

Exploring Solid Electrolytes for Electrochemical Energy Devices: Properties and Mechanisms Governing Ion Conduction

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DECLARATION

I, Diksha N. Karmalkar, hereby declare that this thesis represents work which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

Place: Talcigoa Plateau
Date: -05-2026

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CERTIFICATE

I hereby certify that the above Declaration of the candidate, name of the candidate is true and the work was carried out under my supervision.

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.....
Dedicated,
to my Parents
.....

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Abstract

Solid electrolytes play a crucial role in facilitating ion transport in various electrochemical energy devices. This work focuses in particular on solid electrolytes for applications in all-solid-state sodium-ion batteries (NIBs) and solid oxide fuel cells (SOFCs). In this context, *Chapter 1* introduces different electrochemical energy devices, followed by an overview of state-of-the-art Na^+ -ion and oxide-ion conductors for sodium-ion batteries and intermediate-temperature SOFCs. Moreover, this chapter discusses the factors governing the ion-conduction mechanism in electrolytes and strategies to improve their performance. *Chapter 2* discusses various characterization methods employed to investigate structural (XRD, ND), microstructural (SEM/EDX), local structural (NMR, PALS, EXAFS), thermal (DSC), and electrochemical (EIS, CV, GCD, LSV, DC polarization) properties of the synthesized compositions. It also explains the sample synthesis procedures. This thesis emphasizes three solid electrolyte systems, i.e., NASICON-based ceramic electrolytes, PEO-NASICON-based polymer-ceramic composite electrolytes, and Bi_2O_3 -based ceramic electrolytes. The results on the structural, microstructural, and electrochemical properties of NASICON-type: $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (parent), $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ (Si/P-modified), and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (Sc-doped and Si/P-modified) compositions are presented in *Chapter 3*. Herein, the effect of Si/P ratio, Sc substitution, and synthesis conditions on the bulk and grain boundary conductivity is discussed. The $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ sample exhibits the highest conductivity of 3.2 mS/cm at RT, and the electrochemical cell made with this composition revealed stable performance against sodium metal. *Chapter 4* outlines the synthesis and in-depth characterization of three optimized NASICON ceramic fillers and the fabrication of $(\text{PEO})_{15}\text{-NaNO}_3\text{-}x$ wt% NASICON composite films using these fillers. In this work, a maximum RT conductivity of $\sim 10^{-4}$ S/cm was achieved using a composite prepared with 60 wt% $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ ceramic filler. This high conductivity was primarily attributed to an increased amorphous phase fraction of PEO, along with enhanced bulk conductivity of the filler. The cell performance of this film was also tested, which demonstrated good cycling stability. *Chapter 5* presents an extensive study of the structural, microstructural, and electrochemical properties of V and V, Sr/Ca co-doped Bi_2O_3 -based SOFC materials. In this work, $\text{Bi}_{1-x}\text{V}_x\text{O}_{1.5+x}$ compositions with $x = 0.084\text{-}0.148$ were prepared and characterized. Structural analysis revealed the formation of a rhombohedral phase in low V-doped (0.084-0.09) compositions, whereas a monoclinic phase at high V-doped ($x=0.148$) composition. All compositions with lower V-concentration exhibited promisingly high

conductivity $\sim 10^{-1}$ S/cm at 500 °C. V- and Sr/Ca- co-doped compositions were also prepared, showing conductivity comparable to those with low V-content. Furthermore, the phenomenon of aging was also investigated in this system, wherein excellent aging resistance was observed in V, Sr/Ca co-doped samples relative to single V-doped compositions. The effect of varying Sr content on the properties of these compositions was also explored. Besides, an understanding of the ion-conduction mechanisms has been developed for each of the above systems. *Chapters 6* and *7* of this thesis present the summary and future scope of this work, respectively.

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CHAPTER 1

Introduction

1.1 Electrochemical Energy Storage and Conversion Devices

Recently, energy harvesting from renewable energy resources has become an area of major research for achieving environmentally friendly and sustainable energy generation. However, compared to the existing conventional energy systems, these resources are inherently intermittent and geographically constrained. Therefore, to ensure reliable energy supply from these resources despite their limitations, electrochemical energy storage and conversion devices (ESDs) have emerged as an effective solution for efficient storage and utilization of harvested energy.[1], [2] Among the various energy storage technologies, electrochemical energy storage is regarded as an optimal choice, due to its high energy density, conversion efficiency, and rapid response times.[2], [3]

1.1.1 Role of Solid Electrolytes in ESDs

In ESDs, an electrolyte plays a crucial role by facilitating charge transfer and ionic balance between two electrodes separated by a medium. Thus, it can directly affect the charge storage performance of an ESD and is therefore considered an indispensable component.[4] The desired properties of electrolytes depend on the principles and purposes of ESDs.[5], [6] For an enhanced performance in ESD, an electrolyte should meet following requirements: (1) wide electrochemical window;

(2) high ionic conductivity; (3) high chemical and thermal stability; (4) chemical inertness to other cell components such as the separator, electrode substrates and cell packaging materials; (5) safe, non-toxic, and economically affordable.[6]

In ESDs, liquid electrolytes (specifically based on organic solvents like propylene carbonate (PC), ethylene carbonate (EC)) are commercially sought, because of their favorable bulk and interfacial properties like high ionic conductivity (10^{-3} - 10^{-2} S/cm)[7] and the ability to form stable contact with electrodes.[4], [5] However, these electrolytes present safety concerns particularly associated with flammability, leakage and dendrite formation.[4], [8] In this aspect, solid-state electrolytes (SSEs) offer enhanced safety, high energy density, improved thermal stability and superior electrochemical performance under diverse operational conditions.[4], [5]

Solid electrolytes are generally fast ionic conductors that can attain ionic conductivity comparable to liquids, often several orders of magnitude greater than that of typical solids.[9], [10]. This high conductivity originates from multiscale nature of ionic transport, ranging from atomic scale to the device scale, with each contribution adding to the overall conductivity.[11]

At the atomic scale ($\text{\AA}$), ionic diffusion in solids is best understood based on the classical diffusion model, which describes ionic transport as the hopping of individual ions from one lattice site to another through inter-connected diffusion channels within the crystal framework.[10], [11] In an ideal crystal, at absolute zero, the free energy is dominated by potential energy and is minimized for the perfectly ordered arrangement of ions. This leaves negligible free space for ionic diffusion, allowing only vibrations about their equilibrium positions. However, at finite temperatures, the entropy contributes significantly to the free energy, thereby supporting defect formation. These defects (vacancies and interstitials) provide necessary sites for ion movement and thus play an important role in hopping mechanism.[12] According to the theory of random-walk for defect transport by isolated jumps, the average diffusion coefficient D_{avg} can be expressed as,[13]

$$D_{\text{avg}} = \alpha d^2 \nu_0 \Theta e^{\left(\frac{\Delta S_m}{k_B}\right)} e^{\left(-\frac{\Delta H_m}{k_B T}\right)} \quad (1)$$

Where, α is a geometric factor, d the distance moved during a single jump, ν_0 is the attempt frequency and Θ is the probability of defect species being present at a lattice site. The ΔS_m and ΔH_m terms correspond to entropy and enthalpy of migration, respectively and represent the probability of successful ion jump.

In ionic transport, Θ can be defined as the fraction of defect species that are mobile and can be written as,

$$\Theta = \frac{n}{C} = e^{\left(-\frac{\Delta S_f}{2k_B}\right)} e^{\left(-\frac{\Delta H_f}{2k_B T}\right)} \quad (2)$$

Where, n is the mobile ion density, C is the atomic density and ΔS_f and ΔH_f are the entropy and enthalpy changes for formation of an ionic defect pair (representing the change from perfect to imperfect crystal).[13] Therefore, the mobile ion density can be further simplified as,

$$n = N e^{-\frac{\Delta H_f}{2k_B T}}$$

Where, N is the total ionic defect density

The factor $1/2$ in the above expressions shows that when ion is displaced from a lattice site, a defect is created in pair that maintains the electrical neutrality of the crystal. Thus, after combining equations 1 and 2, the average diffusion coefficient is of the form,

$$D_{\text{avg}} = \alpha d^2 \nu_0 e^{\left(\frac{\Delta S_m + \frac{\Delta S_f}{2}}{k_B}\right)} e^{\left(-\frac{\Delta H_m + \frac{\Delta H_f}{2}}{k_B T}\right)}$$

Or,

$$D_{\text{avg}} = D_0 e^{-\frac{E_a}{k_B T}} \quad (3)$$

Where, D_0 is the frequency factor and E_a is the activation energy

$$D_{\text{avg}} = D_0 e^{-\left(\frac{\Delta H_m + \frac{\Delta H_f}{2}}{k_B T}\right)} \quad \text{and} \quad E_a = \Delta H_m + \frac{\Delta H_f}{2}$$

The activation energy is the sum of migration and formation energies associated with a mobile ion. Therefore, assuming that the charge and mass are transported by the same mobile species, the ionic conductivity can be expressed in terms of particle diffusion coefficient, using Nernst-Einstein relation as,[13]

$$\sigma = \frac{e^2 D_{\text{avg}} N}{k_B T} \quad (4)$$

Where, e is the elementary charge. Upon combining the equations 3 and 4, the temperature dependent conductivity is given by,[13], [14], [15]

$$\sigma = \frac{\sigma_0}{T} e^{-\left(\frac{E_a}{k_B T}\right)}$$

This expression indicates that the ionic conductivity at atomic scale is influenced by several key factors: the concentration of charge carriers, temperature, the availability of vacant-accessible sites (depends on defect density), and the activation energy, which controls the ease of ion migration between lattice sites.[12]

It is also clear that ionic conduction is a thermally activated process and varies across temperature regimes, depending on the underlying defect processes. In intrinsic regime (elevated temperatures), the conductivity is governed by the intrinsic defects (Schottky and Frenkel) by virtue of its activation energy, which includes both, the enthalpy of migration and defect formation. In contrast, at moderate or low temperatures (extrinsic regime), conductivity is dominated by extrinsic defects (introduced by dopants) which are present in much higher concentration than intrinsic defects. Therefore, the corresponding activation energy reflects only the energy of migration.[11], [16], [17]

Furthermore, in certain crystal structures under extrinsic conditions, if the defect concentration exceeds the number of available ground state sites, excess ions can be forced to occupy metastable positions. This can facilitate collective migration

of multiple ions through concerted migration and further reduce the activation energy.[11] Figure 1.1 depicts the single-ion and multi-ion migration and its effect on ion transport energy barrier.

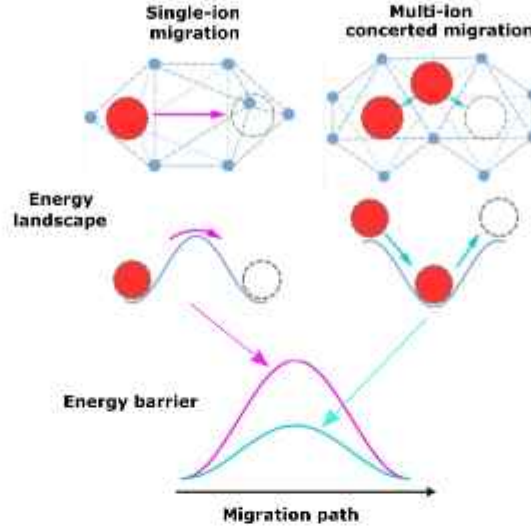


Figure 1.1: Effect of single ion and concerted migration on the activation energy barrier [10]

At the microscale, the ionic conductivity arises as a result of ion dynamics within the bulk and across the microstructural defects, which can affect the macroscopic ion transport in either beneficial or detrimental manner.[18], [19], [20] The microstructural defects include features like grain boundaries, cracks, pores, and secondary phase inclusions.[19], [20] In most cases, grain boundaries have been shown to increase the resistance for ion migration, making them undesirable in macroscopic samples.[20] Strategies to mitigate such defects, often involve optimizing the synthesis process, especially by careful control of sintering temperature. In the case of grain boundaries, sintering can promote grain growth and enhance densification, consequently reducing the grain boundary volume fraction and its contribution to the total conductivity.[21]

1.1.2 Types of Electrochemical Energy Devices

Electrochemical energy storage and conversion system (ESDs) are devices that convert or store energy using electrochemical (redox) reactions. On the basis of their operational principles and targeted applications, these electrochemical devices are broadly classified into batteries, fuel cells, and supercapacitors.[3], [22], [23] The targeted application of ESDs can be understood from the schematic plot shown in Figure 1.2 which compares the performance of energy devices in terms of energy density and power density.

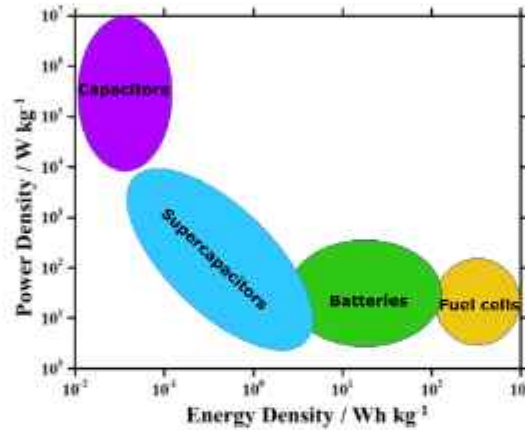


Figure 1.2: Ragone plot showing a comparison between various energy storage devices [24]

Energy density (Wh/kg) is the measure of energy that can be stored in a given mass and is important for applications that require long-term energy storage (i.e. long distance transportation and backup power). On the other hand, power density (W/kg), reflects the rate of energy delivery and is crucial for applications that need rapid bursts of energy (i.e., in emergency power supplies) [25], [26] From the Ragone plot in Figure 1.2, it is evident that capacitors exhibit high power density but low energy density, whereas, fuel cells and batteries are characterized by high energy density but relatively low power density. The supercapacitors lie in region between the conventional capacitors and batteries on the Ragone plot, and thus bridge the gap between them. Therefore, there is a tradeoff between the energy and power density among these devices, and the choice of the technology is based

on specific requirement of the application. In the current thesis work, we choose to focus on the long energy storage aspect of the application with emphasis on batteries and fuel cells.[25], [26]

1.1.2.1 Solids State Batteries (SSBs)

A battery is an electrochemical energy device that stores electricity in the form of chemical energy. Conventional liquid electrolyte batteries, generally consist of four components: cathode, anode, electrolyte, and a separator (to keep the electrodes apart). In case of solid-state battery, however, the electrolyte serves the dual purpose of an electrolyte and separator simultaneously.[27] In addition to the state of art Li^+ -ion and currently developing Na^+ -ion solid state battery, alternative technologies based on elements like Potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn), and aluminium (Al), also exists as a viable option, offering advantages in terms of cost, availability and multivalent charge storage capability.[28]

A working principle of a solid state battery for Na^+ -ion based system is illustrated in Figure 1.3.

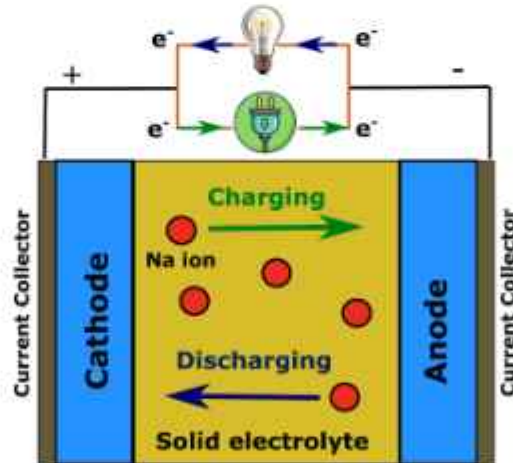


Figure 1.3: Schematic diagram of ASSB of Na^+ -ion [29], [30]

The principle of operation of a sodium-ion based solid state battery (SSB) depends on the reversible migration of sodium ions between the positive (cathode) and negative (anode) electrodes, resulting in storage and release of energy.[30] For the working of the battery, material of both electrodes need to have at least one

redox pair and the redox potential of the positive electrode higher than that of the negative electrode.[27]

During the charging of the battery, the positive electrode undergoes an oxidation reaction, while the negative electrode undergoes a reduction reaction. The sodium ions released during the oxidation of the positive electrode migrates through the electrolyte and enters the negative electrode. Simultaneously, the electrons released from the positive electrode move to the negative electrode through the external circuit, ensuring charge balance. During the discharge, this process is reversed. The Na^+ ions revert from the negative to the positive electrode, while the electrons travel through external circuit, delivering power to the load.[27], [30] Solid electrolytes play an important role in battery operation and are expected to exhibit attributes like high ionic conductivity, broad ESW, chemical compatibility with electrodes and good interfacial contact with electrodes for a superior battery performance.[31]

1.1.2.2 Solid Oxide Fuel cell (SOFCs)

Fuel cells are electrochemical devices that convert the chemical energy from reaction of hydrogen and oxygen into electrical energy with heat and water as byproducts.[32] Similar to the batteries, they consist of an anode, a cathode and an electrolyte that facilitates ion transport between the electrodes. However, unlike batteries, fuel cells do not store reactants internally, instead, fuel and oxidant are supplied continuously from an external source.[26], [32]

Fuel cells are classified based on their operating temperature and electrolyte type. Among different types of fuel cells, Solid oxide fuel cell (SOFCs), belonging to the class of high temperature fuel cells have gathered prominent interest.[33] Because of its elevated temperature of operation, SOFCs exhibit highest electrical conversion efficiency among all fuel cell (up to 90% when waste heat is used by cogeneration).[34] Other advantages include fuel flexibility (hydrogen, carbon dioxide, methane, and other hydrocarbons), superior tolerance to fuel impurities, low emis-

sions, relatively low cost, and high scalability.[34] The basic working mechanism of solid oxide fuel cell is depicted in Figure 1.4.

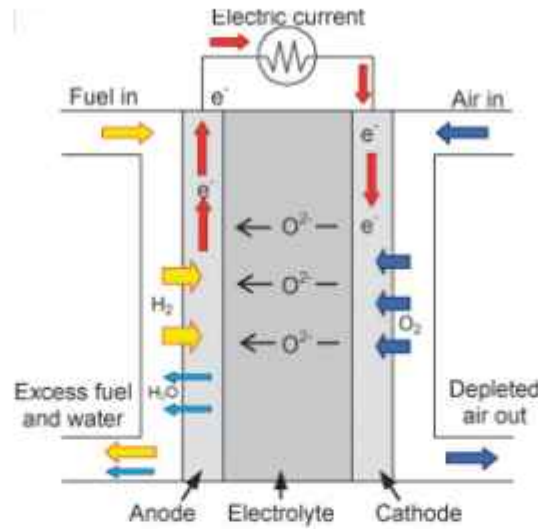


Figure 1.4: Schematic diagram of SOFC operation [35]

In SOFC, fuel (H_2) is supplied at the anode, where it undergoes oxidation, while oxidant (oxygen) is introduced at cathode, where it undergoes reduction. The resulting oxide ions (O^{2-}) at the cathode end are then transported through the electrolyte to the anode. At the anode, when the fuel is supplied, it disperses to electrolyte interface and reacts catalytically with these oxide ions, releasing electrons. These electrons flow through the external circuit to generate electrical power. Meanwhile, at the cathode, oxygen is distributed at electrolyte interface and is reduced by the electrons arriving from the external circuit, producing oxide ions.[36] These oxide ions again diffuse to the anode and complete the reaction, forming H_2O as a byproduct.

SOFCs typically operate in the temperature range of 800-1000°C, depending on the characteristics of component materials.[35] This elevated device operating temperature promotes high conductivity of the electrolyte and a higher rate of electrode reactions, leading to better performance of the fuel cell. However, these conditions also introduce challenges, including material degradation, increased cost and reduced device lifetime. To address these limitations, strategies are pursued, to reduce working temperature of SOFC to intermediate range (500-700 °C).[37]

Operation within this range can ease requirements related to high temperature operation, while still retaining fuel flexibility.[37]

Concurrently, research for solid electrolytes material suitable for IT-SOFC is also active. Suitable attributes for such electrolyte are high ion conductivities (and negligible electronic conductivities) at lower temperatures, together with good chemical stability and sinterability for fabrication.[35]

1.2 Sodium-Ion Based Solid Electrolytes

Currently, Li-ion based batteries dominate the commercial market for applications like portable electronics, electric vehicles and stationary storage systems due to their high energy density, long cycle life, and high output voltage.[31], [38] However, scarcity of lithium resources (0.065% of the earth's crust), its uneven global distribution, higher costs, and inherent safety issues have driven the search for alternative technologies to meet the rising energy demand.[31], [38] In this regard, sodium has emerged as a viable candidate, because of its natural abundance (2.75% of earth's crust), relatively even global distribution, cheaper starting materials and a potential for reduced production costs due to similarity in manufacturing process to that of lithium-ion batteries.[38] Incorporating solid electrolytes with sodium ion batteries can provide additional benefits in terms of safety and energy density, paving way for high-performance all-solid-state sodium ion batteries.[38], [39] Accordingly, the following section highlights the types of solid Na^+ -ion electrolytes commonly employed in all-solid-state sodium ion batteries (ASSSBs).

On basis of their structural state, solid electrolytes developed so far, can be broadly classified into inorganic ceramic/glass ceramic electrolytes, organic polymer electrolytes, and ceramic-polymer composite electrolytes.[27], [38]

1.2.1 Na⁺-ion-based inorganic solid electrolytes

Commonly known classes of inorganic solid electrolytes include sulfide, oxide, halide, complex hydride, and anti-perovskite types.[38] Sulfide-based electrolytes exhibit fast Na⁺-ion conduction at room temperature and can be synthesized at relatively lower temperatures. Owing to their ductile nature, these electrolytes can achieve good interfacial contact with even a simple cold pressing treatment.[27], [40] In addition, the soft texture of sulfide also helps in reducing the grain boundary resistance significantly.[41] Na₃PS₄ is one of the most studied sulfide based electrolytes. In its cubic form (*I* $\bar{4}$ 3*m*), Na₃PS₄ glass-ceramic electrolytes exhibits conductivity of 2×10^{-4} S/cm at room temperature. Later, Na₃PS₄ with improved crystallinity of its cubic phase, was reported to have increased conductivity of 4.6×10^{-4} . [27], [42] This high conductivity was a result of efficient Na⁺ migration pathways present in this phase.[43] Further enhancement in conductivity has been achieved using aliovalent dopants at P site (Si, Se, Sn and Ge) or partial substitution of S²⁻ with heterovalent anions (F⁻, Cl⁻, Br⁻).[38], [43] The ionic doping was employed as a means to generate vacancies in the Na₃PS₄ crystal framework required to support fast sodium ion transport.[44] Another well-known variant of Na₃PS₄ is Na₃PSb₄, which in its cubic phase is reported to have ionic conductivity of 2.8 mS/cm.[39] Cationic doping (Mn, W, and Mo) was also employed in this system, with W-substituted Na_{2.88}Sb_{0.88}W_{0.12}S₄[45] exhibiting exceptionally high ionic conductivity of 0.032 S/cm, one of the highest values reported for sulfide-based electrolytes.[43] Despite its superior conductivity, sulfide-based electrolytes are often unstable in air and react with moisture to release toxic H₂S gas.[27], [44] In addition, they also have narrow electrochemical stability which limits the choice of cathode materials, and are also reactive against the sodium metal anode.[46] Therefore, improvement in stability of sulfide electrolytes is required for their practical application.[27]

Complex hydrides are another class of sodium ion conductors with general formula M(XH_{*n*})_{*m*}, where M represents a metal cation like Na and X is a metal-

lic/nonmetallic element that can form a relatively large anion, e.g., $[\text{BH}_4]^-$, $[\text{AlH}_4]^-$, and $[\text{AlH}_6]^{3-}$. [27] The inherent properties of complex hydrides include, low grain boundary resistance, ion selectivity, reduction stability, ease of device integration, mechanical flexibility and cost-effective manufacturing. However, it is constrained by its relatively low ionic conductivity. [27] Complex hydride solid electrolytes of NaAlH_4 and Na_3AlH_6 were first reported by Oguchi *et al.* [47] with Na^+ transference numbers close to one, but RT ionic conductivities of 2.1×10^{-10} S/cm and 6.4×10^{-7} S/cm, respectively. [43] To improve conductivity, Na^+ ion based complex hydride of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (family of closo-borates) was introduced. However, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ exhibited high superionic conductivity, ≥ 0.1 S/cm only in its disordered cubic phase, which existed above its phase transition temperature of 256°C . [27], [38], [43] This prevented their application in ambient temperature solid state batteries. Therefore, strategies were explored to reduce/eliminate the phase transition temperature. [43] Techniques like anion modification, by replacing B with C in the closo-borate anions, were reported to be effective in lowering the phase transition temperature of $\text{NaCB}_{11}\text{H}_{12}$ to 107°C and improving its ionic conductivity to 0.12 S/cm at 110°C . [27] Another method, involved mixing of poly-borate anions, as in case of $\text{Na}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$ electrolyte, which shows a stable disordered structure at room temperature with an ionic conductivity of 7×10^{-2} S/cm at RT. [43]

In oxide based solid electrolytes, two well-known systems are β -alumina and NASICON materials. [38]

The β -alumina family of solid electrolytes is recognized as a promising type of ion conductor, by virtue of its high ionic conductivity, negligible electronic conductivity of $\sim 10^{-12}$ S/cm and easy availability. [48] The β -alumina has general formula of $\text{Na}_2\text{O}.n\text{Al}_2\text{O}_3$ ($n=5-11$) and its structure is classified into $\beta''\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \cdot (5-7)\text{Al}_2\text{O}_3$) and $\beta\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \cdot (8-11)\text{Al}_2\text{O}_3$), on basis of sodium-to-aluminum ratio. [38] The unit cells of both $\beta\text{-Al}_2\text{O}_3$ (hexagonal, $P6_3/mmc$) and $\beta''\text{-Al}_2\text{O}_3$ (rhombohedral, $R\bar{3}m$) have a layered structure of non-conducting slabs (constitut-

ing Al-based tetrahedra and octahedra) and adjacent conduction planes (constituting loosely packed O^{2-} and mobile Na^+). However, they differ in terms stacking sequence of these two planes.[48] Due to the layered nature of its crystal structure, the Na^+ ion migration occurs only in the 2D conduction planes, while it is blocked along c -axis by the non-conducting spinel block. Therefore, the conductivity in β -alumina compounds is strongly anisotropic.[48] Although in single crystal structure, β - Al_2O_3 and β'' - Al_2O_3 could reach conductivity as high as 0.1 S/cm at RT, in the polycrystalline form, it is lowered to 2 mS/cm corresponding to the combined effect of anisotropic conduction and grain boundary resistance.[48] Among the two, β'' - Al_2O_3 displays higher conductivity due to its larger cell volume and higher concentration of Na^+ ions in the conduction planes.[48] However, β'' - Al_2O_3 is thermodynamically unstable and partially decomposes to give stable β - Al_2O_3 phase and $NaAlO_2$ impurity.[48] In addition, synthesis of pure β'' - Al_2O_3 is also very challenging and often yields a phase fraction of β - Al_2O_3 and β'' - Al_2O_3 along with other impurities.[48] Therefore, efforts to improve conductivity were attempted by enhancing β''/β phase ratio. Several cations with radii less than 0.97 Å (Li^+ , Mg^{2+} , Ni^{2+} , Mn^{2+} , Ti^{4+} and Ta^{5+}) were employed to enter the spinel block (non-conducting plane) and stabilize the β'' - Al_2O_3 phase.[48] Among these, cations with charge lower than Al^{3+} in the spinel block can also simultaneously enhance the Na^+ -ion concentration. The Mg^{2+} doped composition of $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ is known to exhibit ionic conductivity of 0.3 S/cm at 300 °C.[44], [48] Incorporating Mg^{2+} as dopant in synthesis of polycrystalline β'' - Al_2O_3 has been reported to have multiple benefits like, stabilization of up to 95% of β'' phase after high temperature treatment and formation of $MgAl_2O_4$ at the grain boundaries which can reduce porosity.[42] Apart from the tuning of β'' -phase, increasing Na^+ content in the conduction plane is another effective method of improving the conductivity.[48] This is achieved either by reducing sodium loss by reducing sintering temperature or using excess sodium during synthesis.[48] With 6% excess Na_2O , high β'' - Al_2O_3 phase and ionic conductivity of 0.17 S/cm at 300 °C was reported by Li

et al.[49] Despite these advancements, issues like humidity sensitivity and use of energy-intensive synthesis processes like sintering at temperatures above 1497 °C persist.[43] Moreover, achieving phase pure β'' -Al₂O₃ with high yield, low cost, and precise control of microstructure is difficult to accomplish.[38] Furthermore, careful optimization is also needed to balance ionic conductivity and mechanical strength which hinders its practical application.[40], [50] In these context, NASICON type electrolytes emerge as competent rival to traditional β -alumina, offering high ionic conductivities and robust structural properties as their key advantages.[40], [43]

1.2.1.1 NASICON-Type Electrolytes for SIB

Among various classes of solid electrolytes, oxides are considered highly practical, due to factors like electrochemical/thermal/chemical stability, mechanical strength, and ionic conductivity.[51] Specifically, NASICON as a class of oxide-based electrolytes is an promising choice because of its highly reversible Na⁺ ion migration, low thermal coefficient, wide electrochemical stability window, good air stability, and low electronic conductivity.[51]

Figure 1.5 (a) illustrates the relationship of oxides with other well-known classes of solid inorganic electrolytes in the form of radar plot, while Figure 1.5 (b) depicts Arrhenius plot that underscores the potential of NASICON with respect to other well-known Na⁺ ion conductors.

NASICON (Sodium superionic conductor) was first proposed by Goode-nough[55] and Hong[56] in 1976 and is represented by the general formula Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ ($0 \leq x \leq 3$).[57] It was originally derived from the parent compound of NaZr₂P₃O₁₂ by partially substitution of P⁵⁺ with Si⁴⁺. [55], [56] The NASICON crystal structure is three-dimensional framework consisting of interconnected corner-sharing SiO₄/PO₄ tetrahedra and ZrO₆ octahedra (Figure 1.6). This interconnected network creates interstitial sites that are occupied by Na⁺-ions, facilitating three dimensional isotropic conduction.[48] Depending on composition and ambient temperature, Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ typically exhibits two polymor-

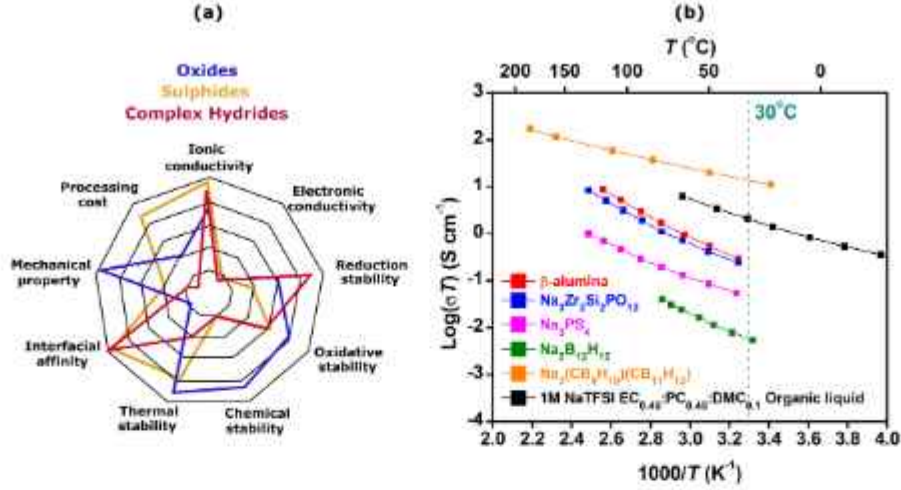


Figure 1.5: (a) Radar plot comparison of properties of oxides, sulfides and hydrides [48] and (b) Arrhenius plot of Na⁺-ion solid inorganic electrolytes.[52], [53], [54]

phic forms corresponding to monoclinic phase (space group $C2/c$) in the x range of $1.8 \leq x \leq 2.2$ and rhombohedral (space group, $R3c$) phase for the rest of the x range.[44], [48], [58] In the rhombohedral crystal structure, Na⁺ ion can reside in two different sites, M_1 and M_2 sites in Figure 1.6 (a), where M_1 is a low-energy site and M_2 is a high-energy site. However, in the $1.8 \leq x \leq 2.2$ range, it undergoes slight rotational distortion to the monoclinic phase. This distortion, is accompanied by splitting of high-energy M_2 site into two new occupied sites (M_2^α and M_2^β) [27], [59], as shown in Figure 1.6 (c).

Ion conduction mechanism in NASICON involves, Na⁺-ion migration through the interconnected channels via hopping between the Na(1)-Na(2) sites in rhombohedral phase or to Na(1)-Na(2)/Na(3) sites in monoclinic phase.[43], [60] To realize ion transport, the Na⁺-ions needs to pass through the triangular bottleneck areas formed by the three oxygen atoms shared between the (Si/P)O₄ tetrahedron and ZrO₆ octahedron pockets.[58], [60] To achieve unhindered Na⁺ ion movement, the smallest diameter of these bottlenecks must exceed the sum of Na⁺-ion and framework O²⁻ ion, which is 2.35 Å.[48] The corresponding bottlenecks between the conduction channels in rhombohedral and monoclinic crystals structures are shown in Figure 1.6 (b, d), respectively.

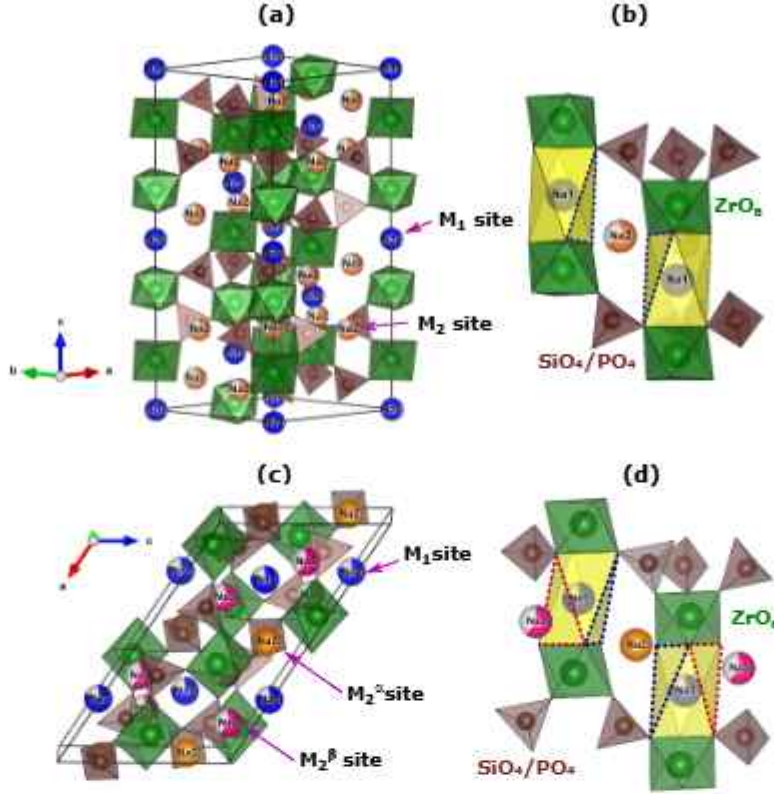


Figure 1.6: Conventional unit cells of NASICON in (a,c) Rhombohedral ($R3c$) and Monoclinic ($C2/c$) crystal structures and (b,d) Bottlenecks for Na^+ ion pathways in rhombohedral and monoclinic structure [27], [59]

In the NASICON structure, the long-range Na^+ transport is assisted by correlated migration mechanism.[48] An optimal concentration of Na^+ ions participating in correlated migration helps to promote the occupancy of high-energy sites, which can induce columbic repulsion between mobile ions and lower the activation energy. However, excess Na^+ concentration reduces the vacancies available for ion transport, thereby leading to lower conductivity. Therefore, optimum concentration of Na^+ -ions and vacancies is essential.[48] In this context, among the two polymorphs, the distorted monoclinic structure exhibits lower activation energy due to the presence of extra high-energy sites and an additional migration pathway leading to higher ionic conductivity.[43], [48] Notably, the monoclinic composition of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ($x=2$) has been reported to have the highest ionic conductivity of 6.7×10^{-4} S/cm at room temperature and 2×10^{-1} S/cm at 300 °C.[43]

1.2.1.2 Limitations and Challenges

A major obstacle to the achieving enhanced conductivity in NASICON composition arises from the interplay of bulk (R_b) and grain boundary resistances (R_{gb}) in a polycrystalline sample.[61] The bulk resistance is an intrinsic property determined by the underlying ion transport mechanism in a material.[61] Consequently, it is dominated by the Na^+ -ion mobility and concentration.[48] On the other hand, grain boundary resistance heavily relies on complex parameters such as the presence of insulating secondary phases, defects, voids, dislocations, and inadequate grain-to-grain contact, which can seriously obstruct ion migration.[61] In NASICON structure, the grain boundary resistance predominates the total conductivity due to the thermal expansion anisotropy.[61], [62] This manifests due to different thermal expansion coefficients along different lattice parameter directions (prominent in lower symmetry structures), resulting in anisotropic contact degradation between grains after sintering.[61] Additionally, the grain boundary resistance also depends on the microstructural feature of the material, such as the grain size distribution. When the sintered grains size results in higher volumetric grain boundary to grain ratio, its effect can become particularly prevalent.[62] Ionic conductivity is also affected by the synthesis process and sintering conditions.[63] Among various preparation methods, solid-state reaction (SSR) is the most reliable for synthesis of NASICON electrolytes for industrial scale applications.[48] The solid-state reaction generally involves two thermal steps, including calcination and sintering for densification. However, higher sintering temperature is often known to cause volatilization of sodium source, formation of impurity phases and abnormal grain growth, whereas lower sintering temperature can hinder densification.[48] Consequently, precise optimization of sintering condition is also very challenging.

1.2.1.3 Strategies for Improvement of conductivity

For high ionic conductivity, NASICON composition should have optimal Na^+ -ion concentration, enlarged bottleneck size, phase purity and minimal grain boundary

defects. Accordingly, several strategies have been adopted including aliovalent substitution and alteration of synthesis conditions.[48]

Although, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) has been widely known, its ionic conductivity is still insufficient for practical application.[64] As a result, it is commonly used as a prototype system for developing strategies to improve conductivity.[64] In NASICON compositions, aliovalent substitution at $\text{Zr}^{4+}/\text{P}^{5+}$ site can effectively increase Na^+ concentration through charge compensation, while also adjusting the bottleneck size using dopants of suitable radii.[48] Several dopants (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) have been used to partially replace Zr^{4+} site to achieve this effect. Mg^{2+} doped composition of $\text{Na}_{3.1}\text{Zr}_{1.95}\text{Mg}_{0.05}\text{Si}_2\text{PO}_{12}$ was reported to have high RT conductivity of 3.5 mS/cm, resulting from enlarged bottleneck size.[52] From further investigations, an optimum dopant ionic radii of 0.72 Å was identified for substitution at Zr site, in order to achieve an optimized bottleneck size.[48], [52] Substitution of P site with dopants like Ge^{4+} , As^{5+} etc., or altering of Si/P ratio, could also help in improvement of conductivity.[48] In addition to bottleneck size, tuning of sodium content is also essential. Guin *et al.*[65] reported the optimal Na content as 3.3-3.55 mol per formula unit to ensure sufficient vacancies for correlated migration and high ionic conductivity.[48] In NZSP composition, low conductivity is often caused by impurities like ZrO_2 which emerge due to the loss of Na/P during high-temperature synthesis.[64] In such a case, introducing an excess sodium source can compensate for the sodium loss, while also providing additional mobile charge carriers.[48], [58] For instance, Naqash *et al.* reported NZSP synthesized with excess sodium source to have improved RT conductivity of 1.6 mS/cm.[66] All these strategies emphasize approaches to enhance the bulk ionic conductivity of NZSP and related compositions; however, improving grain boundary conductivity is equally essential.[48]

Typically, optimized synthesis conditions can control or eliminate the microstructural defects like grain boundaries, pores and micro cracks.[48] To mitigate the effect of these defects in solid state synthesis, sintering aids or inter-granular phases

are often employed.[48] The introduction of low-melting-point sintering aid (eg. oxides,[67] fluoride,[68] silicates,[69] etc.) is known to fill the grain boundaries through capillarity force, thereby enhancing density at reduced sintering temperature.[48] Furthermore, elevated packing density can also be achieved using advanced sintering technologies like hot-pressing sintering (HPS) and spark plasma sintering (SPS).[60] Both HPS and SPS methods involves simultaneous use of high temperature and pressure to mold and sinter the sample, resulting in higher packing density. For example, NZSP composition prepared via SPS, exhibited high RT conductivity of 1.8 mS/cm compared to 0.52 mS/cm in conventional method, due to its higher density.[70] In addition, the density of NZSP is also influenced by the particle size of the NASICON powder. Smaller particle powders possess higher surface energy, which promotes densification by providing stronger driving force for grain growth. Accordingly, an NZSP composition prepared using nano-particle precursors has been reported to exhibit RT conductivity of 1.16 mS/cm, which is higher than that obtained from macro-particle precursors.[71]

Grain boundary modification represents another effective approach, wherein additives that form secondary phases can reinforce inter-grain contact in NASICON, thereby reducing the grain boundary resistance.[61], [62] For example, the $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ modified with 2.5 mol% of $\text{Na}_3\text{LaP}_2\text{O}_8$ exhibits total RT conductivity of 7.2 mS/cm[62] whereas, LaNbO_4 modified composition can achieve up to 9.1 mS/cm[61].

Additionally, employing liquid-based methods for NASICON synthesis, can suppress formation of impurity phases like ZrO_2 , which is very difficult to avoid in solid-state synthesis. Due to its convenience, low-cost, and scalability, the solution-assisted solid-state reaction method is well suited for synthesis of NASICON compositions. This method has also been reported to yield high purity NZSP composition with RT conductivity of 1 mS/cm, making it a strong alternative for solid-state reaction method.[72] NASICON compositions of $\text{Na}_{3.4}\text{Sc}_{0.4}\text{Zr}_{1.6}\text{Si}_2\text{PO}_{12}$ and $\text{Na}_{3.3}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ synthesized using this method, have been reported

to achieve a high RT conductivity of 4 mS/cm and 5.5 mS/cm, respectively.[73], [74]

Integration of the above mentioned strategies can boost the bulk and the grain boundary conductivities simultaneously, effectively increasing the overall ionic conductivity.

1.2.1.4 Strategies to reduce Interfacial resistance

Although, the inorganic solid electrolyte like NASICON addresses the safety issues, its electrochemical performance is limited by the high interfacial resistance that it encounters at the solid-solid interface. Due to its rigid nature, solid electrolytes cannot form tight interfacial contact with the electrode. This can lead to higher interfacial resistance as well as mechanical degradation of the electrolyte during cycling, ultimately degrading its electrochemical performance.[38]

Strategies to improve the interfacial contact include introduction of inter-layers between electrode and electrolyte to accommodate volume changes.[38] Other approaches involve, ion doping for interfacial regulation, co-sintering of electrode and electrolyte and use of liquid based wetting agents.[75] Among these, incorporating flexible polymer electrolyte to form a composite solid electrolyte is particularly effective as it combines mechanical compliance of polymer with high ionic conductivity of NASICON.[38]

1.2.2 Polymer-Ceramic Composite Electrolytes

Solid polymer electrolytes (SPEs), featuring a polymer matrix with a sodium salt dispersed within it, can help to alleviate the interfacial issues of ceramic electrolyte, due to their excellent flexibility, easy processability, good interfacial adhesion and compatibility with electrodes.[76], [77] The comparison of performance of a typical solid composite electrolyte w.r.t inorganic ceramic and solid polymer electrolyte is shown in Radar plot of Figure 1.7 (a).

Typically in a SPEs, sodium salts like NaPF_6 , NaBF_4 , NaClO_4 etc., are dissolved

within a polymer host. Polymer matrix solvates these low lattice-energy salts by forming stable ion-polymer complexes. Movement of the ions then proceeds through hopping mechanism, wherein the Na^+ ions migrate between successive coordination sites along the polymer chains.[77], [78] Effective salt solvation requires the polymer host to have polar functional groups (ether (-O-), carbonyl (C=O), and cyano ($\text{C}\equiv\text{N}$)) in order to interact with mobile Na^+ ions.[31], [40], [78] However, the strength of these interactions needs to be optimally balanced for efficient ion hopping within the polymer. This indicates the interdependence of salt solvation and ion transport processes.[78] Moreover, the ion hopping is closely coupled with structural relaxation of polymer segments (also known as polymer segmental motion) for long-range ionic transport. Increased flexibility of polymer chains enhances the segmental motion and facilitates faster ion transport.[31], [78] Consequently, amorphous regions of the polymer matrix, especially above the glass transition temperature (T_g), offer such flexible pathways and thus promote efficient Na^+ ion transport.[31] The illustration of ion hopping mechanism within solid polymer electrolyte is depicted in Figure 1.7 (b).

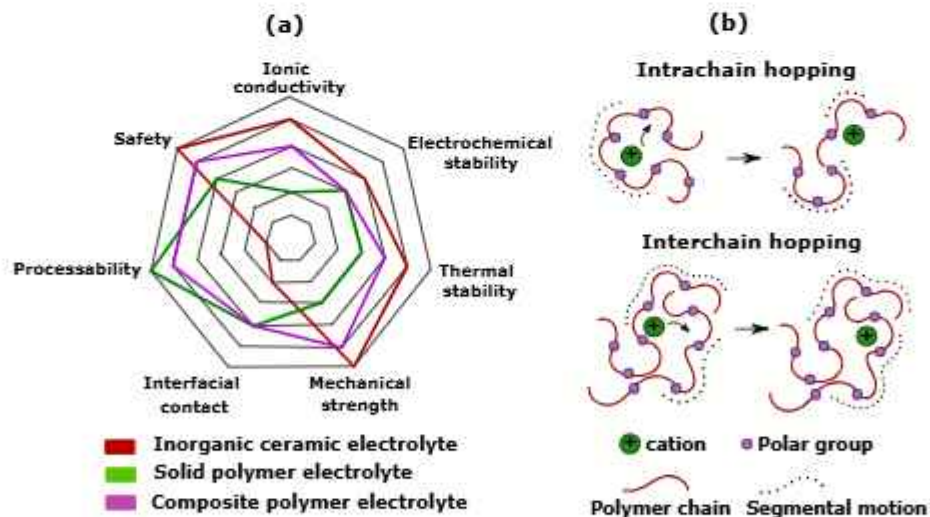


Figure 1.7: (a) Comparison of performance of ceramic, solid polymer (SPEs) and composite polymer electrolytes (CSEs)[79] and (b) Ion conduction in amorphous region of SPE[80]

Among SPE, poly(ethylene oxide) (PEO) is the earliest and most promising polymer host, because of its relatively good viscoelasticity, high ion dissociation capac-

ity and good mechanical properties.[40], [77] To date, several PEO-based polymer electrolytes have been developed using different polymer to sodium ratios (EO/Na) and anionic moieties of sodium salt, such as NaPF₆, [81] NaClO₃, [82] NaCF₃SO₃, [83] NaFSI, [84] and NaTFSI [85].

In general, the PEO complexed with sodium salts, exhibits ionic conductivities of 10^{-8} - 10^{-7} S/cm at RT. This low value of conductivity primarily stems from the high crystallinity of PEO at room temperature, which immobilizes a significant portion of polymer chains and confines ion transport to amorphous regions.[31], [77], [86] To increase conductivity, strategies aim at disrupting the crystallinity of PEO and increasing the fraction of high-conducting amorphous phase.[31] In this regard, use of additives like polymer blends (Polyvinylpyrrolidone, PVP), plasticizers (succinonitrile, SN) and inorganic ceramic fillers is known to suppress crystallinity of the polymeric PEO.[40]

Specifically, the incorporation of fillers to form composite polymer-ceramic electrolytes (CSEs) has emerged as an effective approach to obtain enhanced conductivity while preserving the mechanical strength.[77], [86] Inorganic ceramic fillers can be divided into two groups, i.e., inert and active fillers, depending on their ability to conduct mobile ions. Inert fillers include SiO₂, ZrO₂ and Al₂O₃, while Na⁺ ion conductors like garnet, perovskite, sulfide and NASICON-type belong to the class of active fillers.[87] Inert fillers influence conductivity by disrupting the local crystallization behavior of the polymer matrix, thereby enabling chain mobility.[86] In contrast, active fillers serve dual purpose. Apart from acting as plasticizers, these fillers also provide supplementary ion transport pathways, both at the polymer-ceramic interface and within the filler itself.[87] As a result, composite with active fillers typically show higher conductivity and mobile ion transference number relative to inert fillers.[86]

1.3 Bi₂O₃-Based and Other Electrolytes reported for SOFCs

Lowering the operating temperature of SOFC is essential to ensure its long-term stability and has therefore become developing trend in current research. Achieving efficient operation at intermediate operating temperature requires minimization of electrolyte ohmic resistance as well as the polarization resistance at the electrodes, while maintaining the mechanical and chemical stability.[88] Accordingly, many oxide-ion based systems have been explored for application in intermediate temperature SOFCs (IT-SOFC). Typically, an ideal SOFC electrolyte is expected to fulfill criteria like high ionic conductivity, low electronic conductivity, chemical and physical stability under reducing and oxidizing atmospheres, ease of preparation and cost-effectiveness.[89] The following section highlights few of such solid oxide ion conductor commonly employed in Solid oxide fuel cells (SOFCs).

Fluorite-type oxides are presently the most widely used electrolytes for SOFCs.[88] These oxides possess face-centered cubic arrangement of cations with anions occupying all the tetrahedral sites. In order to generate vacancies to support oxide ion conduction, these are often doped with lower valence cations.[88] The best-known fluorite type oxide is the acceptor-doped ZrO₂. [35] Pure ZrO₂ is not a good oxide ion conductor and, it adopts its cubic fluorite phase only above 2370 °C. Partial substitution of ZrO₂ with cations like Ca²⁺, Y³⁺, Er³⁺ stabilizes cubic phase over a wide range of temperatures, while introducing oxygen vacancies into its structure.[35], [88] Among its various substituted compositions, YSZ (Ytria stabilized zirconia) is the most well-known oxide electrolyte; however, its high working temperature (typically 800-1000 °C) makes unfeasible for IT-SOFC application.[35] Sc-doped ZrO₂ (ScSZ) has been reported with high ionic conductivity of 0.003 S/cm at 500 °C, but its use is limited because of scarcity of Sc source. Doped CeO₂ is another fluorite-type oxide. Similar to ZrO₂, pure CeO₂ is also not a good ion conductor due to negligible oxygen vacancies, although it has stable

cubic phase from RT to its melting point.[88] Thus, trivalent or divalent cations such as Gd^{3+} , Sm^{3+} , Y^{3+} , La^{3+} or Ca^{2+} have been used to improve its conductivity at intermediate temperatures.[35] Typically, ionic conductivity of Sm- and Gd-doped CeO_2 can surpass that of YSZ, particularly at intermediate temperature range (500-700 °C).[35] However, it exhibits substantial amount of electronic conductivity at low oxygen partial pressures and elevated temperatures (< 600 °C), caused by reduction of Ce^{4+} to Ce^{3+} .[35], [88]

LaGaO_3 -based perovskite-type electrolytes is another well explored system for application in IT-SOFCs.[88] Doped LaGaO_3 composition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) has been reported to exhibit high oxide ion conductivity, comparable to doped CeO_2 electrolyte at intermediate temperatures.[88] However, its widespread use is hampered by issues like phase purity, densification, the volatile nature of gallium at high temperatures and high reactivity with Ni metal which is typically used in anodes.[35], [88]

$\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX) represents another class of fast oxide ion conductors.[35] This compound exhibits two polymorphs, the non-conductive monoclinic phase and the highly conductive cubic phase. In its cubic phase, it shows ionic conductivity of 6×10^{-2} S/cm at 800 °C, but this phase exists only above 580 °C.[35], [90] The challenge associated with this phase transition is resolved by doping alkaline (e.g., K and Rb) and alkaline-earth (e.g., Ca, Sr and Ba) cations on the La site, which are known to stabilize the cubic phase at room temperature while maintaining its conductivity. Another limitation is the low chemical stability of $\text{La}_2\text{Mo}_2\text{O}_9$ in low oxygen pressure, which gives rise to mixed valent $\text{Mo}^{5+}/\text{Mo}^{6+}$ phase of $\text{La}_7\text{Mo}_7\text{O}_{30}$, followed by decomposition of the electrolyte.[35]

Lanthanum silicates and germanates with apatite-type structure are also another category of promising candidates. Apatite-type oxides have formula of $\text{M}_{10}(\text{XO}_4)_6\text{O}_{2-y}$, where M is a rare-earth or alkaline-earth cation, X is a p-block element such as P, Si or Ge.[35] The highest conductivities have been reported in germanium-based analogues. However, these systems are hindered by the issue of

germanium volatility.[35], [91]

δ - Bi_2O_3 is another important fast oxide-ion conductor with a fluorite-based structure. Among all solid oxide-ion conductors, the face-centered cubic (fcc) phase of bismuth oxide (δ - Bi_2O_3) is reported to have highest known oxygen ion conductivity.[92] As a result, it has garnered significant attention for application in IT-SOFCs. For reference, Figure 1.8 compares the Arrhenius plots of well-known oxide ion conductors with that of Bi_2O_3 based electrolyte.[89].

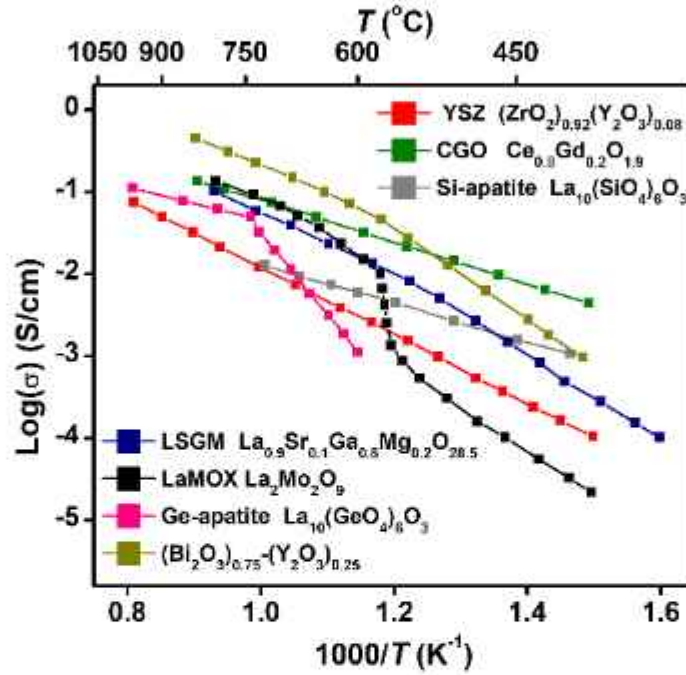


Figure 1.8: Comparison of Arrhenius plots for well-known oxide ion conductors.[35], [93]

1.3.1 Structure of Bi_2O_3 electrolyte

The high conducting nature of bismuth oxide (δ - Bi_2O_3) and its aliovalent metal-doped variants was first reported by Takahashi and his group in 1972.[94] The pristine Bi_2O_3 exhibits several polymorphs, among which the monoclinic α phase is the stable phase at room temperature. At 729°C, this phase undergoes a transition to the high-temperature fcc phase (δ - Bi_2O_3), which remains stable up to its melting point at 824°C. Upon cooling, δ -phase typically transitions to the α -phase through intermediate metastable polymorphs of tetragonal β or bcc γ

phases. However, in some cases, the γ -phase is also found to persist at room temperature.[92] Among all its polymorphs, δ -phase exhibits exceptionally high ionic conductivity of 1 S/cm at 750 °C.[95] The transitions of polymorphic phases alongside their order of conductivity and transition temperatures are depicted in Figure 1.9 (a).

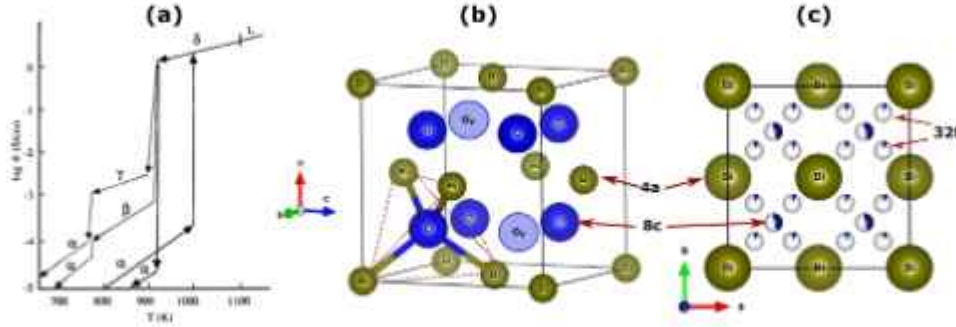


Figure 1.9: (a) Conductivity of α , β , γ and δ polymorphs of Bi_2O_3 [96] and (b, c) Unit cell of $\delta\text{-Bi}_2\text{O}_3$ (oxygen vacancy denoted by O_v) by Harwig [97] and Battle Model[98], respectively

The structure of the $\delta\text{-Bi}_2\text{O}_3$ is highly disordered due to the large transition enthalpy associated with the $\alpha \rightarrow \delta$ transition, which is nearly three times higher than the heat of melting.[96], [99] This high conducting $\delta\text{-Bi}_2\text{O}_3$ phase, adopts a defective fluorite crystal structure ($\text{BiO}_{1.5}\square_{0.5}$), described by cubic close packed (fcc) lattice of Bi^{3+} ions (4a sites), with O^{2-} ions disordered over 6/8 of the tetrahedral sites (8c sites).[100], [101]. This structure is illustrated in the Figure 1.9 (b) and describes the earliest model of $\delta\text{-Bi}_2\text{O}_3$. However, this model was later refined by Battle *et al.*[98], wherein oxides ions were shown to occupy two sites within the $Fm\bar{3}m$ structure. In this Battle model, about 43% of 8c (1/4, 1/4, 1/4) sites are randomly occupied, while the remaining the 1.28 oxide anions per unit cell are displaced along $\langle 111 \rangle$ direction from regular 8c to interstitial 32f site. (0.354, 0.354, 0.354) as depicted in Figure 1.9 (c).[99]

Thus, exceptionally high ionic conductivity of $\delta\text{-Bi}_2\text{O}_3$, stems from the high polarizability of the bismuth framework, highly disordered anion network, presence of 25% intrinsic vacancies, and large ability of bismuth cations to dynamically accommodate asymmetric surroundings.[99], [100] However, despite its superior ionic

conductivity, the phase stability of δ -Bi₂O₃ is only within the narrow temperature range of 730-825 °C. This limited stability range, along with the associated mechanical stress due to the volume change during the phase transitions, results in pure Bi₂O₃ being unsuitable for practical applications. Consequently, considerable efforts have been spared to stabilize the high conducting δ -Bi₂O₃ at room temperature using various cation doping strategies.[99]

1.3.2 Challenges and strategies for performance enhancement

A wide variety of isovalent and aliovalent dopants have been substituted at Bi³⁺ site to retain the highly conductivity form of δ -Bi₂O₃ at intermediate temperatures. These includes oxides of the form M₂O₃ (M: La, Y, Fe, Sb, and rare earth element), M₂O₅ (M: Ta, Nb, Sb, and V), MO₂ (M: Zr, Sn, Te, Ti, and W), and MO (M: Ca, Sr, Ba, and Pb).[102] It has been reported that dopants with ionic radii smaller than Bi³⁺ (1.03 Å) promotes stabilization of cubic phase, by inducing contraction of its open crystal structure. In contrast, introduction of relatively larger cations (La, Nd, Sm, and Gd) tends to form rhombohedral structure in Bi₂O₃. [102] Both these phases exhibit appreciable oxygen-ion conductivities due to the high concentration of oxygen vacancies in their crystal structure.[103] However, their conductivity is typically an order of magnitude lower relative to pure δ -phase. This may be a result of partial cation substitution which may reduce the polarization strength of host Bi³⁺ ion.[101]

Prior studies were mainly based on rare-earth (RE) stabilized Bi₂O₃, which generally have lower ionic radius attributing to reduced lattice constant and therefore, required lower doping content for stabilization. For example, Er³⁺ doped (Bi₂O₃)_{0.80}(Er₂O₃)_{0.20} was able to effectively stabilize the δ -phase with the least amount of doping (15-20 mol%), giving conductivity of the order of 0.023 S/cm at 500 °C.[104], [105] However, recent studies have shifted focus on stabilization using transition metal oxide such as Mo, Cr, W, Nb, and Ta, resulting in fluorite-type

superstructures with local ordering of oxide-ion around the transition metals.[104] The Nb-doped composition of $(\text{Bi}_2\text{O}_3)_{0.85}(\text{Nb}_2\text{O}_5)_{0.15}$ has been reported to have ionic conductivity of 0.011 S/cm at 500 °C.[106]

Despite extensive efforts to stabilize the $\delta\text{-Bi}_2\text{O}_3$ through doping, the phase remains metastable and leads to rapid decline in conductivity upon annealing below $\sim 650^\circ\text{C}$.[104] This decline was attributed to two different mechanisms. In certain doped $\delta\text{-Bi}_2\text{O}_3$, slow phase transformation from high conducting cubic to a lower conducting rhombohedral phase was observed within the intermediate temperature range of 600-650 °C. However, at temperatures below $\sim 600^\circ\text{C}$, another scenario persisted, which was due oxygen sub-lattice undergoing both occupancy and positional ordering, resulting in a decrease in conductivity as well as change in activation energy.[104] This phenomenon is commonly referred to as aging effect and occurs when the phase-stabilized composition is annealed at temperatures below 600 °C. The comparison of phase transformation with aging effect is shown in Figure 1.10 for Y-doped Bi_2O_3 .

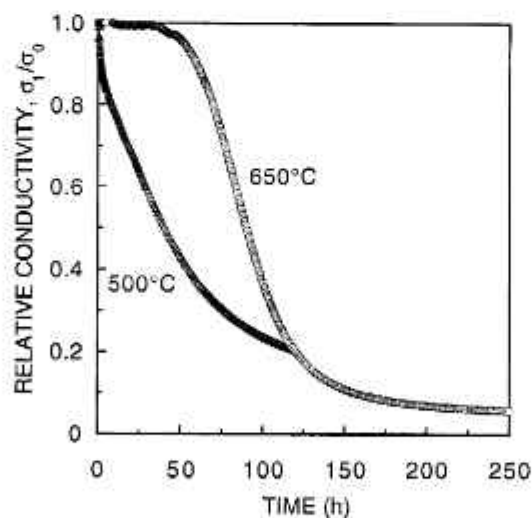


Figure 1.10: Comparison of conductivity decay in $(\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}$ at 500 °C due to aging and 650 °C due to phase transformation [103]

Figure 1.10 shows that the rate of conductivity decay due to aging is faster and distinct relative to that of phase transformation.[103], [104] Both these issues imply that single dopant substitution only quenches the high conducting phase; however, its long term stability is still at risk.[104]

Systematic research has been done to study these effects in rare-earth doped ($\text{Ln} = \text{Dy, Ho, Er, Tm, and Yb}$) Bi_2O_3 , wherein rate of conductivity degradation was found to be dependent on the ionic radii and concentration of the dopant.[103] For higher ionic conductivity, higher disorder of the oxygen sub-lattice is necessary. However, for the fixed concentration of RE dopant, the fcc phase stability and structural stability (pertaining to disordered network) exhibit opposing trends with regards to the cationic radii.[103] Therefore, to ensure both phase and structural stability, it is necessary to understand the factors affecting these phenomena. Both the phenomena, cubic to rhombohedral transformation and ordering of O^{2-} sub-lattice, are governed by cation diffusion, with their different kinetics arising from differences in characteristic diffusion distances involved.[99]

Aging phenomena observes time-dependent conductivity decay, with stability of disordered structure directly governed by ionic radii (via polarizability) and concentration of the dopant. However, lattice parameter plays an indirect role in structure stability, not through the size of unit cell but by its effect on formation of dopant-oxygen associates.[103] In substitutions, with stronger dopant-O bond strength compared to Bi-O bond, such an association can exist and restrict either the mobility of anion vacancies or the concentration of mobile oxide ions.[103]

Typically, dopants with large ionic radii, by virtue of their polarizability, can reduce the tendency of oxygen-vacancies to associate with the Bi^{3+} cation (ordering).[92] But, for the cubic Bi_2O_3 phase stabilization, smaller ionic radii of the dopants is essential. In such as case, a co-doping strategy involving a both a large radii dopant to minimize ordering and small radii dopant to stabilize the cubic phase can serve the purpose. Moreover, this can also increase entropy of the co-doped system, leading to higher disorder in the anion sub-lattice resulting in enhanced conductivity.[92]

Even in cubic to rhombohedral phase transformation (600 to 650 °C), co-doping can play a major role in preserving the isotropic bonding between Bi^{3+} and O^{2-} , which is a requisite of cubic phase, thereby suppressing transformation.[104] An

effective example of this approach involves isovalent co-dopants of Er^{3+} and Y^{3+} , which have been shown to stabilize the cubic phase even at low doping concentration. In contrast, for single dopant systems, the same effect can be achieved by introducing aliovalent dopant like Zr^{4+} , which can increase the effective coordination number of Bi^{3+} , resulting in retention of isotropic bonding and increased energy barrier for phase transition.[104]

So far, several combinations of co-dopants, including Y-Ln (Ln = Er, Gd, Sm, Pr, Nb, Zr), Te-Ln (Ln= La, Sm, Gd, Er), Ca-W, Dy-W, Nb-Ho, and Er-Nb oxides have been studied for stabilization of $\delta\text{-Bi}_2\text{O}_3$. [103] Recent report by Jung *et al.* studying Bi_2O_3 doped with strong polarizable W and Dy dopants, achieved highest conductivity of 0.57 S/cm at 700 °C and 0.098 S/cm at 500 °C.[107]

Another recent method of conductivity enhancement includes high entropy Bi_2O_3 systems, wherein a composition of $(\text{Bi}_{0.8}(\text{Y}_{0.2}\text{Er}_{0.2}\text{Zr}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2})_{0.2})_2\text{O}_{3\pm\delta}$ has been reported with conductivity 1.32×10^{-1} to 1.09×10^{-1} S/cm in 300-550 °C, almost 5.7 times higher than single RE doped Bi_2O_3 ceramic. This enhancement is attributed to the random distribution of multiple cations with various ionic radii, which induces lattice distortions and enhance oxygen vacancy mobility.[108]

Apart from phase and structural stability, the doped Bi_2O_3 phases also encounter the issue of decomposition to metallic Bi at lower oxygen partial pressures. This limitation has been addressed by fabrication of bilayer electrolyte based on doped ceria/stabilized bismuth oxide as reported by Wachsman *et al.*[109] The dense doped cerium oxide layer is expected to shield the Bi_2O_3 layer from the reducing atmosphere. However, ensuring the formation of dense bilayer electrolyte along with its complex preparation process and high cost are major obstacles in this method.[110]

1.4 Research Aims and Objectives

The focus of this thesis work is divided into the investigation of three classes of solid electrolytes: (1) NASICON-type ceramic electrolyte, (2) PEO- NaNO_3 -NASICON

polymer-ceramic composite electrolytes and, (3) Bi_2O_3 -based electrolytes. The NASICON ceramic and composite electrolytes are targeted for application in Na^+ -ion batteries, whereas, Bi_2O_3 -based electrolytes are designed for IT-SOFC applications.

In NASICON ceramic, the study aims to explore different strategies, such as alteration of Si/P ratio, introduction of dopants, and tuning of synthesis process to improve its overall ionic conductivity. Additionally, this work also intends to employ suitable tools to draw correlations among structural features (like crystal structure, microstructure, and defect concentration), ionic conductivity, and the underlying conduction mechanism of the synthesized materials.

In PEO- NaNO_3 -NASICON composite system, work is focused on examining the effect of NASICON ceramic filler weight percentage (wt%) on the ionic conductivity of the composite films. The work also intended to find the optimum limit of filler %, followed by understanding the structure-property correlation and identifying the underlying ion transport mechanism at this optimized weight fraction. In Bi_2O_3 -based system, the objective is to investigate the effect of V concentration on the ionic conductivity of Bi_2O_3 - V_2O_5 composition. Besides, in the optimized V-doped Bi_2O_3 composition, the effect of the addition of Sr/Ca as a co-dopant is planned to be investigated. To verify the effectiveness of the V- and Sr/Ca-doping, this study also expands into the systematic investigation of the as-prepared and aged samples, and finally correlates the structural factors with the conduction property and aging phenomena of V- and Sr/Ca-doped Bi_2O_3 materials.

References

- [1] H. Kim et al., *Advanced Energy Materials*, vol. 6, no. 19, p. 1600943, 2016. DOI: 10.1002/aenm.201600943.
- [2] Y. Yao et al., *ACS Nano*, vol. 19, no. 34, pp. 30568–30687, 2025. DOI: 10.1021/acsnano.4c10091.
- [3] P. Ragupathy, S. D. Bhat, and N. Kalaiselvi, *WIREs Energy and Environment*, vol. 12, no. 2, e464, 2023. DOI: <https://doi.org/10.1002/wene.464>.
- [4] R. Tiwari et al., *Journal of Energy Storage*, vol. 81, p. 110361, 2024, ISSN: 2352-152X. DOI: <https://doi.org/10.1016/j.est.2023.110361>.
- [5] Y. Wang and W. Zhong, *ChemElectroChem*, vol. 2, no. 1, pp. 22–36, 2015. DOI: <https://doi.org/10.1002/celec.201402277>.
- [6] L. Xia, L. Yu, D. Hu, and G. Z. Chen, *Mater. Chem. Front.*, vol. 1, pp. 584–618, 4 2017. DOI: 10.1039/C6QM00169F.
- [7] H. Yang and N. Wu, *Energy Science & Engineering*, vol. 10, no. 5, pp. 1643–1671, 2022. DOI: <https://doi.org/10.1002/ese3.1163>.
- [8] Y. Zhou et al., *ACS Nano*, vol. 19, no. 49, pp. 41419–41458, 2025. DOI: 10.1021/acsnano.5c14335.
- [9] Y. Gao et al., *Chemical Reviews*, vol. 120, no. 13, pp. 5954–6008, 2020. DOI: 10.1021/acs.chemrev.9b00747.
- [10] X. He, Y. Zhu, and Y. Mo, *Nature Communications*, vol. 8, no. 1, p. 15893, Jun. 2017.
- [11] T. Famprikis, P. Canepa, J. A. Dawson, M. S. Islam, and C. Masquelier, *Nature Materials*, vol. 18, no. 12, pp. 1278–1291, 2019.
- [12] P. P. Kumar and S. Yashonath, *Journal of Chemical Sciences*, vol. 118, no. 1, pp. 135–154, 2006.

-
- [13] S. Tammireddy et al., *ACS Energy Letters*, vol. 7, no. 1, pp. 310–319, 2022. DOI: [10.1021/acsenergylett.1c02179](https://doi.org/10.1021/acsenergylett.1c02179).
- [14] C. Wang et al., *Small*, vol. 18, no. 43, p. 2107064, 2022. DOI: <https://doi.org/10.1002/sml1.202107064>.
- [15] S. Ohno et al., *Progress in Energy*, vol. 2, no. 2, p. 022001, Mar. 2020. DOI: [10.1088/2516-1083/ab73dd](https://doi.org/10.1088/2516-1083/ab73dd).
- [16] M. Reddy and M. Fichtner, in *Photonic and Electronic Properties of Fluoride Materials*, A. Tressaud and K. Poeppelmeier, Eds., Boston: Elsevier, 2016, pp. 449–463, ISBN: 978-0-12-801639-8. DOI: <https://doi.org/10.1016/B978-0-12-801639-8.00020-9>.
- [17] H. Tuller, in *Springer Handbook of Electronic and Photonic Materials*, S. Kasap and P. Capper, Eds. Boston, MA: Springer US, 2007, pp. 213–228, ISBN: 978-0-387-29185-7. DOI: [10.1007/978-0-387-29185-7_11](https://doi.org/10.1007/978-0-387-29185-7_11).
- [18] S. Breuer et al., *J. Mater. Chem. A*, vol. 3, pp. 21343–21350, 42 2015. DOI: [10.1039/C5TA06379E](https://doi.org/10.1039/C5TA06379E).
- [19] H. El Khal, A. Cordier, N. Batis, E. Siebert, S. Georges, and M. Steil, *Solid State Ionics*, vol. 304, pp. 75–84, 2017, ISSN: 0167-2738. DOI: <https://doi.org/10.1016/j.ssi.2017.03.028>.
- [20] W. Yu et al., *eScience*, vol. 5, no. 1, p. 100278, 2025, ISSN: 2667-1417. DOI: <https://doi.org/10.1016/j.esci.2024.100278>.
- [21] Q. Xue, X. Huang, J. Zhang, H. Zhang, and Z. Feng, *Journal of Rare Earths*, vol. 37, no. 6, pp. 645–651, 2019, ISSN: 1002-0721. DOI: <https://doi.org/10.1016/j.jre.2018.11.006>.
- [22] I. T. Bello, L. A. Jolaoso, R. A. Ahmed, and A. Bello, *Energy Reviews*, vol. 4, no. 1, p. 100109, 2025, ISSN: 2772-9702. DOI: <https://doi.org/10.1016/j.enrev.2024.100109>.

- [23] A. Kumar, H. K. Rathore, D. Sarkar, and A. Shukla, *Electrochemical Science Advances*, vol. 2, no. 6, e2100187, 2022. DOI: <https://doi.org/10.1002/elsa.202100187>.
- [24] P. Naskar, P. Chakraborty, D. Kundu, A. Maiti, B. Biswas, and A. Banerjee, *ChemistrySelect*, vol. 6, no. 5, pp. 1127–1161, 2021. DOI: <https://doi.org/10.1002/slct.202100049>.
- [25] Almusawi, Muntather et al., *E3S Web Conf.*, vol. 591, p. 01 010, 2024. DOI: [10.1051/e3sconf/202459101010](https://doi.org/10.1051/e3sconf/202459101010).
- [26] M. Winter and R. J. Brodd, *Chemical Reviews*, vol. 104, no. 10, pp. 4245–4270, 2004. DOI: [10.1021/cr020730k](https://doi.org/10.1021/cr020730k).
- [27] H. Si, J. Ma, X. Xia, Q. Wang, S. Geng, and L. Fu, *Chemistry – A European Journal*, vol. 31, no. 5, e202403247, 2025. DOI: <https://doi.org/10.1002/chem.202403247>.
- [28] J. Zhang, X. Yao, R. K. Misra, Q. Cai, and Y. Zhao, *Journal of Materials Science & Technology*, vol. 44, pp. 237–257, 2020, ISSN: 1005–0302. DOI: <https://doi.org/10.1016/j.jmst.2020.01.017>.
- [29] S. Antony Jose et al., *Batteries*, vol. 11, no. 3, 2025, ISSN: 2313-0105. DOI: [10.3390/batteries11030090](https://doi.org/10.3390/batteries11030090).
- [30] P. Bača, J. Libich, S. Gazdošová, and J. Polkorab, *Batteries*, vol. 11, no. 2, 2025, ISSN: 2313-0105. DOI: [10.3390/batteries11020061](https://doi.org/10.3390/batteries11020061).
- [31] Y. Fu, G. Shao, and Y. Lei, *Interdisciplinary Materials*, vol. 5, no. 1, pp. 5–84, 2026. DOI: <https://doi.org/10.1002/idm2.70023>.
- [32] V. Mahadevan, S. R. S. M. A. Rusho, and S. Yishak, *Results in Engineering*, vol. 26, p. 105 589, 2025, ISSN: 2590–1230. DOI: <https://doi.org/10.1016/j.rineng.2025.105589>.
- [33] M. A. Yattoo et al., *MRS Communications*, vol. 13, no. 3, pp. 378–384, Jun. 2023. DOI: <https://doi.org/10.1557/s43579-023-00371-0>.

- [34] A. Talukdar et al., *International Journal of Energy Research*, vol. 2024, no. 1, p. 6443247, 2024. DOI: <https://doi.org/10.1155/2024/6443247>.
- [35] L. Malavasi, C. A. J. Fisher, and M. S. Islam, *Chemical Society reviews*, vol. 39 11, pp. 4370–87, 2010.
- [36] P. Aravind and W. de Jong, *Progress in Energy and Combustion Science*, vol. 38, no. 6, pp. 737–764, 2012, ISSN: 0360-1285. DOI: <https://doi.org/10.1016/j.pecs.2012.03.006>.
- [37] K. A. Kuterbekov et al., *Nanomaterials*, vol. 12, no. 7, 2022, ISSN: 2079-4991. DOI: [10.3390/nano12071059](https://doi.org/10.3390/nano12071059).
- [38] X. Li et al., *Rare Metals*, vol. 44, no. 5, pp. 2871–2899, May 2025.
- [39] L. Huang and C. Huang, *Electrochemical Energy Reviews*, vol. 9, no. 1, p. 6, Feb. 2026. DOI: <https://doi.org/10.1007/s41918-026-00279-y>.
- [40] Y. Wang, S. Song, C. Xu, N. Hu, J. Molenda, and L. Lu, *Nano Materials Science*, vol. 1, no. 2, pp. 91–100, 2019, ISSN: 2589-9651. DOI: <https://doi.org/10.1016/j.nanoms.2019.02.007>.
- [41] H. Yang et al., *Advanced Energy Materials*, vol. n/a, no. n/a, c05208, 2026. DOI: <https://doi.org/10.1002/aenm.202505208>.
- [42] Y. Yang et al., *Advanced Materials*, vol. 36, no. 1, p. 2308332, 2024. DOI: <https://doi.org/10.1002/adma.202308332>.
- [43] D. Lee, A. Kumar Kakarla, S. Sun, P. Joohyun Kim, and J. Choi, *Chem-ElectroChem*, vol. 12, no. 3, c202400612, 2025. DOI: <https://doi.org/10.1002/ce1c.202400612>.
- [44] A. C. Radjendirane et al., *Langmuir*, vol. 40, no. 32, pp. 16690–16712, 2024. DOI: [10.1021/acs.langmuir.4c01845](https://doi.org/10.1021/acs.langmuir.4c01845).
- [45] A. Hayashi et al., *Nature Communications*, vol. 10, no. 1, p. 5266, Nov. 2019.

- [46] Z. Wei, L. F. Nazar, and J. Janek, *Batteries & Supercaps*, vol. 7, no. 7, e202400005, 2024. DOI: <https://doi.org/10.1002/batt.202400005>.
- [47] H. Oguchi, M. Matsuo, S. Kuromoto, H. Kuwano, and S. Orimo, *Journal of Applied Physics*, vol. 111, no. 3, p. 036 102, Feb. 2012, ISSN: 0021-8979. DOI: 10.1063/1.3681362.
- [48] G. Liu, J. Yang, J. Wu, Z. Peng, and X. Yao, *Advanced Materials*, vol. 36, no. 37, p. 2311 475, 2024. DOI: <https://doi.org/10.1002/adma.202311475>.
- [49] H. Li, X. Jiang, J. Zhang, and J. Zhang, *Materials Today Communications*, vol. 34, p. 105 203, 2023, ISSN: 2352-4928. DOI: <https://doi.org/10.1016/j.mtcomm.2022.105203>.
- [50] Z. Li et al., *Energy & Fuels*, vol. 35, no. 11, pp. 9063-9079, 2021. DOI: 10.1021/acs.energyfuels.1c00347.
- [51] A. V. Shinde et al., *Batteries & Supercaps*, vol. 9, no. 4, e202500251, 2026. DOI: <https://doi.org/10.1002/batt.202500251>.
- [52] S. Song, H. M. Duong, A. M. Korsunsky, N. Hu, and L. Lu, *Scientific Reports*, vol. 6, no. 1, p. 32 330, Aug. 2016.
- [53] Q. Ma and F. Tietz, *ChemElectroChem*, vol. 7, no. 13, pp. 2693-2713, 2020. DOI: <https://doi.org/10.1002/celec.202000164>.
- [54] Y. He, X. Zhang, C. Liu, Y. Yang, and X. Rui, *Metals Advances*, 2026, ISSN: 3117-7220. DOI: <https://doi.org/10.1016/j.metadv.2026.02.033>.
- [55] J. Goodenough, H.-P. Hong, and J. Kafalas, *Materials Research Bulletin*, vol. 11, no. 2, pp. 203-220, 1976, ISSN: 0025-5408. DOI: [https://doi.org/10.1016/0025-5408\(76\)90077-5](https://doi.org/10.1016/0025-5408(76)90077-5).
- [56] H. P. Hong, *Materials Research Bulletin*, vol. 11, no. 2, pp. 173-182, 1976, ISSN: 0025-5408. DOI: [https://doi.org/10.1016/0025-5408\(76\)90073-8](https://doi.org/10.1016/0025-5408(76)90073-8).

- [57] C. Li, R. Li, K. Liu, R. Si, Z. Zhang, and Y. Hu, *Interdisciplinary Materials*, vol. 1, no. 3, pp. 396–416, 2022. DOI: <https://doi.org/10.1002/idm2.12044>.
- [58] H. Park, K. Jung, M. Nezaferati, C. Kim, and B. Kang, *ACS Applied Materials & Interfaces*, vol. 8, no. 41, pp. 27 814–27 824, 2016. DOI: [10.1021/acsami.6b09992](https://doi.org/10.1021/acsami.6b09992).
- [59] H. Yang, B. Zhang, K. Konstantinov, Y. Wang, H. Liu, and S. Dou, *Advanced Energy and Sustainability Research*, vol. 2, no. 2, p. 2 000 057, 2021. DOI: <https://doi.org/10.1002/aesr.202000057>.
- [60] Z. Yang, B. Tang, Z. Xie, and Z. Zhou, *ChemElectroChem*, vol. 8, no. 6, pp. 1035–1047, 2021. DOI: <https://doi.org/10.1002/celec.202001527>.
- [61] L. Liu et al., *Journal of Power Sources*, vol. 626, p. 235 773, 2025, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2024.235773>.
- [62] L. Liu et al., *Advanced Energy Materials*, vol. 15, no. 18, p. 2 404 985, 2025. DOI: <https://doi.org/10.1002/aenm.202404985>.
- [63] A. Tiwari, D. Meghnani, R. Mishra, R. K. Tiwari, A. Patel, and R. K. Singh, *Journal of Power Sources*, vol. 580, p. 233 365, 2023, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2023.233365>.
- [64] X. Xu, Z. Ai, Z. Xiu, Y. Shao, Y. Wu, and X. Hao, *Journal of Energy Storage*, vol. 115, p. 116 046, 2025, ISSN: 2352–152X. DOI: <https://doi.org/10.1016/j.est.2025.116046>.
- [65] M. Guin and F. Tietz, *Journal of Power Sources*, vol. 273, pp. 1056–1064, 2015, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2014.09.137>.
- [66] S. Naqash, F. Tietz, E. Yazhenskikh, M. Müller, and O. Guillon, *Solid State Ionics*, vol. 336, pp. 57–66, 2019, ISSN: 0167–2738. DOI: <https://doi.org/10.1016/j.ssi.2019.03.017>.

- [67] Z. Sun et al., *Nano Letters*, vol. 22, no. 17, pp. 7187–7194, 2022. DOI: 10.1021/acs.nanolett.2c02509.
- [68] S. He, Y. Xu, Y. Chen, and X. Ma, *J. Mater. Chem. A*, vol. 8, pp. 12594–12602, 25 2020. DOI: 10.1039/C9TA12213C.
- [69] B. Santhoshkumar, M. B. Choudhary, A. K. Bera, S. M. Yusuf, M. Ghosh, and B. Pahari, *Journal of the American Ceramic Society*, vol. 105, no. 7, pp. 5011–5019, 2022. DOI: <https://doi.org/10.1111/jace.18463>.
- [70] J. Lee, C. Chang, Y. I. Lee, J. Lee, and S. Hong, *Journal of the American Ceramic Society*, vol. 87, no. 2, pp. 305–307, 2004. DOI: <https://doi.org/10.1111/j.1551-2916.2004.00305.x>.
- [71] A. Jalalian-Khakshour, C. O. Phillips, L. Jackson, T. O. Dunlop, S. Margadonna, and D. Deganello, *Journal of Materials Science*, vol. 55, no. 6, pp. 2291–2302, Feb. 2020.
- [72] S. Naqash, Q. Ma, F. Tietz, and O. Guillon, *Solid State Ionics*, vol. 302, pp. 83–91, 2017, ISSN: 0167–2738. DOI: <https://doi.org/10.1016/j.ssi.2016.11.004>.
- [73] Q. Ma, M. Guin, S. Naqash, C. Tsai, F. Tietz, and O. Guillon, *Chemistry of Materials*, vol. 28, no. 13, pp. 4821–4828, 2016. DOI: 10.1021/acs.chemmater.6b02059.
- [74] Y. Liu et al., *Journal of Power Sources*, vol. 518, p. 230765, 2022, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2021.230765>.
- [75] L. Xiang, X. Li, J. Xiao, L. Zhu, and X. Zhan, *Advanced Powder Materials*, vol. 3, no. 3, p. 100181, 2024, ISSN: 2772–834X. DOI: <https://doi.org/10.1016/j.apmate.2024.100181>.
- [76] M. Irfan, K. H. Khan, A. Shah, and H. Hussain, *Mater. Adv.*, 2026. DOI: 10.1039/D5MA01290B.
- [77] F. Wu et al., *Energy Storage Materials*, vol. 33, pp. 26–54, 2020, ISSN: 2405–8297. DOI: <https://doi.org/10.1016/j.ensm.2020.08.002>.

- [78] D. M. Pesko et al., *Solid State Ionics*, vol. 289, pp. 118–124, 2016, ISSN: 0167-2738. DOI: <https://doi.org/10.1016/j.ssi.2016.02.020>.
- [79] H. Pourzolfaghar et al., *Chemical Engineering Journal*, 2024.
- [80] Z. Li et al., *Advanced Science*, vol. 10, no. 10, p. 2201718, 2023. DOI: <https://doi.org/10.1002/advs.202201718>.
- [81] Q. Zhang et al., *Journal of The Electrochemical Society*, vol. 167, no. 7, p. 070523, Feb. 2020. DOI: 10.1149/1945-7111/ab741b.
- [82] R. Chandrasekaran and S. Selladurai, *Journal of Solid State Electrochemistry*, vol. 5, no. 5, pp. 355–361, Jul. 2001.
- [83] M. Sapri and A. Ahmad, *Jurnal Teknologi*, vol. 76, pp. 47–51, Sep. 2015. DOI: 10.11113/jt.v76.5510.
- [84] X. Qi et al., *ChemElectroChem*, vol. 3, no. 11, pp. 1741–1745, 2016. DOI: <https://doi.org/10.1002/celec.201600221>.
- [85] J. Serra Moreno, M. Armand, M. Berman, S. Greenbaum, B. Scrosati, and S. Pancro, *Journal of Power Sources*, vol. 248, pp. 695–702, 2014, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2013.09.137>.
- [86] Z. Zhang et al., *Journal of Power Sources*, vol. 372, pp. 270–275, 2017, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2017.10.083>.
- [87] D. Issayeva, E. Nurgaziyeva, A. Srikkazyyeva, A. Mentbayeva, and S. Kalybekkyzy, *Journal of Power Sources*, vol. 673, p. 239703, 2026, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2026.239703>.
- [88] H. Shi, C. Su, R. Ran, J. Cao, and Z. Shao, *Progress in Natural Science: Materials International*, vol. 30, no. 6, pp. 764–774, 2020, ISSN: 1002-0071. DOI: <https://doi.org/10.1016/j.pnsc.2020.09.003>.
- [89] N. Sammes and Y. Du, in *Fuel Cell Technologies: State and Perspectives*, N. Sammes, A. Smirnova, and O. Vasylyev, Eds., Dordrecht: Springer Netherlands, 2005, pp. 19–34, ISBN: 978-1-4020-3498-5.

- [90] Srijith, Lakhanlal, A. Das, H. P. Dasari, and M. Saidutta, *Ceramics International*, vol. 48, no. 19, Part B, pp. 29 229–29 237, 2022, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2022.05.198>.
- [91] Y. Higuchi, M. Sugawara, K. Onishi, M. Sakamoto, and S. Nakayama, *Ceramics International*, vol. 36, no. 3, pp. 955–959, 2010, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2009.10.022>.
- [92] A. G. Jolley, Q. Bai, R. Jayathilake, Y. Mo, and E. D. Wachsman, *Materials Today*, vol. 86, pp. 247–254, 2025, ISSN: 1369-7021. DOI: <https://doi.org/10.1016/j.mattod.2025.03.030>.
- [93] T. Takahashi, H. Iwahara, and T. Arao, *Journal of Applied Electrochemistry*, vol. 5, no. 3, pp. 187–195, Aug. 1975.
- [94] T. Takahashi, H. Iwahara, and Y. Nagai, *Journal of Applied Electrochemistry*, vol. 2, no. 2, pp. 97–104, May 1972.
- [95] R. Punni, A. M. Feteira, D. C. Sinclair, and C. Greaves, *Journal of the American Chemical Society*, vol. 128, no. 48, pp. 15 386–15 387, 2006. DOI: [10.1021/ja065961d](https://doi.org/10.1021/ja065961d).
- [96] P. Shuk, H. D. Wiemhöfer, U. Guth, W. Göpel, and M. Greenblatt, *Solid State Ionics*, vol. 89, no. 3, pp. 179–196, 1996, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/0167-2738\(96\)00348-7](https://doi.org/10.1016/0167-2738(96)00348-7).
- [97] D. S. Aidhy, J. C. Nino, S. B. Sinnott, E. D. Wachsman, and S. R. Phillpot, *Journal of the American Ceramic Society*, vol. 91, no. 7, pp. 2349–2356, 2008. DOI: <https://doi.org/10.1111/j.1551-2916.2008.02463.x>.
- [98] P. Battle, R. Catlow, J. Drennan, and A. Murray, *Journal of Physics C: Solid State Physics*, vol. 16, p. L561, Nov. 2000. DOI: [10.1088/0022-3719/16/17/003](https://doi.org/10.1088/0022-3719/16/17/003).
- [99] J. C. Boivin and G. Mairesse, *Chemistry of Materials*, vol. 10, no. 10, pp. 2870–2888, 1998. DOI: [10.1021/cm980236q](https://doi.org/10.1021/cm980236q).

- [100] A. Borowska-Centkowska et al., *RSC Adv.*, vol. 9, pp. 9640–9653, 17 2019. DOI: 10.1039/C9RA01233H.
- [101] M. Balci, M. A. Payveren, B. Saatci, and M. Ari, *Micro and Nanostructures*, vol. 194, p. 207944, 2024, ISSN: 2773-0123. DOI: <https://doi.org/10.1016/j.micrna.2024.207944>.
- [102] S. Wang, Y. Hsu, W. Tsai, and H. Lu, *Journal of Power Sources*, vol. 218, pp. 106–112, 2012, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2012.06.056>.
- [103] N. Jiang and E. D. Wachsman, *Journal of the American Ceramic Society*, vol. 82, no. 11, pp. 3057–3064, 1999. DOI: <https://doi.org/10.1111/j.1151-2916.1999.tb02202.x>.
- [104] I. Jeong, H. Yu, D. Lee, K. Roh, E. D. Wachsman, and K. T. Lee, *ACS Applied Materials & Interfaces*, vol. 17, no. 20, pp. 28961–28981, 2025. DOI: 10.1021/acsami.4c21320.
- [105] M. J. Verkerk, K. Keizer, and A. J. Burggraaf, *Journal of Applied Electrochemistry*, vol. 10, no. 1, pp. 81–90, Jan. 1980.
- [106] T. Takahashi, H. Iwahara, and T. Esaka, vol. 124, no. 10, p. 1563, Oct. 1977. DOI: 10.1149/1.2133111.
- [107] D. W. Jung, K. L. Duncan, and E. D. Wachsman, *Acta Materialia*, vol. 58, no. 2, pp. 355–363, 2010, ISSN: 1359-6454. DOI: <https://doi.org/10.1016/j.actamat.2009.08.072>.
- [108] W. Zhang, X. Ping, B. Meng, Q. Yang, H. Wang, and R. Pan, *Ceramics International*, vol. 51, no. 27, Part A, pp. 52359–52365, 2025, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2025.08.441>.
- [109] J. Park and E. D. Wachsman, *Ionics*, vol. 12, no. 1, pp. 15–20, May 2006.
- [110] M. Tian, H. Cao, L. Liu, and J. Xu, *Ceramics International*, vol. 50, no. 15, pp. 26548–26557, 2024, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2024.04.383>.

CHAPTER 2

Experimental Methods

2.1 Introduction

This chapter discusses the synthesis methodologies and the underlying principles of the characterization techniques employed to analyze the prepared materials. The synthesis section describes the sample preparation methods, including the solid state reaction method (SSR), solution assisted solid state reaction method (SA-SSR) and the hydrothermal based solid state reaction method (HT-SSR). For characterization, the phase identification was carried out using X-ray diffraction (XRD), while Neutron powder diffraction (NPD) measurement was employed as a complimentary technique. Microstructural and compositional characterization was performed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX). Thermal analysis of the samples was conducted using differential scanning calorimetry (DSC) study. The defect distribution in NASICON ceramics and free volume in polymer samples were assessed using positron annihilation lifetime spectroscopy (PALS). Furthermore, local structural information was obtained using Magic angle spinning NMR (MAS-NMR) and X-ray absorption spectroscopy (XAS). Electrochemical Impedance spectroscopy (EIS) was measured to analyze the conductivity of the prepared compositions. Finally, electrochemical performance was assessed using cyclic voltammetry (CV) and galvanostatic charge discharge cycling (GCD).

2.2 Synthesis methodologies

Different synthesis methods can be employed to tune the properties of a material and the choice of the method depends on the specific property targeted for optimization. In the present research work, optimizing the ionic conductivity was the primary objective, for which phase purity, densification and microstructure plays an important role.[1] Therefore, in this thesis work, solid state reaction method (SSR), solution assisted solid state reaction method (SA-SSR) and hydrothermal-based solid state reaction method (HT-SSR) were adopted for ceramic material synthesis. In case of the polymer film synthesis, solvent casting method was employed.

2.2.1 Solid state reaction method (SSR)

The solid state reaction (Ceramic) method is the conventionally used for synthesis of polycrystalline solids. It relies on diffusion controlled chemical reaction between solid precursors at elevated temperatures. In practice, stoichiometric amounts of reagents, determined from balanced chemical equation, are weighed and ground using mortar and pestle in presence of a volatile liquid medium, to attain homogeneity and then heated to form well-defined crystalline structures. These reactions initiate at the interface between the particles and proceed through diffusion after the surface layer has reacted. However, since both, the reaction and diffusion are slow at room temperature, elevated temperatures are employed to increase the reaction rate and promote ionic diffusion. Additionally, strategies like fine grinding are used to reduce the particle size and increase the surface contact area, while pelletising the mixed powders can further improve interparticle contact. The reaction is also accelerated by using multiple heating cycles and intermittent grindings to expose fresh surfaces for continued reactions. Despite its widespread use, this method often results in the formation of large particle sizes, resulting in agglomeration and lower homogeneity.[2]

2.2.2 Solution-assisted solid state reaction method (SA-SSR)

Solution-assisted solid state reaction (SA-SSR) is based on aqueous approach, in which water or acid soluble precursor sources such as nitrates, acetates, or carbonates are used to form homogeneous cationic mixtures in liquid medium. This method employs liquid medium for better mixing of precursors, followed by traditional solid state reaction route[3]. The SA-SSR method offers several advantages including, absence of sensitive parameter control and ease of scale-up. It also improves the sinterability of SA-SSR ceramic, consequently reducing the grain boundary resistance[4]. For the synthesis of NASICON compositions in this thesis, SA-SSR method was adopted as reported by Naqash *et al.* and Ma *et al.*

2.2.3 Hydrothermal based solid state reaction method (HT-SSR)

In hydrothermal method of synthesis, reactants are heated in water/steam at high pressures and temperatures. The water/steam serves dual role as a pressure transmitting medium and a solvent.[5] The high pressure condition is expected to increase the reactivity of chemical species in the reaction mixture. For the ceramic preparation in this work, the hydrothermal method was used as an intermediate step within the SA-SSR synthesis route. In HT-SSR approach, the reaction mixture (sol + precipitate) obtained from the SA-SSR method was transferred into a PTFE-lined cylinder, sealed and heated at 150 °C for 7 h. Following this, solid state route was employed. Thus, HT-SSR method combines the advantages of hydrothermal method like increased reactivity and reduced particle size with those of solid state synthesis.

2.3 Characterization techniques

2.3.1 Powder Diffraction

Diffraction technique is based on constructive interference of X-ray/electron/ Neutron waves, after they are elastically scattered from a crystalline sample. Due to the periodic nature of the atoms in a crystal, it effectively behaves as a three-dimensional diffraction grating for the radiation of a suitable wavelength. For the diffraction to occur, the wavelengths used for the study of crystal structure must be comparable to the order of the distance between atoms in crystals.[2], [6]

2.3.1.1 Bragg's law

Figure 2.1, represents a set of parallel lattice planes with inter planar spacing of d . When a monochromatic x-ray beam is incident on the surface of a crystal, it is reflected by the atomic planes within the crystals. The Bragg diffraction occurs when radiation of a wavelength λ is scattered by these planes in specular fashion (mirror-like reflection) and undergoes constructive interference.[7], [8]

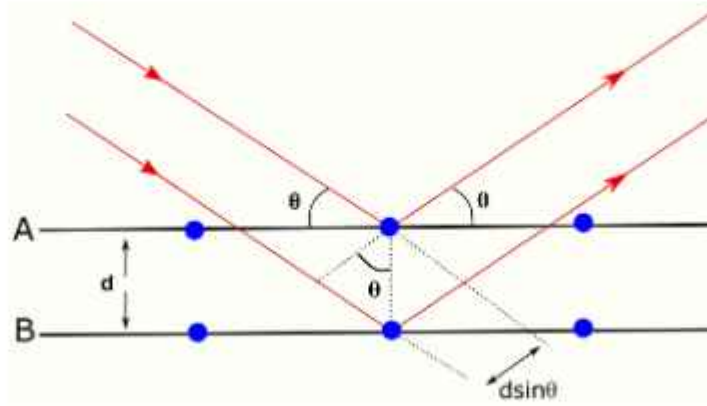


Figure 2.1: Reflection of X-ray from a crystal

For the constructive interference to occur between the rays reflected from successive planes, the path difference between consecutive rays must be an integral

multiple (n) of wavelengths λ . This condition is expressed as:

$$2d \sin \theta = n\lambda, \quad n = 1, 2, \dots$$

Where, θ is the glancing angle and n is the order of reflection. For a given d and λ value, if the angle differs from the Bragg angle, reflected rays remain out of phase with each other and interfere destructively.[7]

The intensity of Bragg reflection diffracted from a set of planes corresponding to miller indices (hkl) is of the form [7],

$$I \sim |F_{hkl}|^2$$

The F_{hkl} is called the structure factor and represents the resultant amplitude of waves scattered by all the atoms within a unit cell in the direction of the hkl reflection,[2]. Accordingly, it can be expressed as,

$$F_{hkl} = \sum_j f_j \exp [2\pi i(hx_j + ky_j + lz_j)]$$

Where, f_j denotes the scattering factor of the j^{th} atom and represents the contribution of scattered amplitude from an individual atom, while x_j , y_j and z_j are its fractional coordinates.[2] The scattering factor/atomic form factor is further expressed as,

$$f_j(q) = \int \rho(\mathbf{r}) e^{i(\mathbf{q} \cdot \mathbf{r})} d^3r, \quad |\mathbf{q}| = \frac{4\pi \sin \theta}{\lambda}$$

Where, q is the scattering wave vector and $\rho(r)$ is the electron density.[7],

X-ray and Neutron diffraction both follow the principle of Bragg's law, but they provide complimentary information. The main difference lies in their scattering mechanisms: X-rays are scattered by the electrons cloud around the nucleus, whereas the neutrons are scattered by the nuclei itself. As indicated by the expression of atomic form factor (f_j), in case of X-ray, the scattering power is proportional to the number of electrons in the scattering atom (electron density). There-

fore, in X-ray diffraction, heavier atom scatters more strongly than the lighter one. In contrast, neutron scattering power is dependent on neutron scattering length and neighboring elements in the periodic table may scatter neutrons with markedly different intensities. In addition, due to the size of the electron cloud relative to the X-ray wavelength, the scattering from different regions of the cloud may not always be in phase and result in decrease of scattering power with $\sin \theta / \lambda$, unlike the neutron scattering power.[2], [5], [9] Therefore, neutron diffraction can help distinguish atoms with similar X-ray scattering power and locate lighter atoms, much more accurately.[5]

2.3.1.2 Structural Analysis by Rietveld refinement

The detailed information about the crystal structure, atomic positions, lattice parameters and site occupancies of atoms within the unit cell of materials, can be extracted from the diffraction pattern by fitting the shape and intensities of the reflections via Rietveld refinement method.[10] Rietveld method involves a whole pattern refinement in which the experimental powder diffraction profile is compared with a calculated profile, and the difference is used to refine the atomic coordinates of the structural model.[5], [11] The calculated intensity at point x_i is given by the equation,

$$y_{C,i}(x_i) = s \sum_k m_k (LP)_k |F_k|^2 P_k \Phi(x_i - x_k) + b(x_i)$$

Where, s is a scale factor, F_k is the structure factor, m_k is the reflection multiplicity, P_k is a function to deal with the preferred orientation of the crystallites, $\Phi(x_i - x_k)$ is a profile function where x_i is the diffraction angle corrected for the 2θ zero error, $b(x_i)$ is the intensity of background and LP are the Lorentz, polarization factors.[10]

The calculated powder XRD profile is generated using a starting structural model that incorporates a description of peak shapes and background parameters.[12] In Rietveld method, there are two groups of refineable parameters, which includes,

the ones that are associated with the structural model (atomic coordinates x_i , y_i and z_i , atomic displacement parameters, unit-cell dimensions) and those related to the instrumental model (angular dependence of the profile parameters, FWHM and shape factors, 2θ -zero position, preferred orientation).[11]

The Rietveld algorithm assesses the validity of the structure by minimizing the weighted sum of squared differences between the observed and computed intensity values, i.e.,

$$\sum_i w_i (y_{C,i} - y_{O,i})^2$$

Where, w_i is $1/\sigma(y_{O,i})^2$ weighting, and $\sigma(y_{O,i})$ is the experimental uncertainty in $y_{O,i}$.

The progress of refinement through the multiple iterative steps is also monitored using the weighted profile R factor, R_{wp} , which should tend to a low value,[12]

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^N w_i (y_{C,i} - y_{O,i})^2}{\sum_{i=1}^N w_i (y_{O,i})^2}}$$

or a quantity such as goodness of fit (GoF) or χ , which relates R_{wp} to the statistically expected value R_{exp} (also known as the best possible R_{wp} value depending on the experimental data quality and correct $\sigma(y_{O,i})$ values)[13],

$$\text{GOF} = \chi = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum_{i=1}^N w_i (y_{C,i} - y_{O,i})^2}{N - P}}$$

Where, N is the number of data points and P the number of parameters. χ should tend to 1 for a good refinement.[12] The quality of a Rietveld fit is determined by viewing the observed and calculated patterns graphically and ensuring that the model used for fitting is chemically plausible.[13]

Powder XRD data presented in this thesis, was recorded using Rigaku Smartlab X-ray diffractometer at Material characterization laboratory (MCL), Goa university. The diffractometer typically operates at 40 kV and 40 mA and the data was collected using Cu k_α radiation in the diffraction angle range of 10 to 80° with step size of 0.02°.

Neutron diffraction powder patterns for the samples at room temperature and high temperature, were recorded using neutron powder diffractometer PD-2 ($\lambda=1.2443 \text{ \AA}$) at Dhruva reactor, BARC, Trombay, India. The structural analysis of both XRD and NPD data was carried out using Fullprof software suite[14].

2.3.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX)

In scanning electron microscopy, a finely focused beam of electrons is scanned in raster pattern across the surface of the sample and the electrons scattered from the surface are detected to produce an image showing the surface topography of the sample.[2] A schematic diagram of scanning electron microscope is shown in Figure 2.2.

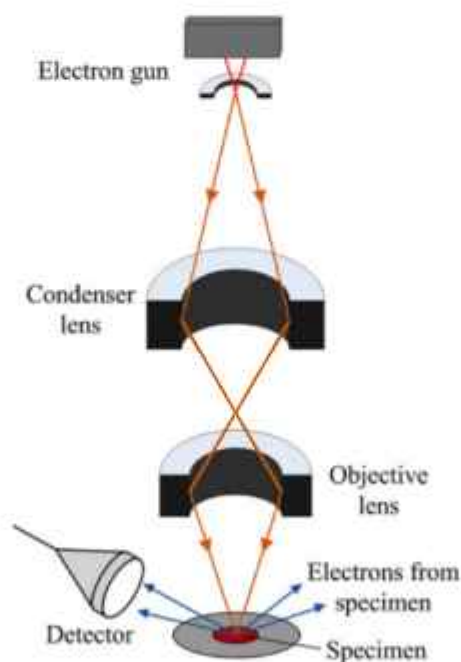


Figure 2.2: Schematic of a scanning electron microscope [15]

In a SEM microscope, the electrons are generated by an electron gun, then accelerated and directed through the condenser and objective lenses, which focus the beam to a diameter of few nanometers. This finely focused beam bombards

the specimen surface, causing interactions which produce various electron signals. These emitted signals are then collected by the detector and converted into an image, with the contrast determined by the intensity of detected electrons.[15]

Different signals produced during the interaction of the electron beam with the sample surface can be broadly classified into elastic and inelastic interactions.[16]

Elastic scattering involves interaction of the incident electron with the atomic nucleus or the outer shell electrons of similar energy, giving rise to the back-scattered electrons (BSE). In contrast, during the inelastic scattering, incident (primary) electron transfer significant energy to the sample electron, which may then be ejected from the atom and emitted as secondary electrons (SEs).[16] The detection of the secondary electrons is the most common mode of imaging in SEM and is used to obtain topographic contrast in the sample (surface texture and roughness) [16], [17], [18]. BSEs, on the other hand, provide both compositional and topographic information in the SEM.[16]

Another class of signals produced by the interaction of the primary electron beam with the specimen is characteristic x-rays.[17] When an inner shell electron is stimulated and ejected, and an outer shell electron drops down to fill the hole, resulting in emission of an x-ray. This characteristic x-ray has energy specific to the element from which it was emitted. Therefore, analysis of this characteristic x-rays can provide chemical information of the sample under study and is called energy dispersive X-ray spectroscopy (EDX).[18]

In conventional SEM, the surface of the sample must be electrically conductive and grounded to prevent accumulation of electrostatic charge at the surface, as it can lead to electrostatically distorted images. To minimize this issue, non conductive samples are sputtered with conductive layer of gold.[2], [18]. The SEM, EDX data in current work were collected at University Science Instrumentation Center (USIC), Goa University, on a Carl-Zeiss SEM setup with EDX facility.

2.3.3 Electrochemical Impedance Spectroscopy (EIS)

In an EIS experiment, small amplitude stimulus (voltage or current) is applied to an electrochemical system and the resulting response (current or voltage, respectively) is measured over a wide range of frequencies.[19] This response shares the frequency of the input, but its phase and amplitude may vary due to the complex impedance of the electrochemical system.[20]

The perturbative excitation signal applied to the electrochemical system at the frequency of ω can be expressed as,

$$E_t = E_0 \sin(\omega t)$$

The resulting response signal I_t , which is shifted in phase (ϕ) and has a different amplitude, I_0 can be expressed as [21],

$$I_t = I_0 \sin(\omega t + \phi)$$

By using an expression analogous to Ohm's Law, impedance of the system can be calculated,[21]

$$Z = \frac{E_t}{I_t} = |Z|e^{-i\phi} = Z' + iZ''$$

Where,

$$Z' = |Z| \cos \phi \quad \text{and} \quad Z'' = -|Z| \sin \phi$$

In the above equation, real part Z' represents resistance on the x-axis and imaginary part Z'' represents reactance on the y-axis.[22] By measuring the impedance over wide range of frequencies, different regions of the material can be separated according to their electrical relaxation times or time constants[23]. In polycrystalline electrolytic system, higher frequency processes often correspond to the response of fastest processes, such as ion migration, while, slow phenomena, such as diffusion, dominates the low frequency.[19], [20] The relaxation time constant,

corresponding to such processes is of form,

$$\tau = RC$$

Where, R is the resistance (Ω) and C is the capacitance (F) of the elements that can be used to model the behaviour of these processes.[20]

The impedance data is commonly presented using Nyquist plot where the imaginary part, $-Z''$, is plotted as a function of the real part, Z' . A schematic representation of Nyquist plot is shown in Figure 2.3.

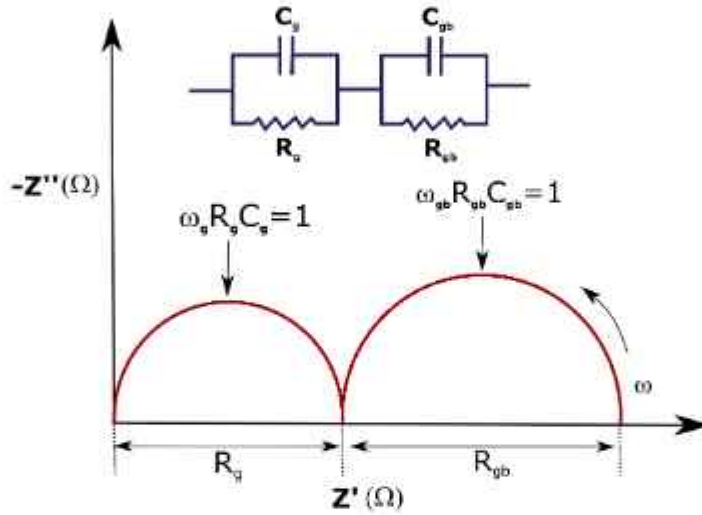


Figure 2.3: Nyquist plot for equivalent circuit containing two parallel RC elements in series [20]

As illustrated in Figure 2.3, Nyquist plot ideally appears as a semicircle for a polarization process characterized by a single RC time constant.[19] The highest arc of this semicircle corresponds to the peak frequency ω_{max} which satisfies the equation, $2\pi f_{max}RC = 1$ and thus help in distinguishing electrochemical regions.[23] In polycrystalline samples, two distinct features corresponding to intra-grain (bulk) and inter-grain (grain boundary) regions are generally observed. In Nyquist plot, these contributions appear as semicircles at high frequency end of the plot with an additional low frequency spike corresponding to the sample-electrode interface.[23] Experimentally, these contributions are identified based on the magnitudes of the capacitances used for modeling the impedance spectra (Nyquist plot). Typically,

capacitance of the order of 10^{-12} F are associated with the bulk region, those with order of 10^{-11} - 10^{-8} F are attributed to grain boundary, whereas values between 10^{-7} - 10^{-5} F correspond to sample-electrode interface.[23]

In some samples, a depressed or broadened semicircle is obtained, which cannot be fitted adequately using simple capacitor element during the equivalent circuit fitting. Therefore, in such cases, impedance data was modeled using constant phase element (CPE) rather than an ideal capacitor. The relationship between the ideal capacitor (C) and CPE is given by,

$$C = R^{\frac{1-n}{n}} C_{CPE}^{1/n}$$

Where, n is the degree of deviation from the ideal capacitor. For a pure capacitor, the n value is equal to 1.[4]

After the data analysis, the ionic conductivity of the sample is extracted from the impedance data using the equation,

$$\sigma_{\text{total}} = \frac{l}{R_{\text{total}} A}$$

Where, l and A are the thickness and area of the sample and $R_{\text{total}} = \frac{1}{R_g + R_{gb}}$, is the total resistance of the sample.[20] The ionic conductivity is temperature-activated and commonly follows Arrhenius-like temperature dependence which is of the form,

$$\sigma_{\text{ionic}} = \frac{\sigma_0}{T} e^{-\frac{E_a}{kT}}$$

where, E_a is the activation energy and k is the Boltzmann constant. σ_0 is a pre-exponential factor.[20]

Impedance data in this thesis, were measured using PSM1735-NumetriQ impedance analyzer (Newtons4th Ltd. UK) at BARC, Trombay and HIOKI IM3570 impedance analyzer (Japan) at SPAS, Goa university. The temperature dependent measurement were carried out in the frequency range of 10 Hz-8 MHz. The obtained EIS data was subsequently analyzed and fitted using EISSA soft-

warc.[24]

2.3.4 Differential Scanning Calorimetry (DSC)

DSC measures the heat absorbed or released by sample by tracking the temperature difference between the sample and a reference material while both are heated at a constant rate.[2], [25] During the occurrence of a thermal event in the sample (melting, decomposition or structural transition), its temperature lags (endothermic) or leads (exothermic) relative to the reference.[5]

When no physical or chemical change occurs in the sample at temperature T , the heat transferred to the sample is,

$$q_p = C_p \Delta T$$

Where, C_p is the specific heat of the sample at constant pressure and ΔT is the temperature difference between the sample and the reference material.

During a thermal event, in order to attain the same change in temperature of the sample as the reference, excess energy needs to be transferred, which can be described as,

$$q_p + q_{p,\text{ext}} = C_{p,\text{ext}} \Delta T$$

Therefore, the enthalpy change associated with the thermal event is,

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ext}} dT$$

Where, T_1 and T_2 are the temperatures at which the thermal event begins and ends. This enthalpy change is depicted graphically as DSC thermogram and can be calculated from the area under the plot of $C_{p,\text{ext}}$ against T . [9]

Samples weighing ~ 7 -10 mg were spread evenly within an aluminium pan and covered with lid. These pans were then sealed using a crimper. Correspondingly, an identical empty aluminium pan was used as reference. The DSC measure-

ments were carried out using DSC-60 (Shimadzu) with heating and cooling rates of 5 °C min, at SPAS, Goa University

2.3.5 Positron annihilation lifetime spectroscopy (PALS)

Positron annihilation lifetime spectroscopy is a characterization method used for probing the local electron density at the site of positron interaction. This method is used to experimentally investigate local structures embedded in the bulk of the material, including missing atoms (vacancies) in ceramics and free volume in polymers.[26] The basic aspects of PALS is illustrated in schematically in Figure 2.4.

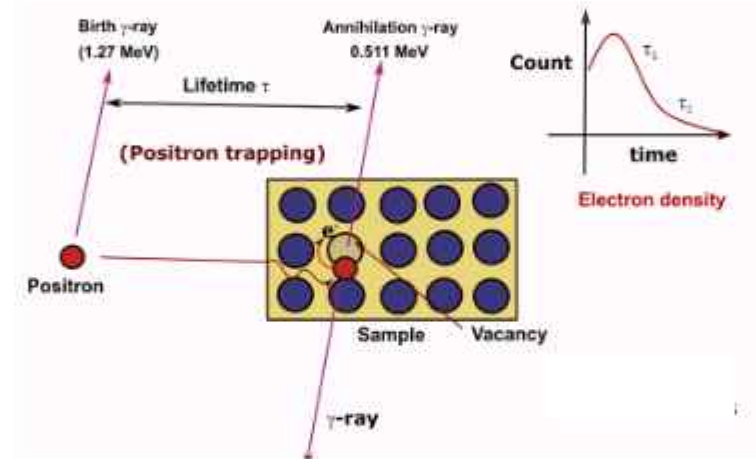


Figure 2.4: Schematic representation of positron annihilation process [27]

In a PALS experiment, positrons emitted from a radioactive nuclei like ^{22}Na are injected into a solid material. After entering the medium, positron rapidly lose their kinetic energy and thermalize within ~ 1 ps. After thermalization, positron annihilates with electrons from the medium. This annihilation results into an emission of two γ rays of 0.511 MeV each. This annihilation rate (inverse of lifetime) depends on the electron density at the site of positron annihilation. Therefore, by measuring the time delay between the birth gamma ray (signaling birth of positron) and the annihilation gamma rays, positron lifetime in the material can be determined.[28] This time delay also depends on the state in which the injected positron exists, within the medium. Figure 2.5 summarizes the alternative annihilation modes of a positron.[26]

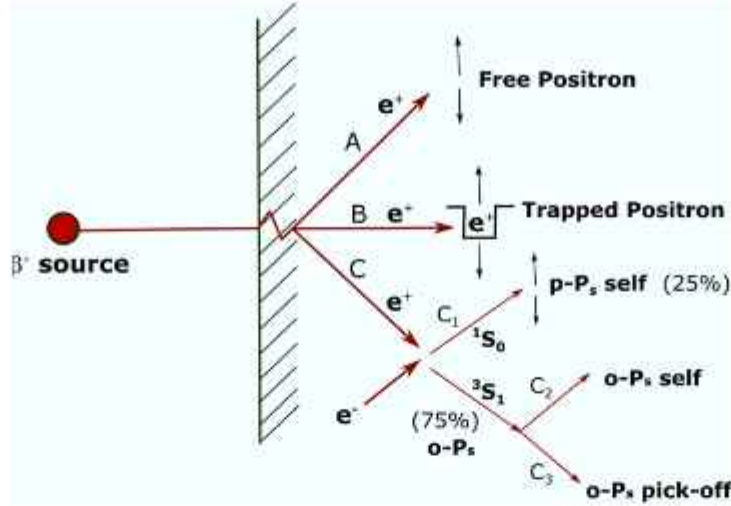


Figure 2.5: Schematic representation of annihilation modes in PAS [26]

When a positron comes in contact with an electron, it may either annihilate into two γ -rays in case of high electron density or form positronium (Ps) in case of low electron density/near surface regions [29]. The free positronium (Ps) has two intrinsic lifetimes depending on the spin combination of the electron-positron pair, i.e, 0.125 ns for para-Ps (p -Ps, antiparallel spins) and 142 ns for ortho-Ps (o -Ps, parallel spins).[30] However, in solids, p -Ps is scarcely influenced by its environment (negligible changes in lifetime) whereas, o -Ps predominantly decays via pick-off annihilation with electron of opposite spin from the medium.[31]

Both, positron and positronium exhibit strong tendency to localize in the regions of low electron density. This localization is reflected in the annihilation characteristic and forms the basis for using positrons as a probe for the study of defects in solids.[30], [32].

A free positron in a crystal lattice experiences strong repulsion from the positively

Table 2.1: Lifetime for Positron annihilation modes

Annihilation mode	Lifetime (τ) (ns)
Free positron	0.1-0.5
Trapped positron	0.2-1.0
p -Ps self	0.125
o -Ps self	140
o -Ps pick-off	0.6-10

charged ion cores. In regions of low electron density, this repulsion is lowered, allowing such regions to act as traps for positron, especially in crystalline solids.[26] The interaction between Ps and matter is also predominantly repulsive due to the electron-electron repulsion. Therefore, in polymeric material, Ps tends to localize in open spaces of the host structure. Thus, as long as its lifetime is less than that of the cavity hosting it, Ps can probe for free volume holes.[33]

A PALS spectrum consists of a sum of number of components, each corresponding to a particular positron state.[33] For a lattice, consisting of k different types of defects with individual positron lifetime τ_i and intensities I_i , the corresponding positron spectrum will contain $k + 1$ terms attributed to these defects including the bulk contribution. The PALS lifetime spectra (+1 for bulk) can be expressed as ,[29]

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} e^{-t/\tau_i}$$

In solids, the positron lifetime (inverse of the annihilation rate) can be attributed to the size of the defect, while its intensity can be correlated to defect concentration. In order to extract the lifetime components, experimental data is fitted with the above equation and two or three lifetime components are commonly used for fitting. The fastest component τ_1 is assigned to free and p -Ps decay, while the longer ones τ_2 and τ_3 , are attributed to pick-off annihilation of o -Ps.[32] Typical range of lifetime values are shown in Table 2.1.

Positron annihilation measurements were performed at Solid State Radiochemistry Division, BARC, Trombay. Measurements were carried out using a ^{22}Na positron source ($\sim 10 \mu\text{Ci}$) and detected using two BaF_2 scintillation detectors connected to a fast-fast coincidence system. The positron source was sealed within the Kapton foil and buried in the electrolyte powder (ceramic samples) or sandwiched between the stack of films (polymer films) and kept between the detectors in 90° configuration. The total number of counts acquired in each spectrum was approximately 10^6 . The fraction of positrons annihilating in source material (Kapton) was corrected by subtracting the source component obtained through acquiring a

positron annihilation lifetime (PAL) spectrum on a reference material (silicon single crystal with positron lifetime 218 ps). The time resolution measured with ^{60}Co in the ^{22}Na energy window settings was 220 ps. The time calibration was kept at 12.5 ps/channel. The obtained PAL spectra was analyzed using the PALSfit analysis program.[34]

2.3.6 Magic angle spinning Nuclear Magnetic resonance spectroscopy (MAS-NMR)

NMR is a spectroscopic technique that manipulates the interactions between nuclei with non-zero magnetic moments and the applied magnetic field. These interactions are strongly influenced by the local electronic environment surrounding the observed nucleus, providing an insight into chemical properties as well as dynamics of the material.[35] Nuclei with non zero spin ($I \neq 0$) possess a magnetic moment μ of the form,

$$\mu = \gamma I$$

Where, γ is the magnetogyric ratio of the specified nucleus.[9] When this nuclei is placed in the external magnetic field, B_0 (field along z axis), the energy of interaction between the nuclear magnetic moment and its external field can be described as [9], [35],

$$E = -\gamma \hbar B_0 m_I$$

In the external magnetic field the degeneracy of the nuclear spin states is lifted, leading to an energy difference of ΔE [36], (also known as Zeeman splitting)

$$\Delta E = \gamma \hbar B_0$$

In its original form, the magnetic resonance experiment involves resonant absorption of radiation by nuclei placed in a magnetic field. If the sample is exposed to radiation of frequency ν , resonance occurs when the energy separations between

the nuclear spin states matches the energy of applied radiation,[9],

$$h\nu_0 = \gamma h B_0$$

This frequency ν_0 is called the Larmor frequency of the nuclear moments. The resonance absorption of the radiation at Larmor frequency is subsequently detected as NMR signal. At the fields commonly applied in NMR experiment (about 7-12 T), these Larmor frequencies typically lie in the radio frequency region of the electromagnetic spectrum.[9]

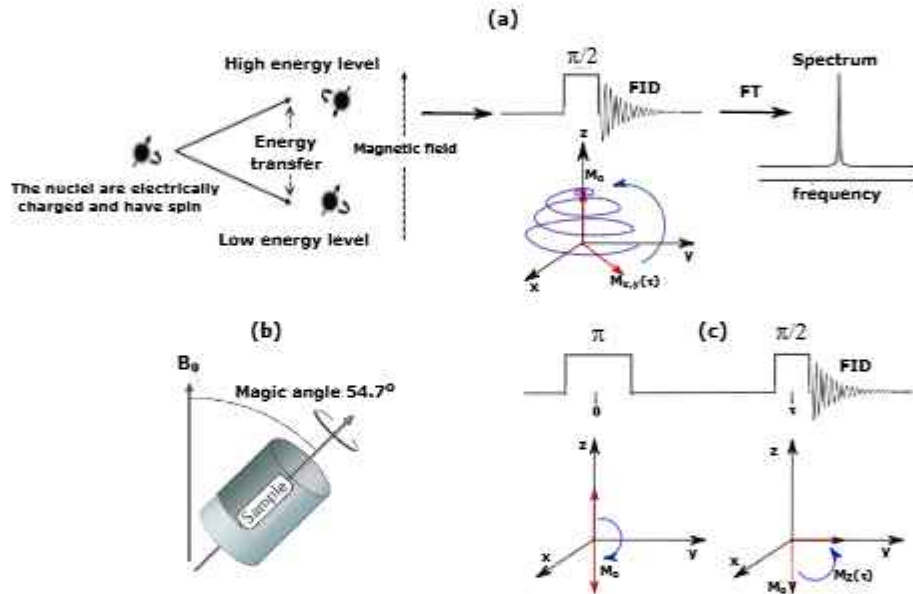


Figure 2.6: Schematic representation of (a) NMR experiment, (b) MAS-NMR technique and (c) Inversion recovery method [35], [36], [37], [38]

Figure 2.6(a) shows the schematic of a typical NMR experiment. In the presence of an external magnetic field (B_0), nuclear magnetic moments align along the direction of the field constituting longitudinal magnetization, M_z . Upon RF irradiation, the net magnetization is tipped into the transverse (x-y) plane, where it rotates around the z axis. This rotating magnetization induces a voltage in the detection coil. Due to internal NMR interactions, transverse magnetization loses coherence while longitudinal magnetization gradually recovers to equilibrium. This causes a decay of the induced voltage, which is measured as the free induction decay (FID)

and subsequently fourier transformed (FT) from time to frequency space to get the NMR spectrum.[39]

In nuclei with $I \neq 0$, the exact resonance frequency of an NMR line is determined not only by the Zeeman interaction, but also by the surrounding electron density (Chemical shift and, for $I > 1/2$, quadrupolar interactions) and direct magnetic dipolar interactions between the nuclei. These interaction are generally anisotropic, i.e., they are dependent on the orientation of the magnetic moment w.r.t static magnetic field or the magnetic moments of the coupled nuclei. In solution-state NMR measurement, these anisotropic interactions are averaged by the rapid tumbling of molecules, resulting in well resolved spectral line. However, in solid-state NMR, they are retained, resulting in broadening of spectral lines.[40] Thus, the resonance frequency of a nuclei in a solid-state NMR can be expressed as a sum of various orientation dependent nuclear magnetic interactions, given by

$$\nu(\Omega) = \nu_0 + \nu_{CS}(\Omega) + \nu_Q(\Omega) + \nu_{DD}(\Omega)$$

Where, ν_0 stands for the Larmor frequency (the Zeeman interaction term), ν_{CS} is the chemical shift of the frequency, ν_Q is the quadrupolar interaction term (existing only for spins $I > 1/2$) and ν_{DD} is the dipolar interaction term. The symbol Ω in above equation is a notation for the orientation dependence of the frequencies. [40], [41]

The chemical shift contribution $\nu_{CS}(\Omega)$ is the small modification of the fundamental Larmor frequency ν_0 caused by the shielding of the electron density surrounding the observed nucleus. The local magnetic field experienced by the target nuclei may differ from the applied magnetic field, because the latter induces circulation of electronic currents, which gives rise to a small additional field at the nucleus.[9] As a result, the net magnetic field experienced by the nuclei is altered, leading to a shift in the NMR signal.[9], [35], [39].

The chemical shift is defined as the difference between the resonance frequency, ν ,

of the nucleus under observation and that of a reference standard, ν_0 , [9]

$$\delta = \frac{\nu - \nu_{ref}}{\nu_{ref}} \times 10^6$$

The quadrupole interaction (ν_q) is an electrical interaction between the non-symmetric charge distribution of the nucleus (existing for spins $I > 1/2$) and the charge distribution of the electronic surroundings, while the dipolar interaction (ν_{DD}) describes the interaction of the nuclear magnetic moments with each other. [40]

In order to eliminate the orientational dependence of the NMR anisotropic interactions in solid-phase samples, the magic-angle spinning (MAS) NMR technique is generally employed. As illustrated in Figure 2.6(b), during the MAS-NMR technique the sample is physically spun around an axis inclined at 54.7° relative to static magnetic field, thereby averaging out anisotropy of nuclear interactions. [36], [39], [41]

The investigation of NMR relaxation time can be effectively used in the study of dynamics in materials. [37], [42] NMR relaxation refers to the process by which magnetization perturbed by radio frequency excitation, returns to the equilibrium position. [37], [42] In current work, spin-lattice relaxation rate (SLR) measurements were used for characterization and measured using inversion recovery method. [37] As illustrated in Figure 2.6(c), inversion recovery method begins with 180° pulse which inverts all signals/magnetization, followed by a variable delay time (v_d) during which relaxation towards the equilibrium is allowed to occur, and finally 90° pulse that flips the recovered longitudinal magnetization into transverse plane for spectral acquisition. [43] This experiment produces a series of spectra of differing signal intensity as a function of variable delay time. The T_1 relaxation is then obtained by fitting a plot of signal intensity as a function of variable delay time (v_d) with one (or a series of) exponential functions as shown by the following equation,

$$M_z(\tau) = |M_0| (1 - 2e^{-\tau/\tau_1})$$

Where M_0 and τ represent the equilibrium magnetization, and the time elapsed after the completion of the radio frequency excitation field.[37]

Solid-state MAS NMR measurements of the samples in current work, were carried out at Dr. Harisingh Gour University, Madhya Pradesh. ^{23}Na MAS-NMR spectra were collected on a JEOL ECX 500 MHz spectrometer with the use of a 4 mm probe. The obtained data was processed using Topspin and spectra were analyzed using the DMFIT program.[44]

2.3.7 X-ray absorption fine structure spectroscopy (XAFS)

X-ray absorption fine structure (XAFS) is the modulation of X-ray absorption probability, at energies near and above the binding energy of a core-level electron in an atom.[45] The absorption coefficient μ represents the probability of X-rays absorption and is described by Beer-Lambert Law as,

$$I = I_0 e^{-\mu t}$$

Where, I_0 is the X-ray intensity incident on a sample, t is the sample thickness, and I is the intensity transmitted through the sample. The absorption coefficient μ is a smooth function of energy and depends on the sample density ρ , the atomic number Z , atomic mass A , and the X-ray energy E as,[45]

$$\mu \approx \frac{\rho Z^4}{AE^3}$$

When the energy of incident X-ray is equal to that of the binding energy of a core-level electron, there is a sharp rise in absorption. This gives rise to an absorption edge corresponding to the transition of the core level electron to the continuum. In XAFS measurement, the energy dependence of μ is examined, at energies near and just above these absorption edges. Since μ has strong dependence on both Z and E , XAFS works as an element specific probe, where target element can be chosen by tuning the X-ray energy to an appropriate absorp-

tion edge.[45] The X-ray absorption spectrum has two regimes: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS). XANES is typically probed within 30 eV of the main absorption edge and is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom. In contrast, EXAFS is examined few keV past the absorption edge and provides information about the local structure like inter-atomic distances, coordination number, and species of the neighbors surrounding the absorbing atom.[45]

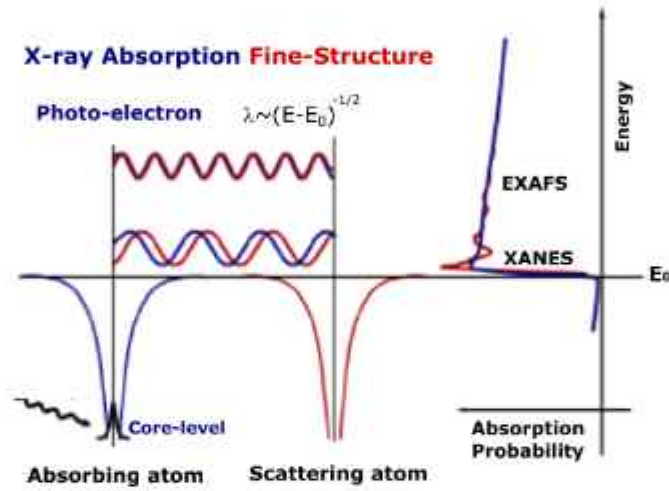


Figure 2.7: Back scattering of ejected photoelectron wave to the absorbing atom and the representation of XAFS spectrum [45]

As shown in Figure 2.7, at energy above the absorption edge, the absorption coefficient exhibits a fine structure due to the interference of outgoing and back-scattered photoelectron wave, attributed to the presence of neighboring atoms. This interference, results in oscillations in the $\mu(E)$, which is the EXAFS fine structure $\chi(E)$. As a result, the absorption coefficient above the absorption edge is defined as,[46]

$$\mu(E) = \mu_0(E) (1 + \chi(E))$$

where $\mu(E)$ is the measured absorption coefficient, $\mu_0(E)$ is a smooth background function representing the absorption of an isolated atom. The isolated XAFS is

usually written as,

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu}$$

where, $\Delta\mu$ is the measured jump in the absorption $\mu(E)$ at the threshold energy.[45] EXAFS is best understood in terms of the wave behavior of the photoelectron created in the absorption process. Therefore, X-ray energy is commonly converted from E space to k space. The final EXAFS function used to model and interpret the experimental data is of the form,[45]

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin(2kR_j + \delta_j(k))$$

Where, the summation is taken the over shells of neighboring atoms. Provided, the scattering properties of the neighboring atoms i.e, $f(k)$ (scattering amplitude), $\delta(k)$ (phase shift) and $\lambda(k)$ (mean free path) are known, one can determine the coordination number of neighboring atoms (N), the distance to the neighboring atom (R) and the mean square disorder of the neighbor distance (σ^2). The S_0^2 parameter represents amplitude reduction factor and is determined from a standard (sample with a well known structure) and applied as a scale factor to a set of unknowns.[45]

The Bi L_3 -edge EXAFS and V K -edge XANES spectra of the samples were recorded at the XAFS beamline at Elettra synchrotron Trieste, Italy. The measurements near the Bi L_3 -edge were carried out in transmission mode, whereas the V K -edge XANES measurements were conducted in fluorescence mode. For room temperature measurements, the absorbers were prepared by meticulously spreading the sample powder over scotch tape to achieve uniformly thick layer, which were then stacked (in an appropriate number) to achieve an edge jump, $\Delta\mu t \leq 1$. For higher temperature measurements, pellets were prepared by mixing sample and boron nitride powder (BN) in an appropriate ratio. The obtained data was then processed and analyzed using the DEMETER suite[47].

2.3.8 DC polarization method

The transference number gives quantitative information of the extent of ionic and electronic (electron and holes) contribution to the total conductivity (σ_T). The transference number can be defined as,[48]

$$t_{\text{ionic}} = \frac{\sigma_{\text{ionic}}}{\sigma_T} = \frac{I_{\text{ionic}}}{I_T}$$

Where,

$$\sigma_T = \sigma_{\text{ionic}} + \sigma_{(e,h)}$$

The ionic transference number is widely and conveniently determined using Wagner's polarization method.[48] During the DC polarization test, a symmetric two electrode cell in a ion-blocking (silver electrodes) configuration is polarized by applying a small constant potential difference. The initial current (I_0) observed in the polarization experiment is determined by the conductivity of the electrolyte (constitutes both ionic and electronic conductivities, if present). After a certain time, the charge transport is limited only to the species being reversible against the electrodes (electrons) and the current falls to a steady-state value I_{SS} . [49] The transference numbers t_{ionic} and t_e is then determined from the polarization current versus time plot using the equations,

$$t_{\text{ionic}} = \frac{(I_0 - I_{SS})}{I_{SS}}$$

The sample pellets were coated with silver paste which served as ion blocking electrode and DC polarization curves were obtained by recording the variation in current w.r.t time using Keithley 6514 electrometer.

2.3.9 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a powerful electrochemical technique, commonly employed to investigate the reduction and oxidation processes of molecular

species.[50] In CV experiment, a cyclic potential sweep is imposed on an electrode (working electrode) and current response is observed. Analysis of this current response can give information of the thermodynamics and kinetics of electron transfer at the electrode-electrolyte interface.[51] The potential sweep is described by its initial (E_i), switching (E_s), final (E_f) potentials and sweep rate (ν). The potentials as a function of time is of the form,[51]

$$E = E_i + \nu t \quad (\text{during the forward sweep})$$

$$E = E_s - \nu t \quad (\text{during the reverse sweep})$$

This applied input voltage is a triangular waveform, due to its linear ramping and is schematically shown in Figure 2.8 (a).

The current resulting from the electron transfer at an active reaction site as a function of applied potential is used to construct the current-potential plot known as cyclic voltammogram.[52] During the forward sweep, the oxidized species is reduced, while on the reverse sweep the reduced species near the electrode is re-oxidized.[51] As the potential is scanned during the CV experiment, the concentration of the redox species near the electrode varies with time in accordance with the Nernst equation.[50] For a reversible redox reaction,



The Nernst equation is of the form,

$$E = E_0 + \frac{2.303RT}{nF} \log \left(\frac{[\text{Ox}]}{[\text{Red}]} \right)$$

Where, E is the applied potential, E_0 is the standard potential of a species, $[\text{Red}]$ and $[\text{Ox}]$ are the concentrations of the reduced and oxidized species, respectively, R is the gas constant, T the temperature, F the Faraday constant and n is the amount of electrons exchanged during the redox reaction.[50]

In a cyclic voltammogram, as shown in Figure 2.8 (b), a typical one electron reversible reduction process exhibits the oxidation/reduction of redox active species in the form of peaks during forward and backward potential scanning.[52] The peak resulting from the reduction process is called the cathodic peak and is observed at $E - E_{pc}$ (F point) with peak current of $i_{p,c}$. During the reverse scan, oxidation occurs, producing anodic peak at $E - E_{pa}$ with corresponding peak current of $i_{p,a}$. [51]

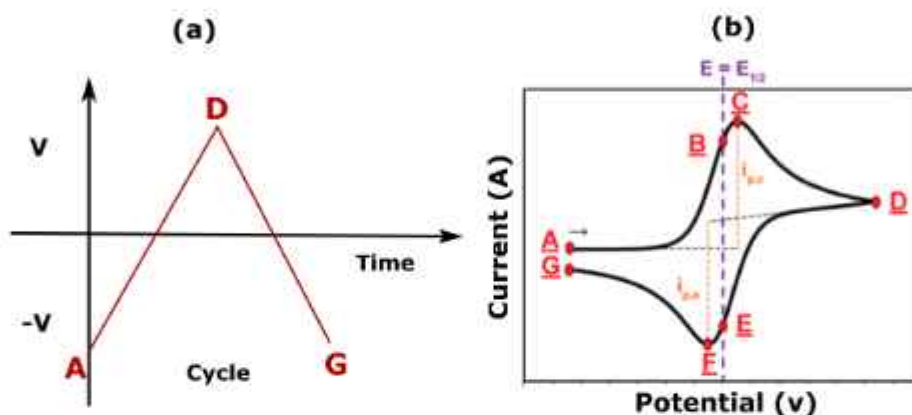


Figure 2.8: Schematic representation of (a) CV potential waveform and (b) corresponding cyclic voltammogram [50]

2.3.10 Galvanostatic Charge-Discharge Cycling (GCD)

Galvanostatic cycling is technique used to evaluate battery performance. During a galvanostatic charge discharge (GCD) experiment, a constant current is applied to the battery, to charge it to a set voltage, followed by discharging at the same current. The voltage response is recorded as a function of time, during both charging and discharging cycles. Figure 2.9 shows the applied current waveform and the corresponding voltage response for a single charge-discharge cycle. The voltage profile appears as an oblique line with plateau region, arising due to intercalation/de-intercalation process and facilitated by crystallographic phase transformation of the electrode material.[53], [54]

The voltage response includes a charging process in which the voltage rises from

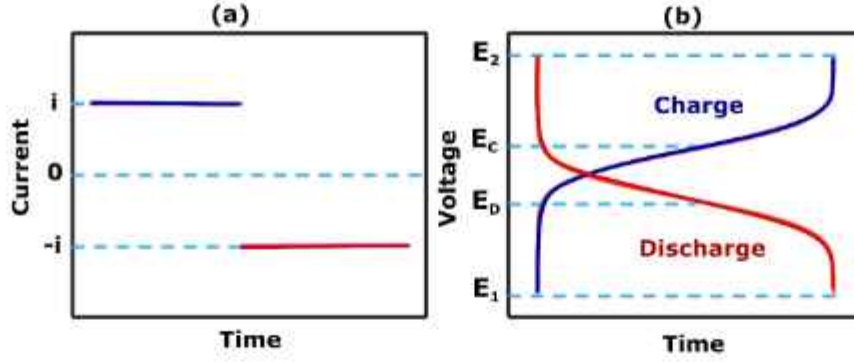


Figure 2.9: Schematic representation of (a) applied current profile and (b) corresponding voltage response vs. time [53], [54]

lower cutoff potential (E_1) to higher cut off potential (E_2) (cut-off voltages), followed by a discharge process where the trend reverses. The average charging and discharging voltage, denoted by E_C and E_D , exhibits an hysteresis gap due to internal resistance/polarization effects within the system.[54] Repetition of such GCD cycles can be used to assess the cycle life and stability of the battery for its long-term performance.[55]

In addition, GCD data can also provide insights into key battery performance parameters, such as specific capacitance and energy density.[55]

The specific capacitance (C_s) and specific energy density (E) can be calculated from GCD data using equations (1) and (2) as:

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \dots (1)$$

where, I , Δt , ΔV and m corresponds to discharge current (A), discharge time (s), potential window (V) and the mass of active materials (g), respectively.

$$E = \frac{1}{2} C_s (\Delta V)^2 \dots (2)$$

where, ΔV is operational voltage window and C_s is the specific capacitance of fabricated electrode.[56]

The Cyclic voltammetry (CV), Linear sweep voltammetry (LSV) and GCD mea-

surements, were recorded using K-Lyte 1.0 potentiostat (Kanopytech). The measurements were performed at Material characterization laboratory, SPAS, Goa university.

References

- [1] R. Marzouki, Y. Ben Smida, M. Jemmali, B. Marzougui, and M. Triki, in *Crystallization and Applications*, Y. Ben Smida and R. Marzouki, Eds., London: IntechOpen, Apr. 2021.
- [2] L. E. Smart and E. A. Moore, 4th ed. roken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742: CRC Press, Taylor & Francis Group, 2012, ISBN: 9780429105173. DOI: 10.1201/b12047.
- [3] Q. Ma, M. Guin, S. Naqash, C.-L. Tsai, F. Tietz, and O. Guillon, *Chemistry of Materials*, vol. 28, no. 13, pp. 4821–4828, 2016. DOI: 10.1021/acs.chemmater.6b02059.
- [4] S. Naqash, Q. Ma, F. Tietz, and O. Guillon, *Solid State Ionics*, vol. 302, pp. 83–91, 2017, ISSFIT12., ISSN: 0167-2738. DOI: <https://doi.org/10.1016/j.ssi.2016.11.004>.
- [5] A. R. West, 2nd ed. John Wiley & Sons, Ltd, 2014.
- [6] C. G. Shull and E. O. Wollan, *Science (New York, N. Y.)*, vol. 108, no. 2795, pp. 69–75, 1948. DOI: <https://doi.org/10.1126/science.108.2795.69>.
- [7] M. A. Omar, in New York: Addison-Wesley, 1993, ch. X-ray, Neutron and Electron Diffraction in Crystals, pp. 35–46.
- [8] C. Kittel, in 8th ed. John Wiley & Sons, 2005, ch. Wave Diffraction and the Reciprocal Lattice, pp. 24–25.
- [9] P. Atkins and J. de Paula, 9th ed. Oxford University Press, 2010.
- [10] R. Dinnebier and M. Müller, in *Modern Diffraction Methods*. John Wiley & Sons, Ltd, 2012, ch. 2, pp. 27–60, ISBN: 9783527649884. DOI: <https://doi.org/10.1002/9783527649884.ch2>.

- [11] D. Lou  r, in *Encyclopedia of Spectroscopy and Spectrometry (Third Edition)*, J. C. Lindon, G. E. Tranter, and D. W. Koppenaal, Eds., Third Edition, Oxford: Academic Press, 2017, pp. 723–731, ISBN: 978-0-12-803224-4. DOI: <https://doi.org/10.1016/B978-0-12-803224-4.00257-0>.
- [12] J. S. O. Evans and I. R. Evans, *J. Chem. Educ.*, vol. 98, no. 2, pp. 495–505, Feb. 2021.
- [13] B. H. Toby, *Powder Diffraction*, vol. 21, no. 1, pp. 67–70, 2006.
- [14] O. Arcelus et al., *Journal of Applied Crystallography*, vol. 57, no. 5, pp. 1676–1690, Oct. 2024. DOI: 10.1107/S1600576724006885.
- [15] F. Zhu, Q. Wang, X. Zhang, W. Hu, X. Zhao, and H. Zhang, *Nanotechnology*, vol. 25, no. 18, p. 185705, Apr. 2014. DOI: 10.1088/0957-4484/25/18/185705.
- [16] W. Zhou, R. Apkarian, Z. L. Wang, and D. Joy, in *Scanning Microscopy for Nanotechnology: Techniques and Applications*, W. Zhou and Z. L. Wang, Eds. Springer New York, 2007, pp. 1–40, ISBN: 978-0-387-39620-0. DOI: 10.1007/978-0-387-39620-0_1.
- [17] A. Micheals, in *Encyclopedia of Forensic Sciences (Second Edition)*, J. A. Siegel, P. J. Saukko, and M. M. Houck, Eds., Second Edition, Waltham: Academic Press, 2013, pp. 483–493, ISBN: 978-0-12-382166-9. DOI: <https://doi.org/10.1016/B978-0-12-382166-9.00153-7>.
- [18] A. Barhoum and M. Luisa Garc  a-Betancourt, in *Emerging Applications of Nanoparticles and Architecture Nanostructures*, ser. Micro and Nano Technologies, A. Barhoum and A. S. H. Makhoulouf, Eds., Elsevier, 2018, pp. 279–304, ISBN: 978-0-323-51254-1. DOI: <https://doi.org/10.1016/B978-0-323-51254-1.00010-5>.
- [19] A. C. Lazanas and M. I. Prodromidis, *ACS Measurement Science Au*, vol. 3, no. 3, pp. 162–193, 2023. DOI: 10.1021/acsmeasuresciau.2c00070.

- [20] P. Vadhva et al., *ChemElectroChem*, vol. 8, no. 11, pp. 1930–1947, 2021. DOI: <https://doi.org/10.1002/celec.202100108>.
- [21] J. R. Macdonald and W. B. Johnson, in *Impedance Spectroscopy*. John Wiley & Sons, Ltd, 2018, ch. 1, pp. 1–20, ISBN: 9781119381860. DOI: <https://doi.org/10.1002/9781119381860.ch1>.
- [22] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, and L. Pilon, *The Journal of Physical Chemistry C*, vol. 122, no. 1, pp. 194–206, 2018. DOI: 10.1021/acs.jpcc.7b10582.
- [23] J. T. S. Irvine, D. C. Sinclair, and A. R. West, *Advanced Materials*, vol. 2, no. 3, pp. 132–138, 1990. DOI: <https://doi.org/10.1002/adma.19900020304>.
- [24] A. S. Bondarenko and G. A. Ragoisha, in *Progress in Chemo-metrics Research*, A. L. Pomerantsev, Ed., Program available at <http://www.abc.chemistry.bsu.by/vi/analyser/>, New York: Nova Science Publishers, 2005, pp. 89–102.
- [25] P. Gill, T. T. Moghadam, and B. Ranjbar, *Journal of biomolecular techniques : JBT*, vol. 21 4, pp. 167–93, 2010.
- [26] F. Tuomisto and I. Makkonen, *Rev. Mod. Phys.*, vol. 85, pp. 1583–1631, 4 Nov. 2013. DOI: 10.1103/RevModPhys.85.1583.
- [27] J. Swaminathan, in *Metal Oxide Defects*, scr. Metal Oxides, V. Kumar, S. Som, V. Sharma, and H. C. Swart, Eds., Elsevier, 2023, pp. 27–60, ISBN: 978-0-323-85588-4. DOI: <https://doi.org/10.1016/B978-0-323-85588-4.00013-1>.
- [28] C. Sundar, *Bulletin of Materials Science*, vol. 17, no. 7, pp. 1215–1232, 1994.
- [29] B. Sahoo, Tech. Rep., Jun. 2014. DOI: 10.13140/RG.2.1.1981.8965.
- [30] Y. C. Jean, J. D. Van Horn, W.-S. Hung, and K.-R. Lee, *Macromolecules*, vol. 46, no. 18, pp. 7133–7145, 2013. DOI: 10.1021/ma401309x.

-
- [31] R. Krause-Rehberg and H. S. Leipner. Springer Science & Business Media, 1999.
- [32] R. Krishnan and D. D. Upadhyaya, *Pramana*, vol. 24, no. 1, pp. 351–359, Jan. 1985.
- [33] G. Consolati, D. Nichetti, and F. Quasso, *Polymers*, vol. 15, p. 3128, Jul. 2023. DOI: 10.3390/polym15143128.
- [34] J. V. Olsen, P. Kirkegaard, and M. Eldrup, Department of Energy Conversion and Storage, Technical University of Denmark, Tech. Rep., 2022, Version 3.251.
- [35] A. Borisov, P. Hazendonk, and P. Hayes, *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 20, pp. 183–212, Jun. 2010. DOI: 10.1007/s10904-010-9358-5.
- [36] B. Reif, S. E. Ashbrook, L. Emsley, and M. Hong, *Nature Reviews Methods Primers*, vol. 1, no. 1, p. 2, Jan. 2021. DOI: 10.1038/s43586-020-00002-1.
- [37] C. C. Fraenza, S. G. Greenbaum, and S. N. Suarez, *International Journal of Molecular Sciences*, vol. 24, no. 12, 2023, ISSN: 1422-0067. DOI: 10.3390/ijms241210373.
- [38] R. Cao et al., *Food Chemistry*, vol. 342, p. 128 258, 2021, ISSN: 0308-8146. DOI: <https://doi.org/10.1016/j.foodchem.2020.128258>.
- [39] O. Pecher, J. Carretero-González, K. J. Griffith, and C. P. Grey, *Chemistry of Materials*, vol. 29, no. 1, pp. 213–242, 2017. DOI: 10.1021/acs.chemmater.6b03183.
- [40] T. Bräuniger, *Molecules*, vol. 29, no. 17, 2024, ISSN: 1420-3049. DOI: 10.3390/molecules29174148.
- [41] T. Polenova, R. Gupta, and A. Goldbourt, *Analytical Chemistry*, vol. 87, no. 11, pp. 5458–5469, 2015. DOI: 10.1021/ac504288u.

- [42] V. Epp and M. Wilkening, in *Handbook of Solid State Batteries*, 2nd. WORLD SCIENTIFIC, 2015, ch. Chapter 5, pp. 133–190. DOI: 10.1142/9789814651905_0005.
- [43] G. Foran, N. Verdier, D. Lepage, C. Malveau, N. Dupré, and M. Dollé, *Polymers*, vol. 13, no. 8, 2021, ISSN: 2073-4360. DOI: 10.3390/polym13081207.
- [44] D. Massiot et al., *Magnetic Resonance in Chemistry*, vol. 40, no. 1, pp. 70–76, 2002. DOI: <https://doi.org/10.1002/mrc.984>.
- [45] M. Newville, *Reviews in Mineralogy and Geochemistry*, vol. 78, no. 1, pp. 33–74, Jan. 2014, ISSN: 1529-6466. DOI: 10.2138/rmg.2014.78.2.
- [46] D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen, and D. E. Ramaker, *Topics in Catalysis*, vol. 10, no. 3, pp. 143–155, May 2000.
- [47] B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, vol. 12, no. 4, pp. 537–541, Jul. 2005. DOI: 10.1107/S0909049505012719.
- [48] R. C. Agrawal, *Indian Journal of Pure & Applied Physics*, vol. 37, pp. 294–301, 1999.
- [49] M. Sickierski, M. Bukat, M. Ciosek, M. Piszcz, and M. Mroczkowska-Szerszeń, *Polymers*, vol. 13, p. 895, Mar. 2021. DOI: 10.3390/polym13060895.
- [50] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, *Journal of Chemical Education*, vol. 95, no. 2, pp. 197–206, 2018. DOI: 10.1021/acs.jchemed.7b00361.
- [51] D. K. Gossler. VCH New York, 1993, vol. 43.
- [52] N. Bhuvanendran, S. Ravichandran, Q. Xu, T. Maiyalagan, and H. Su, *International Journal of Hydrogen Energy*, vol. 47, no. 11, pp. 7113–7138, 2022, ISSN: 0360-3199. DOI: <https://doi.org/10.1016/j.ijhydene.2021.12.072>.

- [53] X. Yang and A. L. Rogach, *Advanced Energy Materials*, vol. 9, no. 25, p. 1900747, 2019. DOI: <https://doi.org/10.1002/aenm.201900747>.
- [54] Y. Liu, S. Jiang, and Z. Shao, *Materials Today Advances*, vol. 7, p. 100072, 2020, ISSN: 2590-0498. DOI: <https://doi.org/10.1016/j.mtadv.2020.100072>.
- [55] J. García-Torres, *Journal of Chemical Education*, vol. 102, no. 2, pp. 821–828, 2025. DOI: [10.1021/acs.jchemed.4c01217](https://doi.org/10.1021/acs.jchemed.4c01217).
- [56] S. Sharma and P. Chand, *Results in Chemistry*, vol. 5, p. 100885, 2023, ISSN: 2211-7156. DOI: <https://doi.org/10.1016/j.rechem.2023.100885>.

CHAPTER 3

NASICON-based ceramic electrolytes

3.1 Introduction

Sodium (Na) Super-Ionic CONductor (NASICON) with the general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, first reported by Goodenough's group, exhibited ionic conductivity exceeding 100 mS/cm at 300 °C for $x=2$. [1], [2]. This high conductivity originates from its framework of corner-sharing Si/ PO_4 tetrahedra and ZrO_6 octahedra, which creates interconnected three-dimensional channels for fast Na^+ -ion transport. [3] Despite these, at room temperature, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ shows ionic conductivity typically of the order of 10^{-4} S/cm, which is insufficient for practical application in solid-state sodium ion batteries (SSBs). [1], [2] Therefore, compositional and processing optimization are required for enhanced performance of NASICON electrolytes. In the present work, various strategies have been explored to tune both structure and morphology of NASICON, including adjustments of Si/P ratio [4], substitution of aliovalent cations at Zr^{4+} site [5], [6], [7], and adoption of alternative synthesis routes. [8], [9] Based on these optimization approaches, three compositions have been prepared - $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$, and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$. Variations in Si/P ratio and Sc^{3+} substitution create a charge imbalance, compensated by additional Na^+ -ions to maintain neutrality. Sc^{3+} was chosen as a dopant because of its ionic radius closely matching that of Zr^{4+} ($r_{\text{Zr}^{4+}} = 0.72 \text{ \AA}$ and $r_{\text{Sc}^{3+}} = 0.745 \text{ \AA}$), minimizing lattice distortion.

Additionally, two different synthesis routes have also been employed for these compositions - conventional solid state reaction (SSR) and hydrothermal-based solid state reaction (HT-SSR). The HT-SSR method was employed with an expectation of facilitating better reactivity of precursors, ensuring homogeneity of mixing through the use of a liquid medium.

The objectives of the present investigation are thus:

- Verifying the influence of systematic structural tuning on Na^+ -ion conductivity of proposed NASICON compositions
- Comparing the impact of the HT-SSR method over the SSR method on the microstructure of NASICON compositions.
- Understanding the role of structure in ionic conduction and establishing a structure-composition-property relationship.
- Determining Na^+ -ion migration pathway in the proposed system.
- Evaluate the electrochemical performances.

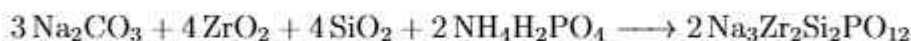
3.2 Methods and experimental design

3.2.1 Synthesis

The NASICON compositions of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ in the current work were synthesized by two different synthesis approaches – the solid-state reaction method (SSR) and the hydrothermal-based solid-state reaction method (HT-SSR).

Nominal polycrystalline NASICON compositions were prepared by a solid-state procedure using Na_2CO_3 (Sigma Aldrich, 99.0 %), ZrO_2 (Sigma Aldrich, 99.0 %), SiO_2 (Alfa Aesar, 99.9 %), Sc_2O_3 (Sigma Aldrich, 99.0 %), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 99.9 %) as precursors. The starting materials were ground and preheated to get rid of moisture that may be present. Stoichiometric amounts of the precursors

were mixed using isopropanol in an agate mortar and pestle. Dried mixtures were calcined at 1100 °C for 10 h. Later, the calcined powders were ground manually and pressed to form pellets of 10 mm diameter and ~ 2 mm thickness, applying a pressure of 250 MPa for 5 min. Finally, the pellets of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ were sintered at 1220 °C for 10 h, and $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ were sintered at 1260 °C for 5 h. The chemical reaction of the synthesised composition of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ is as follows:



In the HT-SSR method, NASICON compositions were prepared using NaNO_3 (Alfa Aesar, 99.0 %), Sc_2O_3 (Sigma Aldrich, 99.9 %), $\text{ZrO}(\text{NO}_3)_2$ (Sigma Aldrich, 99.0 %), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Alfa Aesar, 99.0 %), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 99.9 %) as precursors. Before the synthesis, all the powders were finely ground to avoid lumps while mixing. Furthermore, NaNO_3 , Sc_2O_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were heated above 100 °C to eliminate any moisture that may be present in the powder. After the preliminary treatment, required amounts of NaNO_3 , $\text{ZrO}(\text{NO}_3)_2$, and Sc_2O_3 (for $\text{Na}_{3.4}\text{ZSSP}_{0.8}$) were first dissolved in deionized water and mixed into one solution. To facilitate the solubility of Sc_2O_3 in the solution, nitric acid was added. Subsequently, a stoichiometric amount of $\text{Si}(\text{OC}_2\text{H}_5)_4$ was added to the solution along with a small amount of nitric acid to dissolve the silicon source. On hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$, a required amount of $\text{NH}_4\text{H}_2\text{PO}_4$ was added, which transformed the homogeneous solution into a mixture of colloidal sol and precipitate. This mixture was then stirred overnight. The resulting mixture was transferred into an autoclave and treated at 150 °C for 7 hours. This reaction product was dried at 100 °C for 24 hours, yielding a white powder. The obtained powder was then calcined at 800 °C. The calcined powder was ground using ethanol as a medium, and the dried powder was then pressed into 10 mm pellets with a pressure of 250 MPa for 5 min. Pellets of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ were sintered at 1250 °C for 5 h, whereas $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ and $\text{Na}_{3.4}\text{Sc}_{0.2}\text{Zr}_{1.8}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ were sintered at 1260 °C for 5

h. The schematic diagrams of the SSR and HT-SSR methods are outlined in Figure 3.1.

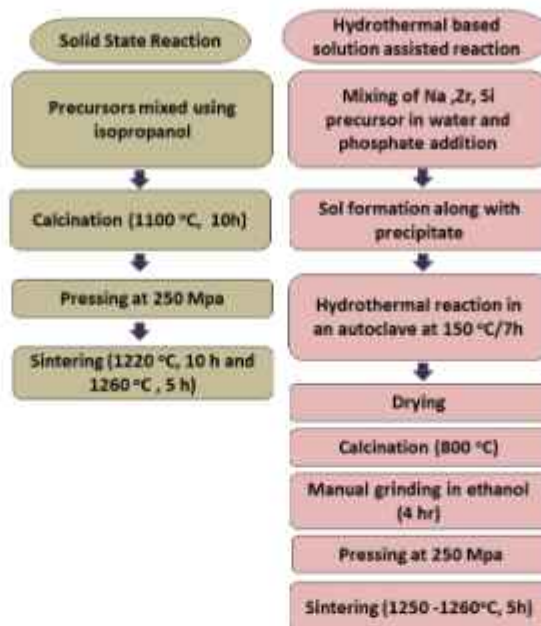


Figure 3.1: Synthesis scheme of the solid state reaction (SSR) method and the hydrothermal-based solid state reaction (HT-SSR) method

The following short names - N_3ZSP , $N_{3.4}ZSP_{0.6}$, and $N_{3.4}ZSSP_{0.8}$ have been used for $Na_3Zr_2Si_2PO_{12}$, $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$, and $Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O_{12}$ compositions, respectively, followed by the term ‘SSR’ or ‘HT-SSR’ depending on the employed synthesis method.

3.2.2 X-ray and Neutron powder diffraction study

Room temperature X-ray diffraction (XRD) measurement of the powder samples was performed on a Rigaku diffractometer, using $Cu K_\alpha$ radiation. Data were collected in a 2θ range of 10° - 80° with the step size of 0.02° . Neutron powder diffraction (NPD) data were recorded at room temperature using PD-2 diffractometer ($\lambda = 1.2443 \text{ \AA}$) equipped with five linear position-sensitive He3 detectors at the Dhruva reactor, Trombay, India. For NPD, the powder sample was filled inside a cylindrical vanadium can and placed on the neutron beam for this measurement. The diffraction pattern was corrected for instrumental background and normalized with the vanadium standard sample.

Crystalline phase and structural refinements for XRD/NPD data were carried out using the Rietveld method in Fullprof software[10]. In the refinements, a pseudo-Voigt function was used to describe the line shape of diffraction peaks. In the first step, scale factors, background coefficients, 2θ zero positions, line widths, and peak shapes were determined. The second step deduced positional parameters and site occupancies.

3.2.3 Impedance spectroscopy (EIS) and scanning electron microscopy (SEM)

Electrical conductivity was determined with electrochemical impedance spectroscopy (EIS) using two different impedance analyzer setups, PSM1735 NumetriQ, UK, and Hioki IM3570, Japan. An AC amplitude of 121 mV and frequency range of 10 Hz - 8 MHz was used to record the impedance data in the temperature range of RT-120 °C. Before the EIS measurements, the sintered pellets were coated with silver paste on the parallel surfaces and fired at 500 °C for 2 h to establish electric contact. For equivalent circuit fitting of the impedance data, EISSA software[11] was used. EIS measurement at low temperature was performed using an ice bath, and the temperature at the sample site was probed by an external thermocouple.

The microstructure was examined using SEM measurements on a Carl Zeiss setup. In order to create a thin conducting layer on the surface of the non-conducting sample, pellets were sputtered with gold. To find the average particle size from the SEM images, the ImageJ software[12] was used.

3.2.4 Positron annihilation lifetime spectroscopy

The PALS measurements were performed using two BaF₂ scintillation detectors connected to fast-fast coincidence system. A ²²Na positron source (~ 10 μ Ci) sealed within a thin Kapton foil (5mm $\times$ 5mm $\times$ 8 μ m) was put inside the powder sample and kept in an aluminum vial. Subsequently, the vial was kept between

two BaF₂ detectors in 90° configuration. The time resolution measured with ⁶⁰Co in the ²²Na energy window settings was 220 ps. The time calibration was kept 12.5 ps/channel. The total number of counts acquired in each spectrum was approximately 1 x 10⁶.

3.2.5 Electrochemical performance - Cyclic voltammetry, Galvanostatic cycling, and DC polarization

The electrochemical measurements, including cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) cycling, were performed on NASICON compositions using a potentiostat/galvanostat (K-Lyte, Kanopy, India). The cell configuration of Ag|electrolyte|Na and Na|electrolyte|Na was used for CV and GCD, respectively. The DC polarization curves for NASICON ceramic were recorded using an Ag|electrolyte|Ag cell with a Keithley 6514 electrometer under an applied voltage of 0.8 V.

3.3 Results

3.3.1 Phase identification and structure determination

The crystal structure of the prepared NASICON compositions was investigated using X-ray and neutron powder diffraction. XRD was used to confirm the phase formation and assess the influence of sintering conditions. On the other hand, NPD was used to accurately determine the occupancies and positions of light atoms such as oxygen, silicon, phosphorus, and sodium. Room temperature XRD pattern of SSR prepared NASICON compositions at sintering temperature of 1220 °C is shown in Figure 3.2.

In NASICON compositions, high-temperature sintering is required to densify the pellets and minimize grain boundary resistance; however, it often leads to volatilization of sodium and phosphorus, which in turn promotes the formation of

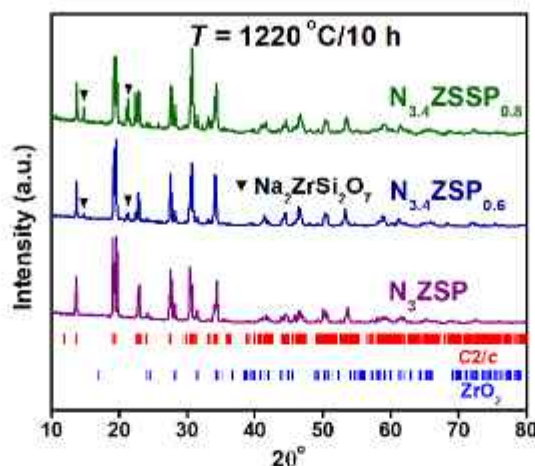


Figure 3.2: XRD pattern of the NASICON compositions synthesized by the SSR method with sintering temperature of $T = 1220\text{ }^{\circ}\text{C}$ for 10 h

impurity phase(s) such as ZrO_2 and Na_3PO_4 . Therefore, an optimum temperature is important for balancing densification with phase purity. Noi *et al.* reported a sintering condition of $1220\text{ }^{\circ}\text{C}/10\text{ h}$ as optimum for N_3ZSP composition [13], and therefore, it was initially adopted in the SSR synthesis. Under this sintering condition, the SSR synthesised N_3ZSP composition formed the desired NASICON phase, and its ionic conductivity presented in section 3.3.3, closely matched the reported value.[13] However, $\text{N}_{3.4}\text{ZSP}_{0.6}$ and $\text{N}_{3.4}\text{ZSSP}_{0.8}$ compositions contained a substantial amount of $\text{Na}_2\text{ZrSi}_2\text{O}_7$ as a secondary phase, along with traces of unreacted ZrO_2 phase observed across all three compositions. The presence of $\text{Na}_2\text{ZrSi}_2\text{O}_7$ phase [14], possibly arising from the incomplete solid state reaction, suggested that $1220\text{ }^{\circ}\text{C}/10\text{ h}$ was insufficient for complete phase formation of these two compositions. The sintering condition of $1260\text{ }^{\circ}\text{C}/5\text{ h}$ was considered, after noting it as another optimum condition reported by several groups [3], [15], [16]. Therefore, the NASICON compositions of $\text{N}_{3.4}\text{ZSP}_{0.6}$ and $\text{N}_{3.4}\text{ZSSP}_{0.8}$ were re-prepared and sintered at $1260\text{ }^{\circ}\text{C}$ for 5 h. The corresponding XRD patterns of these compositions are shown in Figure 3.3.

From Figure 3.3, the re-sintered compositions were found to be free of $\text{Na}_2\text{ZrSi}_2\text{O}_7$ phase. This confirmed that the optimum sintering condition is composition-dependent. In case of HT-SSR compositions also, slightly different sintering tem-

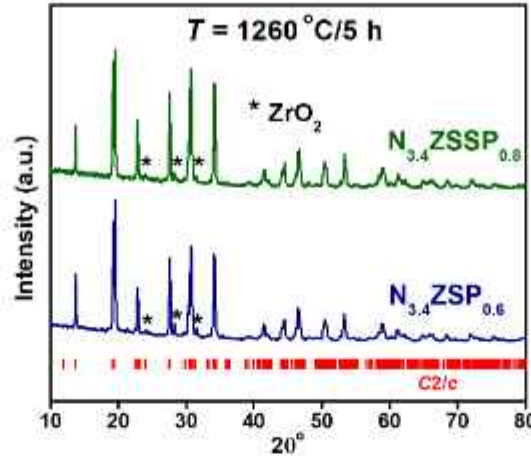


Figure 3.3: XRD pattern of the NASICON compositions synthesized by the SSR method and with sintering temperature of $T = 1260\text{ }^{\circ}\text{C}/5\text{ h}$

peratures were used for N_3ZSP and $\text{N}_{3.4}\text{ZSP}_{0.6}$, $\text{N}_{3.4}\text{ZSSP}_{0.8}$ as prescribed by previous reports [15], [16], [17]. The HT-SSR-based N_3ZSP composition was sintered at $1250\text{ }^{\circ}\text{C}$ while the $\text{N}_{3.4}\text{ZSP}_{0.6}$ and $\text{N}_{3.4}\text{ZSSP}_{0.8}$ were subjected to $1260\text{ }^{\circ}\text{C}$ for 5 hours. The XRD patterns of the HT-SSR compositions are shown in Figure 3.4.

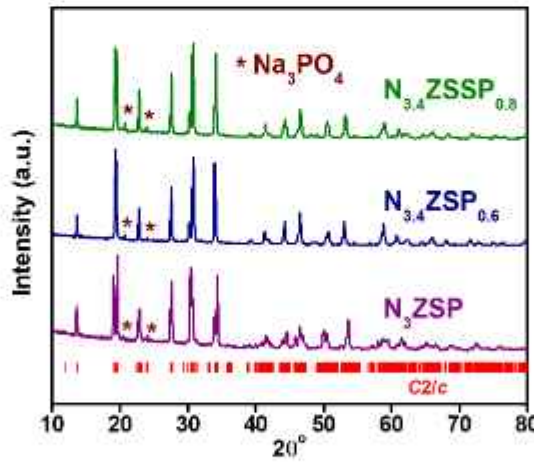


Figure 3.4: XRD pattern of the NASICON compositions prepared by the HT-SSR method and with sintering temperature of $T = 1250\text{ }^{\circ}\text{C} - 1260\text{ }^{\circ}\text{C}/5\text{ h}$

It was observed that, despite the use of optimum sintering temperatures, small amounts of ZrO_2 and/or Na_3PO_4 impurity phases were still present. The presence of the ZrO_2 phase is commonly linked to the limited reactivity of the zirconia precursor, particularly in the solid-state reaction route. However, even in the HT-SSR route, where zirconia precursor is used in a more reactive form, impurity remained.

This persistence may be attributed to the loss of sodium and phosphorus at the employed sintering temperatures, which may disturb the stoichiometry and create Zr-rich regions, making its complete elimination challenging.

The Rietveld refinement was performed on the prepared compositions to determine the crystal structure and quantify the phase fraction. The Rietveld refined spectra of the SSR and HT-SSR based NASICON compositions are shown in Figure 3.5 and Figure 3.6, respectively.

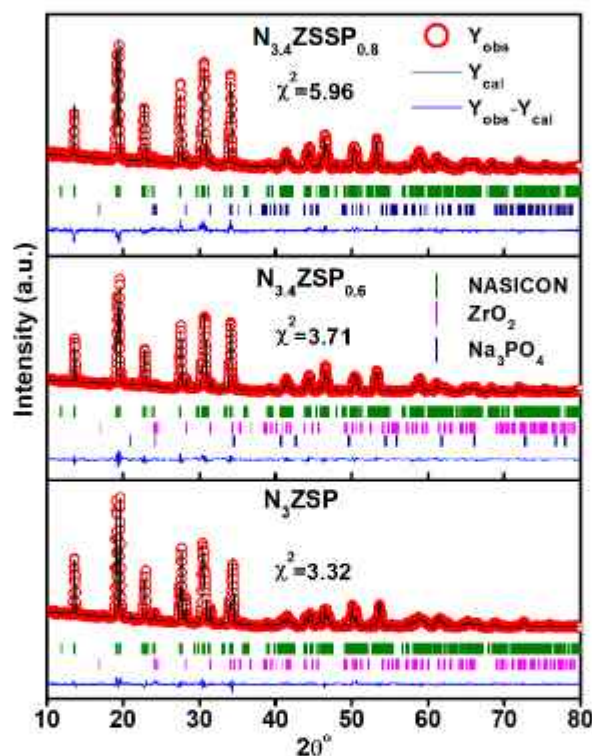


Figure 3.5: The Rietveld fit to the XRD pattern of SSR-based NASICON compositions

The sodium sublattice in NASICON has been described using different structural models, each proposing distinct site locations and occupancies with varying numbers of Na sites. Initial refinements based on the commonly used three-site model [18] did not provide a satisfactory fit to the present diffraction data. Therefore, Rietveld refinement for all compositions was carried out using the five-site Na model proposed by Zhang *et al.*[19] The refined values of structural parameters for the $N_{3.4}ZSSP_{0.8}$ composition and the lattice parameters of impurity phases are shown in Table 3.1 and Table 3.2, respectively.

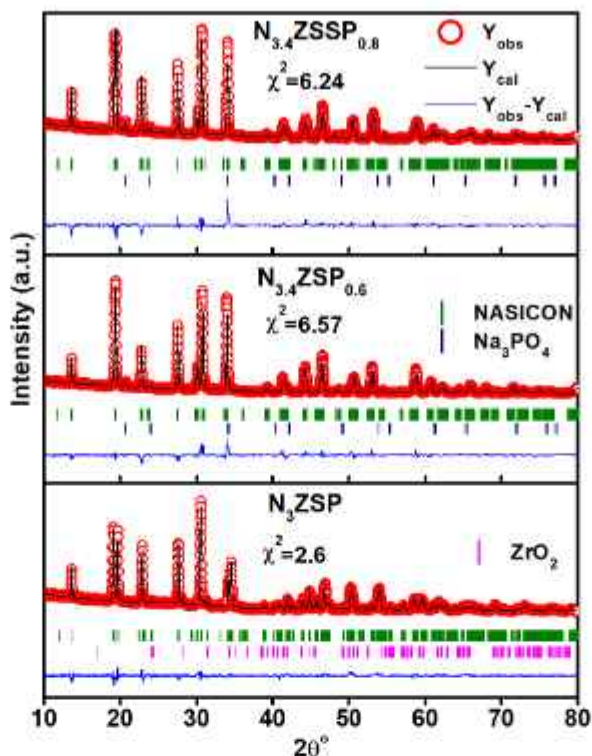


Figure 3.6: The Rietveld fit to the XRD pattern of HT-SSR-based NASICON compositions

For refinement, the thermal parameters were kept at fixed values, and only the occupancies of the Na site were varied. Rietveld fitting of all the compositions (prepared by SSR and HT-SSR) was satisfactorily indexed to the monoclinic $C2/c$ symmetry with a small amount ($< 5\%$) of monoclinic ZrO_2 and/or Na_3PO_4 phase. The unit cell parameters and impurity phase contents after final refinement are shown in Table 3.3.

The volume of the unit cells of the $N_{3.4}ZSP_{0.6}$ and $N_{3.4}ZSSP_{0.8}$ samples was observed to be slightly larger compared to that of the N_3ZSP compositions. Figure 3.7 shows the RT NPD pattern with Rietveld refinement for HT-SSR-based $N_{3.4}ZSSP_{0.8}$ composition. The Rietveld refined Na1-5 occupancies, and Na content/formula unit are listed in Table 3.4.

For $N_{3.4}ZSSP_{0.8}$ composition, the final sodium site occupancy factor, cell volume, lattice parameters, atomic positions, and Na-content/f.u. estimated from NPD data were found to align well with the refined XRD parameters. NPD refinement also revealed a phase fraction of $N_{3.4}ZSSP_{0.8}:Na_3PO_4 = 92:8$, which was higher

Table 3.1: Structural parameters of monoclinic $C2/c$ phase in nominal HT-SSR prepared $N_{3.4}ZSP_{0.8}$ obtained from Rietveld analysis of XRD

Atom	Wyckoff position	x	y	z	Occupancy	U_{iso} ($\text{\AA}^2$)
Na1	4d	0.25	0.25	0.5	0.248(7)	0.006
Na2	4e	0	0.395(9)	0.25	0.470(2)	0.006
Na3	8f	0.332(5)	0.424(6)	0.321(8)	0.365(8)	0.006
Na4	8f	0.191(8)	0.138(5)	0.555(4)	0.416(8)	0.006
Na5	8f	0.704(5)	0.533(5)	0.828(1)	0.304(6)	0.006
Zr1	8f	0.100(7)	0.248(1)	0.056(3)	0.892(9)	0.006
Sc1	8f	0.100(7)	0.248(1)	0.056(3)	0.098(3)	0.006
Si1	4e	0	0.046(2)	0.25	0.371(6)	0.006
P1	4e	0	0.046(2)	0.25	0.134(7)	0.006
Si2	8f	0.357(4)	0.111(6)	0.259(7)	0.818(5)	0.006
P2	8f	0.357(4)	0.111(6)	0.259(7)	0.263(2)	0.006
O1	8f	0.148(4)	0.433(6)	0.221(4)	1	0.006
O2	8f	0.436(3)	0.480(8)	0.074(7)	1	0.006
O3	8f	0.252(3)	0.185	0.210(6)	1	0.006
O4	8f	0.377(1)	0.137(1)	0.101(2)	1	0.006
O5	8f	0.553(4)	0.187(6)	0.062(9)	1	0.006
O6	8f	0.085(4)	0.148(6)	0.245(8)	1	0.006
$a = 15.739(4) \text{ \AA}$, $b = 9.095(5) \text{ \AA}$, $c = 9.181(3) \text{ \AA}$, $\beta = 124.6^\circ$, $V = 1082.4 \text{ \AA}^3$						

Table 3.2: Refined lattice parameters of impurity phases of ZrO_2 and Na_3PO_4

Compositions	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	β ($^\circ$)	V ($\text{\AA}^3$)
ZrO_2 ($P2_1/c$)	5.328(5)	5.210(10)	5.177(12)	80.9(2)	141.4(1)
Na_3PO_4 ($Fm\bar{3}m$)	7.431(6)	7.413(6)	7.431(6)	-	410.4(2)

than that determined from XRD. Such a difference is usually expected, as neutron diffraction offers higher sensitivity and stronger contrast for light elements as well as minimal absorption effects, enabling more accurate quantification of minor phases. Refined Na-content per formula unit was found to increase for $N_{3.4}ZSP_{0.6}$ and $N_{3.4}ZSP_{0.8}$ samples, in agreement with their nominal compositions. As shown in Table 3.4, the general trend of sodium site occupancy for each synthesis route showed that Na2 was the highest occupied site, while Na5 was the lowest. With increasing sodium content, the occupancies of Na1 and Na5 sites increased, Na4 site decreased, and Na3 site remained approximately unchanged.

Table 3.3: Refined lattice parameters of NASICON phase in SSR and HT-SSR compositions and corresponding impurity phase fraction

Samples	SSR-prepared			HT-SSR-prepared		
	Lattice parameters	ZrO ₂ (%)	Na ₃ PO ₄ (%)	Lattice parameters	ZrO ₂ (%)	Na ₃ PO ₄ (%)
N ₃ ZSP	$a = 15.629(2) \text{ \AA}$ $b = 9.040(8) \text{ \AA}$ $c = 9.210(1) \text{ \AA}$ $\beta = 123.7^\circ$	4.70	—	$a = 15.539(2) \text{ \AA}$ $b = 8.983(2) \text{ \AA}$ $c = 9.246(7) \text{ \AA}$ $\beta = 123.8^\circ$	1.79	—
N _{3.4} ZSP _{0.6}	$a = 15.723(9) \text{ \AA}$ $b = 9.092(8) \text{ \AA}$ $c = 9.181(8) \text{ \AA}$ $\beta = 124.3^\circ$	2.51	1.98	$a = 15.796(2) \text{ \AA}$ $b = 9.126(7) \text{ \AA}$ $c = 9.162(2) \text{ \AA}$ $\beta = 124.8^\circ$	—	2.86
N _{3.4} ZSSP _{0.8}	$a = 15.720(3) \text{ \AA}$ $b = 9.089(9) \text{ \AA}$ $c = 9.195(1) \text{ \AA}$ $\beta = 124.3^\circ$	—	2.08	$a = 15.739(4) \text{ \AA}$ $b = 9.095(5) \text{ \AA}$ $c = 9.181(3) \text{ \AA}$ $\beta = 124.6^\circ$	—	3.33

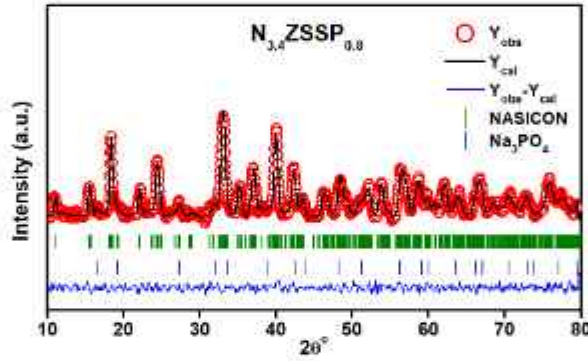
Figure 3.7: The Rietveld refined fit for RT NPD pattern of N_{3.4}ZSSP_{0.8} sample, prepared by the HT-SSR method

Table 3.4: Refined Na (Na1-5) site occupancy factors and Na content of SSR and HT-SSR compositions

Synthesis route	Sample	Na content (/f.u.)	Na occupancy factors				
			Na1	Na2	Na3	Na4	Na5
SSR	N ₃ ZSP	2.95	0.117(2) (23.4%)	0.436(4) (87.3%)	0.369(2) (36.9%)	0.422 (42.2%)	0.129(3) (12.9%)
	N _{3.4} ZSP _{0.6}	3.35	0.237 (47.0 %)	0.454(5) (90.9%)	0.368 (36.8%)	0.383(6) (38.4%)	0.24 (24 %)
	N _{3.4} ZSSP _{0.8}	3.39	0.247(1) (49.4%)	0.487(9) (95.6 %)	0.331(5) (33.1%)	0.320(2) (34.5 %)	0.310 (31.0 %)
HT-SSR	N ₃ ZSP	2.99	0.121(4) (24.3%)	0.425(5) (87.3%)	0.369(5) (36.9 %)	0.425(1) (42.5%)	0.116(9) (11.7%)
	N _{3.4} ZSP _{0.6}	3.39	0.242(7) (48.5%)	0.439(4) (87.9%)	0.412(6) (41.2%)	0.380(2) (38%)	0.222 (22%)
	N _{3.4} ZSSP _{0.8}	3.39	0.321(7) (64.3%)	0.460(8) (92.2%)	0.438 (43.8%)	0.240(5) (24%)	0.230(3) (23%)
	N _{3.4} ZSSP _{0.8} (from NPD)	3.35	0.291(8) (58.4%)	0.450(2) (90%)	0.371(4) (37.1%)	0.362(4) (36.2 %)	0.197(5) (19.7%)

3.3.2 Microstructural studies using SEM

The microstructure of a solid-state reacted NASICON plays a decisive role in determining its electrical performance, with sintering conditions strongly controlling the microstructural development. The microstructural defects, like grain boundaries, can scatter the charge carriers, leading to reduced mobility and increased resistivity in ion-conducting ceramics. Optimized sintering conditions promote grain growth and densification, while the particle size of the pre-sintered (calcined) powder also serves a critical role in enhancing the sintering behavior. Notably, different synthesis routes can significantly affect this particle size.

Figure 3.8 presents the micrographs of calcined powders for all compositions prepared by the HT-SSR method, along with the SSR-prepared $N_{3.4}ZSSP_{0.8}$ composition for comparison (Figure 3.9). The corresponding particle size distributions are also included.

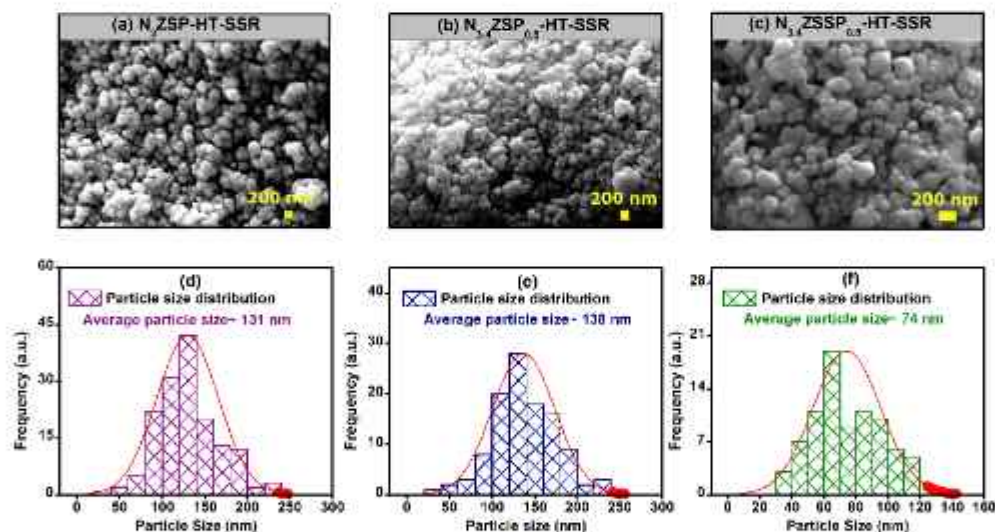


Figure 3.8: (a, b, c) The SEM images of HT-SSR prepared NASICON, and (d, e, f) the corresponding particle size distribution

The SEM analysis of HT-SSR compositions revealed calcined powders that were homogeneous in appearance, with nearly spherical morphology and some degree of agglomeration. In contrast, the SSR prepared $N_{3.4}ZSSP_{0.8}$ powder displayed relatively different morphology and a wider distribution of particle sizes, accompanied by visible clumping around the agglomerates.

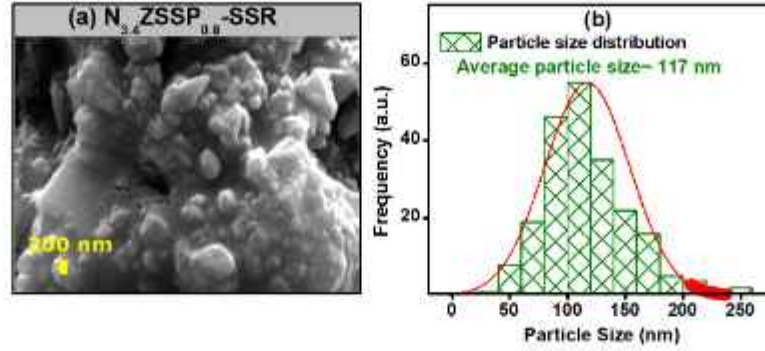


Figure 3.9: (a) The SEM image of SSR prepared $N_{3.4}ZSSP_{0.8}$ NASICON, and (b) the corresponding particle size distribution

Although agglomeration was observed in powders of both synthesis routes, it was strongly influenced by precursor homogeneity. In the SSR method, dry mixing of coarser precursors may cause localized clustering, leading to larger agglomerates. Conversely, in the HT-SSR method, wet chemistry-derived precursors could ensure uniform cation distribution at the molecular level, enabling consistent nucleation and grain growth during calcination.

The particle sizes were determined from the SEM images of the compositions and presented in the form of a histogram. The average particle size was then derived from the position of the primary peak of the particle size distribution. Primary peak for HT-SSR derived $N_{3.4}ZSSP_{0.8}$ powder was centered at 74 nm, consistent with an earlier report where the SA-SSR synthesized $Na_{3.4}Sc_{0.4}Zr_{1.6}Si_2PO_{12}$ composition exhibited a mono-modal distribution with calcined particles <50 nm. In contrast, the SSR-derived $N_{3.4}ZSSP_{0.8}$ exhibited a broader distribution with a peak at 117 nm. The average particle sizes of the remaining HT-SSR compositions are displayed in Table 3.5.

Table 3.5: Average particle size of HT-SSR NASICON composition and corresponding pellet density

Composition	Average particle size (nm)	Relative pellet density (%)
N_3ZSP	131	86
$N_{3.4}ZSP_{0.6}$	138	85
$N_{3.4}ZSSP_{0.8}$	74	94

The sinterability of the pre-sintered powders was also evaluated by estimating the relative density of the composition pellets using Archimedes' principle (Table 3.5). The HT-SSR-derived, $N_{3.4}ZSSP_{0.8}$ composition, with an average particle size of 74 nm, exhibited the highest relative density ($\sim 94\%$) among the sintered pellets. Whereas the N_3ZSP and $N_{3.4}ZSP_{0.6}$ compositions, with their higher average particle sizes of 131, 138 nm, respectively, showed lower densities. This correlation between finer average particle size and improved densification highlights the importance of pre-sintered powder characteristics in optimizing the microstructure.

3.3.3 Electric conductivity measurements of the NASICON compositions using EIS and DC polarization

The charge transport in an ideal ceramic electrolyte should be predominantly ionic, with minimal electronic contribution to ensure efficient ion conduction. To evaluate this behavior in NASICON compositions, electrochemical impedance spectroscopy (EIS) was used to probe the ionic conductivity and distinguish its underlying contributions. Meanwhile, DC polarization measurement was used to estimate the ionic transference number, to quantify the extent of ionic contribution to the total conductivity of the compositions.

The impedance data were recorded for all the NASICON compositions in the temperature range of 25 to 120 °C and are presented in the form of Nyquist plots. The room temperature Nyquist plots for the SSR-based NASICON compositions are shown in Figure 3.10 (a-c), and those for HT-SSR compositions are shown in Figure 3.11 (a-c).

The Nyquist plots of all compositions displayed a large semicircle in the high-frequency region, followed by a spike at low frequencies. In ceramic electrolytes, two distinct semicircles are typically observed at higher frequencies, corresponding to grain and grain boundary resistances, while the low-frequency spike is attributed to electrode polarization. In this study, broadening of semicircles was observed, suggesting an overlap of grain and grain boundary contributions. To resolve these

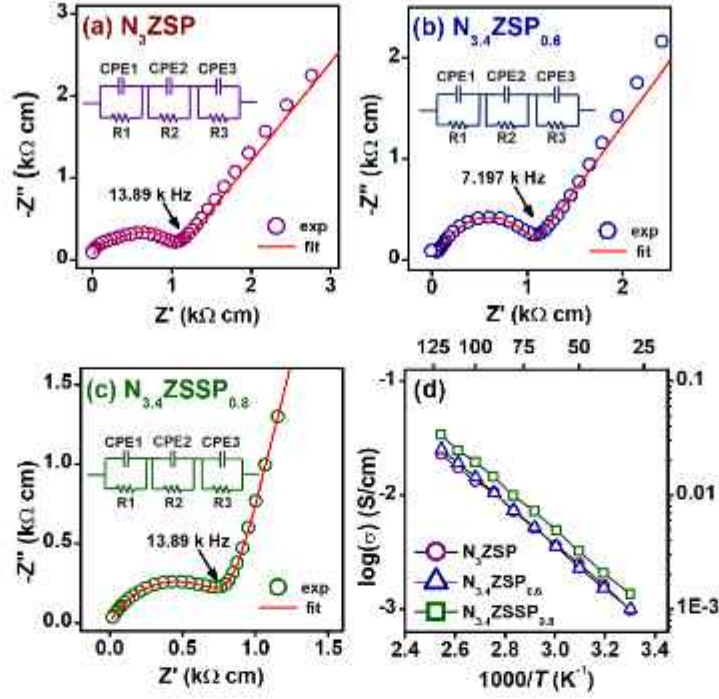


Figure 3.10: RT Nyquist plot for SSR-based (a) N_3ZSP , (b) $N_{3.4}ZSP_{0.6}$, (c) $N_{3.4}ZSSP_{0.8}$, and (d) Arrhenius plot

contributions, impedance measurement was carried out in N_3ZSP -SSR composition at 4.2°C , as shown in Figure 3.12.

At 4.2°C , two separate semicircles were clearly distinguished, confirming their association with grain and grain boundary resistances. At low temperatures, the grain-boundary contribution dominates the total impedance, forming a larger semicircle in the Nyquist plot that allows its separation.[20] Similar measurements were also performed in $N_{3.4}ZSP_{0.6}$ and $N_{3.4}ZSSP_{0.8}$; however, at $T = 4.2^\circ\text{C}$, grain boundary contribution was not resolved in these compositions, and temperatures lower than 4.2°C were not achievable using the current experimental setup.

The grain and grain boundary resistances (R_g , R_{gb}) were determined by fitting the complex impedance data with an equivalent circuit, as shown in the insets of the figures. For HT-SSR-based samples, an additional inductive element was included in the circuit model to account for the different experimental setup employed during their impedance measurements. The contributions of R_g and R_{gb} were distinguished based on their characteristic capacitance values, with $CPE \sim 10^{-12} \text{ F/cm}$ attributed to grain and $CPE \sim 10^{-9} \text{ F/cm}$ associated with the grain

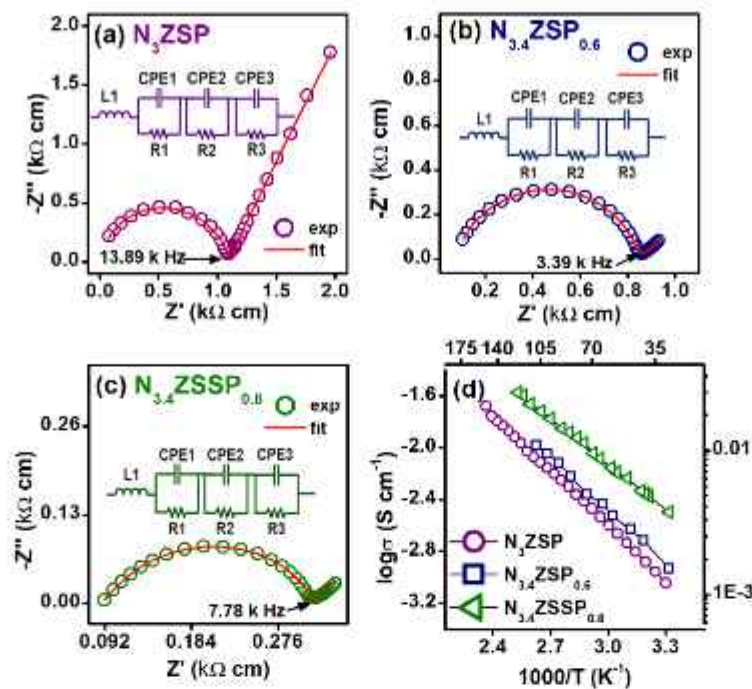


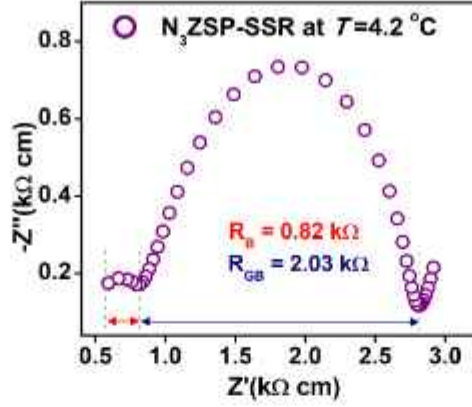
Figure 3.11: RT Nyquist plot for HT-SSR-based (a) N_3ZSP , (b) $N_{3.4}ZSP_{0.6}$, (c) $N_{3.4}ZSSP_{0.8}$, and (d) Arrhenius plot

boundary.[21] Simulated lines due to the circuit models are shown with solid lines in Figure 3.10 and Figure 3.11. Further, the experimental total ionic conductivity (σ_{total}) was calculated using the equation, $\sigma_{total} = \frac{1}{R_g + R_{gb}}$ and the values of grain and grain boundary conductivities (σ_g and σ_{gb}) obtained from equivalent circuit models are listed in Table 3.6.

Table 3.6: The grain and grain-boundary conductivity values of NASICON compositions

Synthesis route	Si/P=2:1 N_3ZSP			Si/P=2.4:0.6 $N_{3.4}ZSP_{0.6}$			Si/P=2.2:0.8 $N_{3.4}ZSSP_{0.8}$		
	σ_g (mS/cm)	σ_{gb} (mS/cm)	σ_{total} (mS/cm)	σ_g (mS/cm)	σ_{gb} (mS/cm)	σ_{total} (mS/cm)	σ_g (mS/cm)	σ_{gb} (mS/cm)	σ_{total} (mS/cm)
SSR	3.90	1.30	0.99	4.20	1.35	1.02	7.70	1.37	1.16
HT-SSR	4.17	1.18	0.92	6.21	1.45	1.18	9.34	4.93	3.22

The total room-temperature conductivity (σ_{total}) of the SSR-synthesized N_3ZSP composition was estimated to be 0.99 mS/cm. This value closely matched the previously reported conductivity by Noi *et al.*[13], confirming that the total conductivity obtained in this study represents the maximum achievable for the N_3ZSP composition.

Figure 3.12: Nyquist plot for SSR-based N_3ZSP at $T = 4.2^\circ C$

For the Na-rich compositions, $N_{3.4}ZSP_{0.6}$ exhibited a σ_{total} of 1.02 mS/cm, which increased to 1.16 mS/cm in $N_{3.4}ZSSP_{0.8}$. A closer analysis of the grain conductivity ($\sigma_g = 1/R_g$) revealed a systematic trend. In SSR-based compositions, increasing the Na content from 3.0 to 3.4 per formula unit (f.u.) by modifying Si/P ratio from 2:1 to 2.4:0.6 resulted in a modest rise in σ_g from 3.9 to 4.2 mS/cm. In $N_{3.4}ZSSP_{0.8}$ composition, σ_g increased more significantly to 7.7 mS/cm, likely due to the combined effect of the optimum Si/P ratio (2.2:0.8), as reported by Samice *et al.*[22] and scandium incorporation. The grain boundary conductivity ($\sigma_{gb} = 1/R_{gb}$) showed only a marginal improvement in SSR-derived compositions. In case of HT-SSR compositions, σ_{total} values were higher than those of the corresponding SSR-based samples, except for the parent N_3ZSP composition. For N_3ZSP , σ_{total} remained comparable between the two synthesis routes, with the HT-SSR sample (0.92 mS/cm) closely matching the 1.0 mS/cm reported by Naqash *et al.*[23] for SA-SSR synthesis. For HT-SSR-derived $N_{3.4}ZSP_{0.6}$ and $N_{3.4}ZSSP_{0.8}$ compositions, σ_{total} increased from 1.18 to 3.22 mS/cm, respectively. Analysis of the grain contributions revealed that, similar to SSR compositions, the grain conductivity increased across the series; however, the values were consistently higher than those of SSR samples. This improvement can be attributed to reduced sodium loss during the lower temperature calcination at 800 °C, compared to 1100 °C for SSR synthesis. For the HT-SSR compositions, σ_g increased from 4.17 mS/cm for N_3ZSP to 6.21 mS/cm for $N_{3.4}ZSP_{0.6}$, and reached 9.34 mS/cm for $N_{3.4}ZSSP_{0.8}$.

The grain boundary conductivity (σ_{gb}) also showed a gradual increase, rising from 1.18 to 1.45 mS/cm, and reaching a maximum of 4.93 mS/cm for $N_{3.4}ZSSP_{0.8}$. The highest conductivity was observed for the HT-SSR $N_{3.4}ZSSP_{0.8}$ composition. This indicates that the optimized sintering conditions and composition enhance grain conductivity, while the improved microstructure achieved through the HT-SSR route increases grain boundary conductivity. Together, these factors contribute to the high total conductivity of 3.22 mS/cm.

The temperature dependence of σ_{total} for the SSR-based samples is presented in Figure 3.10(d), while for the HT-SSR samples is shown in Figure 3.11(d). All compositions exhibited Arrhenius-type behaviour. The σ_{total} values of N_3ZSP and $N_{3.4}ZSP_{0.6}$ for both SSR and HT-SSR compositions showed minimal variation across the measured temperature range. The SSR-based $N_{3.4}ZSSP_{0.8}$ exhibited a slight increase compared to the other two compositions, whereas HT-SSR $N_{3.4}ZSSP_{0.8}$ showed a pronounced enhancement in σ_{total} values across the temperature range. The activation energy for $N_{3.4}ZSSP_{0.8}$ composition was estimated to be 0.36 eV for the SSR route and 0.23 eV for the HT-SSR route. This lower activation energy in the HT-SSR sample further confirms reduced grain-boundary resistance due to its improved microstructure. To estimate the contributions from ionic charge carriers towards the measured total conductivity, DC-polarization experiment was carried out in an $Ag|N_3ZSP|Ag$ and an $Ag|N_{3.4}ZSSP_{0.8}|Ag$ cell with an applied constant potential of 0.8 V. The variation of total current as a function of time is shown in Figure 3.13.

The ionic transference numbers were determined for N_3ZSP and $N_{3.4}ZSSP_{0.8}$ using the equation, $t_i = \frac{I_t - I_e}{I_t}$, where I_t represents the total (ionic plus electronic) current measured at $t \approx 0$ s and I_e corresponds to the steady state electronic current measured at $t \approx 7200$ s. The calculated values of t_i were 0.97 for N_3ZSP and 0.99 for $N_{3.4}ZSSP_{0.8}$. The magnitude of these values being close to unity confirms that both N_3ZSP and $N_{3.4}ZSSP_{0.8}$ possess predominant ionic conduction with very low electronic conductivity.

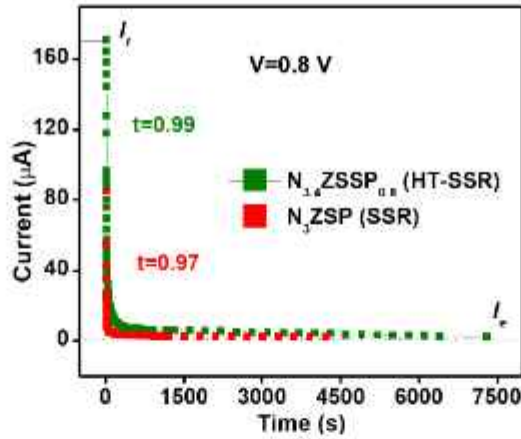


Figure 3.13: DC polarization response of Ag|N₃ZSP|Ag and Ag|N_{3.4}ZSSP_{0.8}|Ag cell

3.3.4 Investigation of Na⁺ defect distribution using positron annihilation lifetime spectroscopy (PALS)

In a solid, the lifetime of thermalized positrons is governed by the local electron density at the annihilation site, making PALS a powerful tool for probing cationic vacancies. Consequently, cationic vacancies, due to their reduced electron density, lead to an elongated positron lifetime compared to that of bulk crystals. In our study, N_{3.4}ZSP_{0.6} and N_{3.4}ZSSP_{0.8} compositions maintain a fixed Na-content/f.u. of 3.4, which is reported to be optimal. However, this content is distributed across five distinct sodium sites as observed from XRD/NPD results (Section 3.3.1). Such a distribution of Na defects can alter the pathways available for Na⁺-ion transport, making it essential to characterize both these defects and their spatial arrangement, for which PALS was used.

The PALS spectra measured at room temperature in SSR-based N₃ZSP and HT-SSR-based N_{3.4}ZSP_{0.6} and N_{3.4}ZSSP_{0.8} compositions are shown in Figure 3.14.

A typical positron lifetime spectrum can be described as a sum of decaying exponentials, with each exponential representing a distinct positron state in the material. As shown in Figure 3.14, the slopes of the exponential decay regions varied across different compositions. This variation reflected that the local annihilation environments experienced by the positrons in the defect regions can vary

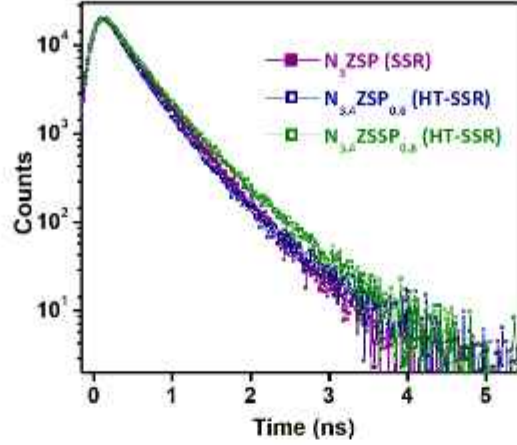


Figure 3.14: Experimental PAL spectra of N_3ZSP , $N_{3.4}ZSP_{0.6}$, and $N_{3.4}ZSSP_{0.8}$ samples

with composition. To resolve these annihilation modes, PAL spectra were analyzed using PALSfit program[24], which mathematically models the experimental data using the following expression,

$$F(t) = \sum_{i=1}^k \frac{I_i}{\tau_i} e^{-t/\tau_i}$$

Where, $F(t)$ is the number of counts at time t , k is the number of exponential decay components and τ_i is the lifetime of the i^{th} component having intensity I_i . In present study, the experimental spectra were best fitted into three discrete lifetime components, with fitting variance close to unity. A representative fitted spectrum for N_3ZSP composition is shown in Figure 3.15 and the corresponding positron annihilation lifetime components (τ_1 , τ_2 , and τ_3) and intensities (I_1 , I_2 , and I_3) are summarised in Table 3.7.

Table 3.7: Positron annihilation lifetime and intensity parameters

Compositions	Component-1		Component-2		Component-3	
	$\tau_1 \pm 0.015$ (ns)	$I_1 \pm 3.6$ (%)	$\tau_2 \pm 0.015$ (ns)	$I_2 \pm 3.4$ (%)	$\tau_3 \pm 0.015$ (ns)	$I_3 \pm 3$ (%)
N_3ZSP (SSR)	0.180	13.9	0.354	75.6	0.608	10.5
$N_{3.4}SP_{0.6}$ (HT-SSR)	0.152	16.3	0.330	76.3	0.793	7.4
$N_{3.4}SSP_{0.8}$ (HT-SSR)	0.131	6.1	0.339	75.0	0.656	18.9

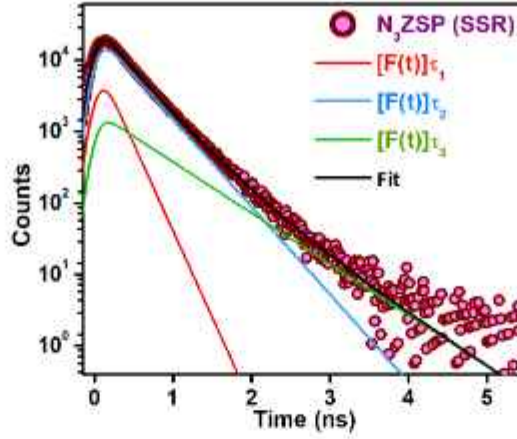


Figure 3.15: The fit of experimental PAL spectra for N_3ZSP with three components

In principle, when the PALS spectra are fitted using only positron components, a material containing a single type of lattice defect (such as mono-vacancy-like defects) yields two lifetime components. The first component τ_1 corresponds to positron annihilation in the defect-free bulk region along with trapping into mono-vacancies, while the second component (τ_2) arises from positron annihilating after being trapped in these vacancies. In a case where two types of defects are present, such as vacancy-like defects and vacancy clusters, the spectra in principle can be resolved into three lifetime components: (i) free positron annihilation in the bulk and trapping into the vacancy-like defects, (ii) annihilation in vacancy-like defects, and (iii) annihilation in vacancy clusters. However, in practice, decomposing PALS spectra into three positron components often introduces large uncertainties in the extracted lifetimes and intensities.[25]

Therefore, to achieve reliable fitting, the present PALS spectra were decomposed into two positron lifetime components (τ_1 and τ_2) and one positronium component (τ_3), which provided the best χ^2 values. In this fitting, the third component (τ_3) exhibits a lifetime between 0.5 ns and 1.0 ns, which cannot be attributed solely to the pick-off annihilation of ortho-positronium (o -Ps) formed in the large voids by multiple grain boundaries. Instead, it likely represents a combination of o -Ps annihilation and trapped positronium annihilation in surface defects. Furthermore, a fraction of thermalized positrons diffusing into grain boundaries can form positro-

nium, which becomes trapped in large boundary voids, giving rise to a pick-off lifetime exceeding ~ 1.0 ns. Hence, in the present three-component fitting, the first lifetime component (τ_1) corresponds to a weighted average of states (i) and (ii), while the second component (τ_2) represents the state (iii). In all three compositions, the obtained τ_2 values are higher than the typical trapped positron lifetime in mono-vacancy-like defects. The relatively high estimated errors observed in I_1 and I_2 across all samples indicate a distribution in the number density of these voids.

To better interpret these observations, the defect states were also correlated with the Na-site occupancies in the monoclinic NASICON structure shown in Figure 3.16(a).

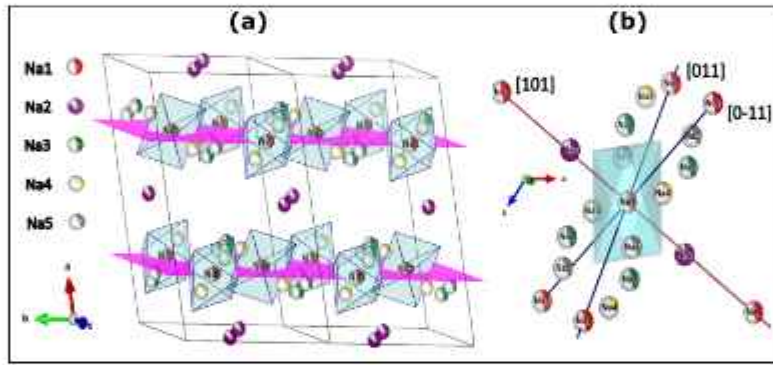


Figure 3.16: (a) Monoclinic NASICON unit cell showing site arrangement along the bc plane and (b) Enlarged view of Na sites.

The Na atoms occupied five distinct crystallographic sites (Na1-Na5), where Rietveld refinement of diffraction data revealed the highest occupancy at Na2 sites (~ 0.87) and the lowest at Na5 sites (~ 0.13) in the N_3ZSP composition (Table 3.4). With increasing Na content per formula unit, the occupancy of certain Na sites increased, leading to two different categories of vacancy formation: (i) mono-vacancy pairs (Schottky defects) at unoccupied Na2 sites, and (ii) vacancy clusters formed by unoccupied Na1, Na3, Na4, and Na5 sites (both Schottky and Frenkel defects) located around the bc planes (Figure 3.16(b)). Within this framework, τ_1 was attributed to positron trapping at Na2 site vacancies, while τ_2 represented trapping at vacancy clusters. The consistency between the estimated intensity values of

I_1 and I_2 and Na site occupancies further supported this interpretation. In the PALS, intensity reflects the concentration of defects while lifetime indicates their size. For the N_3ZSP composition, I_1 contributed only 13.8 % due to the higher occupancy (~ 0.87) of the Na2 site, whereas I_2 dominated with 75.6 % due to much lower occupancies of Na1, Na3, Na4, and Na5 sites. These consistencies between the PALS and XRD/NPD results support the validity of the model used for PALS fitting and the correct interpretation of the PALS components.

3.3.5 Electrochemical performance study by CV and GCD

Interfacial stability is a critical factor in the operation of an assembled solid-state battery. Since the sodium metal serves as the primary anode in practical applications, the compatibility of $N_{3.4}ZSSP_{0.8}$ HT-SSR with sodium metal foil was evaluated using the cyclic voltammetry (CV) curve of $Ag|N_{3.4}ZSSP_{0.8}|Na$ cell. The CV profile is shown in Figure 3.17.

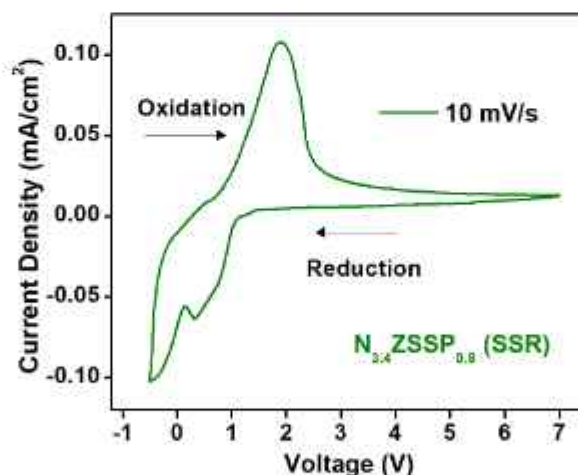


Figure 3.17: Cyclic voltammetry profile obtained on the $Ag|N_{3.4}ZSSP_{0.8}|Na$ cell

The CV curve in Figure 3.17 exhibited a pair of redox peaks at 0.32 and 1.9 V, which can be attributed to the sodium plating and stripping process. These observed redox potentials are also in close agreement with values reported for $Ag|N_3ZSP|Na$. [26] Additionally, no other peaks were detected up to 7 V, which shows a wider electrochemical stability window of this composition versus Na^+/Na .

To further evaluate its practical performance, a symmetric $\text{Na}|\text{N}_{3.4}\text{ZSSP}_{0.8}|\text{Na}$ swagelok-type cell was fabricated and subjected to galvanostatic cycling under constant current densities of 10 and 20 $\mu\text{A cm}^{-2}$.

The voltage response was continuously monitored over an extended duration to assess the stability and reversibility of the electrode-electrolyte interface. The corresponding GCD profile is shown in Figure 3.18.

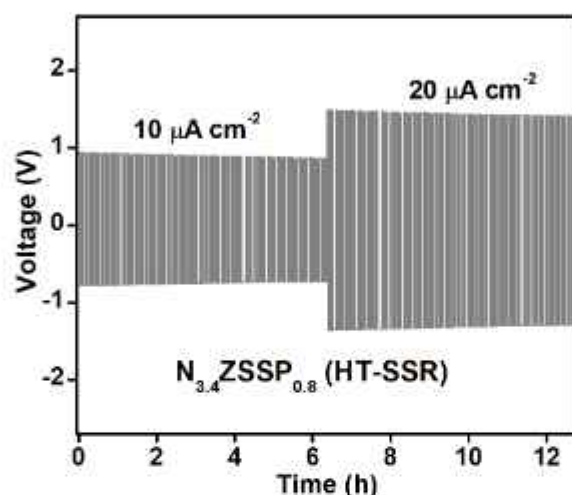


Figure 3.18: Galvanostatic cycling of $\text{Na}|\text{N}_{3.4}\text{ZSSP}_{0.8}|\text{Na}$ symmetric cell.

The galvanostatic voltage profile demonstrated stable polarisation voltage throughout the measurement duration. This result qualifies $\text{N}_{3.4}\text{ZSSP}_{0.8}$ composition for application in battery material. However, further electrochemical study employing a suitable cathode material may be addressed as a part of the future scope for the current study.

3.4 Identification of conduction channels in NASICON composition

Ion transport in NASICON-type compositions is governed by the interplay of crystallographic, microstructural, and synthesis-dependent parameters, as substantiated by the experimental results of this study. Structural features such as increased Na content, favorable site occupancy distribution, aliovalent Sc^{3+} substitution, and

an optimized Si/P of 2.2:0.8 were found to enhance conductivity. Furthermore, the superiority of HT-SSR over conventional SSR synthesis highlighted the influence of synthesis in controlling microstructure. Consequently, total ionic conductivity improved due to the combined contributions of grain conductivity, determined by intrinsic structural factors, and grain boundary conductivity influenced by microstructural characteristics. To systematically probe these structure-property relationships, variations of key structural parameters, such as unit cell volume, refined Na-content/f.u., Na-site distribution, and bottleneck sizes, were closely analyzed across compositions and synthesis methods.

In the $R\bar{3}c$ polymorph of NASICON structure, ^{23}Na MAS NMR study on $\text{Na}_{3+x}\text{Sc}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ composition has reported three-dimensional Na^+ -ion migration occurring primarily via the Na1 site.[5] Given that the monoclinic $C2/c$ phase observed for currently synthesized NASICON compositions is also a subgroup of $R\bar{3}c$ structure, the possible migration pathways were identified using the results of XRD/NPD and PALS.

Figure 3.19(a) illustrates the spatial distribution of Na sites around the Na1 site and the possible migration pathways in $\text{N}_{3.4}\text{ZSSP}_{0.8}$ composition. From the structural model, it was identified that each Na1 site was coordinated to two Na2 sites ($3.5 \text{ \AA}$), two Na4 sites ($1.60 \text{ \AA}$), and two Na5 sites ($2.5 \text{ \AA}$), with remaining inter-Na distances listed in Table 3.8.

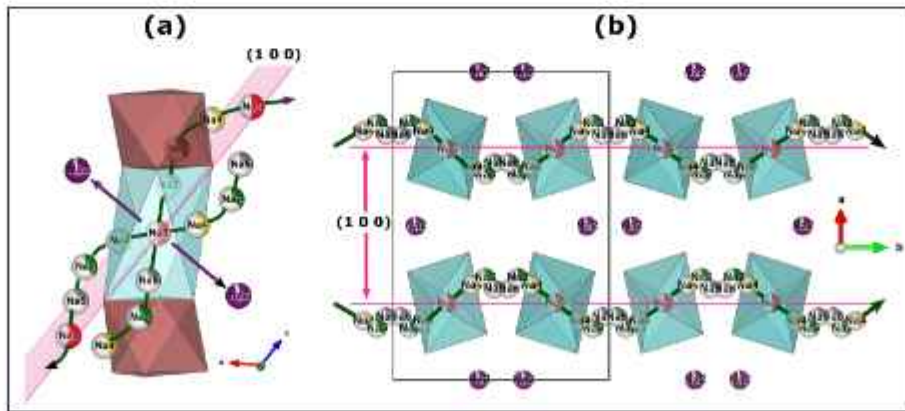


Figure 3.19: (a) Na^+ -ion migration pathways and (b) Correlated migration along (100) plane in $\text{N}_{3.4}\text{ZSSP}_{0.8}$ HT-SSR

Table 3.8: Bond lengths and bottleneck sizes for SSR and HT-SSR $N_{3.4}ZSSP_{0.8}$ composition

Path	Bond distance (Å)		Bottleneck size (Å)	
	SSR	HT-SSR	SSR	HT-SSR
Na1-Na2	3.508(2)	3.502(2)	2.392(7)	2.385(5)
Na1-Na4	1.627(8)	1.629(7)	2.313(8)	2.305(1)
Na4-Na3	1.495(1)	1.495(2)	2.261(4)	2.257(1)
Na3-Na5	1.668(1)	1.479(9)	2.353(9)	2.349(9)
Na5-Na1	2.409(9)	2.468(4)	2.385(1)	2.377(5)

Analysis of the migration channels revealed that Na^+ ions primarily migrate through the Na2-Na1-Na2 pathway along the $[101]$ direction via an ion hopping mechanism (Purple arrows), whereas correlated migration occurs along the Na1-Na4-Na3-Na5-Na1 pathway in the bc plane along the (100) direction (Green arrows). The Na1-Na2 hopping distance of 3.5 Å supports efficient single-ion jumps along $[101]$ direction, whereas shorter inter-Na distances along the bc plane suggest correlated migration as the dominant mode of ion transport there.

In both modes of transport mechanisms, Na^+ -ion must transverse through a bottleneck area, which requires a minimum incircle diameter exceeding the sum of Na^+ and O^{2-} radii (2.35 Å). Therefore, the bottleneck sizes for SSR and HT-SSR synthesized $N_{3.4}ZSSP_{0.8}$ composition were determined, and corresponding values are shown in Table 3.8.

The bottleneck size for Na1-Na2, Na3-Na5, and Na5-Na1 pathways was found to exceed 2.35 Å , indicating easier migration of Na^+ -ion between these sites, while the slightly smaller Na1-Na4 and Na4-Na3 bottlenecks ($< 2.35 \text{ Å}$) implied comparatively less favourable migration across these sites. However, occupancy factors for these Na sites showed a strong preference for low low-energy Na2 site (Occupancy $\sim 92 \%$ in $N_{3.4}ZSSP_{0.8}$), which reduces hopping along the Na2-Na1-Na2 pathway despite its favorable bottleneck size. As a result, Na^+ -ion conduction becomes anisotropic, with Na1-Na4-Na3-Na5-Na1 pathway as the primary route for long-range migration. This migration pathway is illustrated across two unit cells in Figure 3.19(b).

3.5 Conclusion

In the present work, we have investigated the system of three NASICON compositions on the basis of their structure, composition, and synthesis route. Using N_3ZSP as the prototype composition, stepwise enhancements in ionic conductivity were achieved. First, increasing the Na-content by adjusting the Si/P ratio from 2.0/1.0 to 2.4/0.6 enhanced the grain conductivity. Further improvement was achieved by partially substituting Sc^{3+} for Zr^{4+} while maintaining the Si/P ratio at 2.2/0.8. In addition, optimized sintering conditions and microstructural tuning of pre-sintered powders via HT-SSR method, further boosted the grain boundary conductivity. As a result, HT-SSR prepared $\text{N}_{3.4}\text{ZSSP}_{0.8}$ composition exhibited highest total ionic conductivity of 3.2 mS/cm at 25 °C (approximately three times higher than that of pristine N_3ZSP) with DC polarization confirming negligible electronic conductivity.

Electrochemical evaluation using cyclic voltammetry demonstrated stable interfacial stability vs. Na metal up to 7 V, and galvanostatic charge-discharge (GCD), showed consistent and reversible cycling performance. Finally, XRD/NPD and PALS analysis identified the dominant Na^+ -ion migration pathway, revealing correlated migration primarily along (100) plane. Overall, this established a clear structure-composition-synthesis-property relationship and provided valuable guidelines for designing new high performance electrolytes.

References

- [1] H. Hong, *Materials Research Bulletin*, vol. 11, no. 2, pp. 173–182, 1976.
- [2] J. B. Goodenough, H. Hong, and J. A. Kafalas, *Materials Research Bulletin*, vol. 11, no. 2, pp. 203–220, Feb. 1976.
- [3] A. G. Jolley, G. Cohn, G. T. Hitz, and E. D. Wachsman, *Ionics*, vol. 21, no. 11, pp. 3031–3038, Nov. 2015.
- [4] L. Liu et al., *Materials Today Chemistry*, vol. 30, p. 101495, 2023, ISSN: 2468–5194. DOI: <https://doi.org/10.1016/j.mtchem.2023.101495>.
- [5] B. Santhoshkumar et al., *Chemical Physics Letters*, vol. 776, p. 138706, 2021, ISSN: 0009–2614. DOI: <https://doi.org/10.1016/j.cplett.2021.138706>.
- [6] J. Yang et al., *ACS Energy Lett.*, vol. 5, no. 9, pp. 2835–2841, Sep. 2020.
- [7] Y. Liu et al., *Journal of Power Sources*, vol. 518, p. 230765, 2022. DOI: [10.1016/j.jpowsour.2021.230765](https://doi.org/10.1016/j.jpowsour.2021.230765).
- [8] A. Clearfield, M. Subramanian, W. Wang, and P. Jerus, *Solid State Ionics*, vol. 9-10, pp. 895–902, 1983, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/0167-2738\(83\)90108-X](https://doi.org/10.1016/0167-2738(83)90108-X).
- [9] Q. Ma, M. Guin, S. Naqash, C.-L. Tsai, F. Tietz, and O. Guillon, *Chem. Mater.*, vol. 28, no. 13, pp. 4821–4828, Jul. 2016. DOI: [10.1021/acs.chemmater.6b02059](https://doi.org/10.1021/acs.chemmater.6b02059).
- [10] O. Arcelus et al., *Journal of Applied Crystallography*, vol. 57, no. 5, pp. 1676–1690, Oct. 2024. DOI: [10.1107/S1600576724006885](https://doi.org/10.1107/S1600576724006885).
- [11] A. S. Bondarenko and G. A. Ragoisha, in *Progress in Chemo-metrics Research*, A. L. Pomcrantsev, Ed., Program available at <http://www.abc.chemistry.bsu.by/vi/analyser/>, New York: Nova Science Publishers, 2005, pp. 89–102.

- [12] C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, *Nature Methods*, vol. 9, no. 7, pp. 671–675, Jul. 2012.
- [13] K. Noi, K. Suzuki, N. Tanibata, A. Hayashi, and M. Tatsumisago, *Journal of the American Ceramic Society*, vol. 101, no. 3, pp. 1255–1265, 2018. DOI: <https://doi.org/10.1111/jace.15288>.
- [14] Y. B. Rao, K. K. Bharathi, and L. Patro, *Solid State Ionics*, vol. 366–367, p. 115671, 2021, ISSN: 0167–2738. DOI: <https://doi.org/10.1016/j.ssi.2021.115671>.
- [15] Q. Ma, C.-L. Tsai, X.-K. Wei, M. Heggen, F. Tietz, and J. T. S. Irvine, *J. Mater. Chem. A*, vol. 7, pp. 7766–7776, 13 2019. DOI: 10.1039/C9TA00048H.
- [16] A. Chakraborty, R. Thirupathi, S. Bhattacharyya, K. Singh, and S. Omar, *Journal of Power Sources*, vol. 572, p. 233092, 2023, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2023.233092>.
- [17] Y. Lu, J. A. Alonso, Q. Yi, L. Lu, Z. L. Wang, and C. Sun, *Advanced Energy Materials*, vol. 9, no. 28, p. 1901205, 2019. DOI: <https://doi.org/10.1002/aenm.201901205>.
- [18] W. Baur, J. Dygas, D. Whitmore, and J. Faber, *Solid State Ionics*, vol. 18–19, pp. 935–943, 1986, ISSN: 0167–2738. DOI: [https://doi.org/10.1016/0167-2738\(86\)90290-0](https://doi.org/10.1016/0167-2738(86)90290-0).
- [19] Z. Zhang et al., *Advanced Energy Materials*, vol. 9, no. 42, p. 1902373, 2019. DOI: <https://doi.org/10.1002/aenm.201902373>.
- [20] H. Park, K. Jung, M. Nezaferati, C.-S. Kim, and B. Kang, *ACS Applied Materials & Interfaces*, vol. 8, no. 41, pp. 27814–27824, 2016. DOI: 10.1021/acsami.6b09992.
- [21] J. T. S. Irvine, D. C. Sinclair, and A. R. West, *Advanced Materials*, vol. 2, no. 3, pp. 132–138, 1990. DOI: <https://doi.org/10.1002/adma.19900020304>.

- [22] M. Samice et al., *Journal of Power Sources*, vol. 347, pp. 229–237, 2017, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2017.02.042>.
- [23] S. Naqash, Q. Ma, F. Tietz, and O. Guillon, *Solid State Ionics*, vol. 302, pp. 83–91, 2017, ISSN: 0167-2738. DOI: <https://doi.org/10.1016/j.ssi.2016.11.004>.
- [24] J. V. Olsen, P. Kirkegaard, and M. Eldrup, Department of Energy Conversion and Storage, Technical University of Denmark, Tech. Rep., 2022, Version 3.251.
- [25] A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kauppila, and P. Moser, *Phys. Rev. B*, vol. 25, pp. 762–780, 2 Jan. 1982. DOI: 10.1103/PhysRevB.25.762.
- [26] Y. Ruan, F. Guo, J. Liu, S. Song, N. Jiang, and B. Cheng, *Ceramics International*, vol. 45, no. 2, Part A, pp. 1770–1776, 2019, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2018.10.062>.

CHAPTER 4

PEO- NaNO_3 -NASICON-based composite electrolytes

4.1 Introduction

Inorganic conductors and organic polymers are the most commonly explored classes of solid electrolyte materials for application in all-solid-state batteries (ASSBs).[1] Among inorganic systems, NASICON (**Na Super Ionic CONductor**) type ceramics are notable for their high ionic conductivity ($> 10^{-4} \text{ S cm}^{-1}$), excellent thermal stability, broad electrochemical window ($> 5 \text{ V}$) and predominantly single-ion conduction, which minimizes concentration polarization.[2] However, their practical application is often hindered by poor electrolyte-electrode interfacial contact, leading to high interfacial resistance and limited cycling stability. Conversely, polymer electrolytes provide good mechanical flexibility and intimate contact with the electrode surfaces, making them suitable for flexible battery architectures; yet, their application is limited by low room-temperature ionic conductivity ($< 10^{-5} \text{ S cm}^{-1}$).[3] To address these limitations, integrating ceramic fillers into the polymer matrix has emerged as an effective strategy to form composite electrolytes (CEs).

Among various polymer hosts explored, poly(ethylene oxide) (PEO) has garnered significant attention because of its ability to coordinate alkali metal cations and support ion transport when complexed with a suitable salt. In present work, NaNO_3 is selected as sodium salt, owing to its cost effectiveness and relatively

easy handling compared to commonly used salts like NaTFSI [4], [5] and NaClO₄ [6], [7]. Nevertheless, the high crystallinity ($> 60\%$) of PEO at ambient temperature restricts its ionic conductivity to $\sim 10^{-6} \text{ S cm}^{-1}$, necessitating operation at elevated temperatures (50-80 °C) to enhance segmental mobility.[3] To address these limitations, integrating ceramic fillers into the polymer matrix has emerged as an effective strategy to form composite electrolytes (CEs). Introduction of both, passive (e.g., SiO₂, Al₂O₃) and active (Na⁺-ion conducting) fillers can disrupt crystalline domains of PEO and lower its glass transition temperature.[8], [9], [10], [11] However, active fillers also provide an additional advantage by contributing Na⁺-ion conduction pathways at polymer-ceramic interface, thereby improving the overall conductivity of the composite electrolytes.

Based on this approach, Na⁺-ion conducting PEO-NaNO₃-NASICON composite electrolytes (CEs) have been developed by incorporating three highly conductive NASICON-type ceramic fillers of Na_{3.4}Zr_{1.9}Zn_{0.1}Si_{2.2}P_{0.8}O₁₂, Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.6}O₁₂, and Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂, while maintaining PEO:NaNO₃ molar ratio at 15:1. Additionally, the optimized ceramic compositions are synthesized by three different approaches - solid state reaction (SSR) for Na_{3.4}Zr_{1.9}Zn_{0.1}Si_{2.2}P_{0.8}O₁₂, solution assisted solid state reaction method (SA-SSR) for Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.6}O₁₂ and hydrothermal based solid state reaction method (HT-SSR) for Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂. Consequently, the ion transport behavior of the composite electrolytes (CEs) synthesized by using these fillers was investigated to evaluate the influence of their particle size and composition.

The objectives of the present investigation are thus:

- Synthesis and characterization of the three optimized NASICON compositions - Na_{3.4}Zr_{1.9}Zn_{0.1}Si_{2.2}P_{0.8}O₁₂, Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.6}O₁₂, and Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂.
- Investigating the effect of optimized NASICON ceramic composition, particle size and weight percentage (wt%) in tailoring the polymer crystallinity, ionic conductivity and polymer-ceramic interfacial interactions in composite

electrolyte films.

- Assessing the electrochemical performance of the composite electrolyte films in terms of their electrochemical stability and cycling behavior.
- Determining Na^+ -ion migration pathway in the proposed system.

4.2 Methods and experimental design

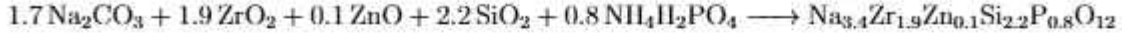
4.2.1 Synthesis of NASICON ceramic fillers

The NASICON ceramic fillers with stoichiometric compositions of $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$, $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$, and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ were synthesized using the solid state reaction method (SSR), solution-assisted solid state reaction method (SA-SSR), and hydrothermal-based solid state reaction method (HT-SSR), respectively. The detailed descriptions of each synthesis procedure are discussed in the following sections.

4.2.1.1 Solid state reaction for synthesis of $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$

Nominal polycrystalline NASICON composition of $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ was prepared by a solid-state reaction procedure using Na_2CO_3 (Sigma-Aldrich, 99.0%), ZrO_2 (Sigma-Aldrich, 99.0%), SiO_2 (Alfa Aesar, 99.9%), ZnO (SDFCL, 99.0%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 99.9%) as precursors. The precursors were ground and preheated to get rid of moisture that may be present. Stoichiometric amounts of the precursors were mixed thoroughly using isopropanol in an agate mortar and pestle. Dried mixtures were calcined at 900°C for 10 h. Later, calcined powders were ground manually and pressed to form pellets of 10 mm diameter and ~ 2 mm thickness by applying a pressure of 250 MPa for 2 min. The sample pellets were sintered at 1250°C for 5 h. Calcination/sintering temperature (duration) was used as proposed by Yang *et al.*[12]

The chemical reaction of the synthesized composition of Na_{3.4}Zr_{1.9}Zn_{0.1}Si_{2.2}P_{0.8}O₁₂ is as follows:



4.2.1.2 Solution-assisted state reaction (SA-SSR) for synthesis of Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.6}O₁₂

The niobium-doped composition of Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.6}O₁₂ was synthesized via a solution-assisted route, using NaNO₃ (Alfa Aesar, 99.0%), ZrO(NO₃)₂ (Sigma-Aldrich, 99.0%), Si(OC₂H₅)₄ (Alfa Aesar, 99.0%), NH₄H₂PO₄ (Alfa Aesar, 99.9%), and NH₄NbO(C₂O₄)₂ (Sigma-Aldrich, 99.99%) as precursors. NaNO₃ and ZrO(NO₃)₂ were first dissolved in the distilled water and stirred until a clear solution was obtained. Nitric acid was then added, and the mixture was stirred for one hour. Subsequently, Si(OC₂H₅)₄ and NH₄H₂PO₄ were added, followed by NH₄NbO(C₂O₄)₂. The resulting mixture was stirred overnight and dried at 80 °C for 24 h. The obtained dried powder was calcined at 800 °C for 3 h, ground in ethanol for 24 hours, and finally sintered at 1260 °C/5h. The synthesis procedure followed the route proposed by Liu *et al.*[13]

4.2.1.3 Hydrothermal-based solid-state reaction (HT-SSR) for synthesis of Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂

The synthesis of Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂ was carried out by a hydrothermal combined solid-state reaction method (HT-SSR), and the detailed synthesis steps are outlined in section 3.3.1.2 of chapter 3. The final NASICON powders were manually ground for 48 hours before mixing them as ceramic fillers in the composites. For convenience, the compositions of Na_{3.4}Zr_{1.9}Zn_{0.1}Si_{2.2}P_{0.8}O₁₂, Na_{3.4}Zr_{1.9}Nb_{0.1}Si_{2.4}P_{0.4}O₁₂, and Na_{3.4}Zr_{1.8}Sc_{0.2}Si_{2.2}P_{0.8}O₁₂ are referred to as NZ-ZSP, NZNSP, and NZSSP in the following sections, respectively.

4.2.2 Synthesis of PEO- NaNO_3 -NASICON polymer composite films

The preparation of ceramic-composite polymer electrolytes in this work was carried out using the solution casting method. PEO (Sigma-Aldrich, ($M_w = 2 \times 10^5$ g/mol) and NaNO_3 (Alfa Aesar, 99.0%) were preheated at 40°C and 150°C for 24 hours, respectively, to remove moisture. NaNO_3 was first dissolved in 16.77 mL of methanol and stirred for an hour. Subsequently, PEO and NASICON ceramic powders were added to the solution and stirred at 40°C for 2 hours. After switching off the heat, stirring was continued for a week, with small amounts of methanol added intermittently to maintain adequate viscosity. The resulting viscous mixture was then sonicated for 20 minutes to ensure its homogeneity, before being cast into a petridish. The solvent was allowed to evaporate at room temperature for three days, followed by drying at 40°C for 24 hours to obtain uniform composite films. The prepared membranes were then stored in a vacuum desiccator to prevent moisture absorption, and an argon atmosphere was maintained during the synthesis steps. A schematic illustration of these synthesis steps is shown in Figure 4.1.

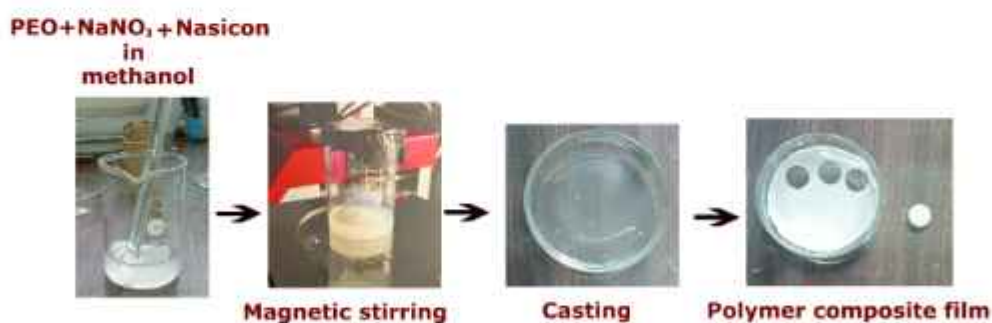


Figure 4.1: Schematic diagram of the synthesis of composite polymer electrolyte films

A pure PEO- NaNO_3 film was prepared with an EO/Na molar ratio maintained at 15:1 and denoted as PE. For the Zn-doped composition (NZZSP), composite films were fabricated by varying PEO:NASICON weight percentage as 85:15, 70:30,

55:45, 40:60, and 25:75, corresponding to PE- x wt% NZZSP formulations. In addition, composite films incorporating Nb-doped (NZNSP) and Sc-doped (NZSSP) ceramics at a fixed ceramic loading of 60 wt% were prepared in later stages to examine the influence of the ceramic composition and particle size on the composite electrolyte properties. The abbreviations of the synthesized films alongside their composition are shown in Table 4.1.

Table 4.1: The composition and abbreviation of the composite films

Composition	Abbreviation
PEO:NaNO ₃	PE
85 wt% PE:15 wt% NZZSP	CE15Zn
70 wt% PE:30 wt% NZZSP	CE30Zn
55 wt% PE:45 wt% NZZSP	CE45Zn
40 wt% PE:60 wt% NZZSP	CE60Zn
25 wt% PE:75 wt% NZZSP	CE75Zn
40 wt% PE:60 wt% NZNSP	CE60Nb
40 wt% PE:60 wt% NZSSP	CE60Sc

4.2.3 X-ray powder diffraction and Differential scanning calorimetry study

The phase content of both the powdered ceramic fillers (NZZSP and NZNSP) and the polymer composite films was examined using room temperature X-ray diffraction (XRD) measurement, carried out on a Rigaku diffractometer using Cu K α radiation. The diffraction data were collected over a 2θ range of 10°–80° with the step size of 0.02°. Identification of the crystalline phases along with the structural refinement of the ceramic XRD data was performed using the Rietveld method implemented in the Fullprof software[14]. A pseudo-Voigt function was used to describe the diffraction peak shape. The refinement parameters included scale factors, background coefficients, 2θ zero positions, line widths, and peak shapes, along with positional and site occupancy parameters. For the polymer composite films, the Bragg reflections were compared with those of the individual constituents, i.e. PEO, NaNO₃, and NASICON, to determine the phase of the

composites.

Thermal analysis of the polymer composite films was carried out using Differential Scanning Calorimetry (DSC) measurement performed in a Shimadzu DSC-60 thermal analyzer. The measurements were performed in the temperature range of RT-100 °C at a scan rate of 5°/min. Sample weighing $\sim$ 8-10 mg was sealed in the aluminium pan and analyzed under a constant flow of nitrogen gas (100 ml/min). The melting peak was normalized using the melting enthalpy of pure PEO (213 J/g)[5] to estimate crystallinity (χ_c) of the polymer composites.

4.2.4 Impedance spectroscopy (EIS) and scanning electron microscopy (SEM) study

Electrical conductivity was evaluated using electrochemical impedance spectroscopy (EIS) on a Hioki IM3570 impedance analyzer (Japan), operating in the frequency range of 10 Hz to 8 MHz with an AC amplitude of 121 mV. Before the measurement, polymer-ceramic composite films were coated on both sides with plain silver paste and dried overnight at room temperature to ensure good electrical contact. For ceramic pellets, a conventional silver paste containing an organic binder was applied, followed by heating at 500 °C for 2 h to remove the organic binder. Plain silver paste was avoided for ceramic pellets because it exhibited poor adhesion on the smooth sintered ceramic surface. EIS measurements for the CEs were conducted at room temperature, while those for ceramics were performed in the temperature range of RT-120 °C. The acquired impedance data of both ceramic and CEs were fitted using appropriate equivalent circuit models in EISSA software.[15]

The microstructural characterization was assessed using scanning electron microscopy (SEM) on a Carl Zeiss instrument. Non-conducting surfaces of the sample were coated with a thin conducting layer of gold by sputtering to prevent surface charging. The average particle size of the final ceramic powder, after $\sim$ 48 hours of manual grinding, was estimated from the SEM images using Im-

ageJ software.[16] Furthermore, the elemental distribution in polymer composites was probed by energy-dispersive X-ray spectroscopy (EDX) with SmartEDX EDS Analysis System.

4.2.5 Positron annihilation lifetime spectroscopy (PALS)

Positron annihilation spectroscopy was used to estimate the free volume of the polymer composite films. The PALS measurements were carried out using a pair of BaF_2 scintillation detectors connected to a fast-fast coincidence system. A ^{22}Na positron source ($\sim 10\ \mu\text{Ci}$) was sealed within a thin Kapton foil ($5\text{mm}\times 5\text{mm}\times 8\ \mu\text{m}$) and placed between a stack of two polymer sample films. This foil was positioned between two BaF_2 detectors in a 90° configuration. The time resolution measured with ^{60}Co in the ^{22}Na energy window settings was 220 ps. The time calibration was kept at 12.5 ps/channel. The total number of counts acquired in each spectrum was approximately 1×10^6 . The fraction of positrons annihilating in source material (Kapton) was corrected by subtracting the source component obtained through acquiring a positron annihilation lifetime (PAL) spectrum on a reference material (silicon single crystal with positron lifetime 218 ps). The PAL spectra have been analyzed using the PALSfit analysis program.[17]

4.2.6 Solid-state magic-angle spinning nuclear magnetic resonance (ss-MAS-NMR)

MAS-NMR was employed to investigate the local Na^+ -ion environment and its dynamics between polymer and ceramic phases of the composite electrolyte. ^{23}Na MAS-NMR spectroscopy measurements were performed on polymer composite films, using a JEOL ECX 500 MHz spectrometer equipped with a 4 mm probe. Single-pulse spectra were recorded at a MAS frequency of 10 kHz, and the chemical shift was referenced with a 1M NaCl solution. Spectral fitting and deconvolution of the NMR spectra were carried out using DMFit software.[18] To assess the influence of battery cycling on Na^+ -ion transport behavior, spectra from pristine

and GCD cycled composite electrolyte were compared. In addition, ^{23}Na spin-lattice relaxation time measurement was performed using the inversion recovery method to estimate the migration rates of the Na^+ -ions within the different phases of the composites.

4.2.7 Electrochemical performance by Cyclic voltammetry, Galvanostatic cycling, and DC polarization studies

The DC polarization measurements for both NASICON ceramics (NZZSP and NZNSP) and polymer-ceramic composites were performed using a symmetric cell configuration of $\text{Ag}|\text{electrolyte}|\text{Ag}$ and measured with an electrometer (Keithley 6514) at a voltage of 0.8 V. The electrochemical characterizations, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and galvanostatic charge-discharge (GCD) cycling of the NASICON ceramics and polymer-ceramic composites, were carried out using a potentiostat and galvanostat (K-Lyte, Kanopy, India). LSV measurements were employed to determine the electrochemical stability window (ESW) using a configuration of $\text{Ag}|\text{electrolyte}|\text{Ag}$ cell. To evaluate the compatibility of the electrolyte with sodium metal, CV measurements were performed using an $\text{Ag}|\text{electrolyte}|\text{Na}$ cell. Subsequently, GCD cycling was conducted in a symmetric $\text{Na}|\text{electrolyte}|\text{Na}$ cell to assess cycling behavior over the experimental duration. A photograph of the assembled Swagelok cell used for the electrochemical measurement is shown in Figure 4.2.

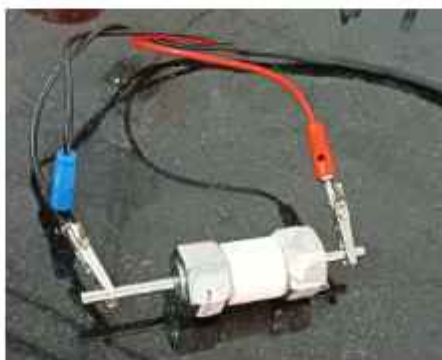


Figure 4.2: Swagelok cell during electrochemical measurement

4.3 Results

4.3.1 Characterization of NASICON ceramic filler

In this section, the results for the $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZZSP) and $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ (NZNSP) NASICON compositions are presented. The characterization of $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZSSP) has already been discussed in Chapter 3 and is therefore not repeated here.

4.3.1.1 Phase identification and structure determination

The crystal structures of the synthesized NASICON filler compositions, $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZZSP) and $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ (NZNSP), were investigated using X-ray powder diffraction. Rietveld refinement was performed to determine the structural parameters and quantify the phase fractions, employing a five-sodium site model. The Rietveld refined spectra of the NZZSP and NZNSP compositions are shown in Figure 4.3.

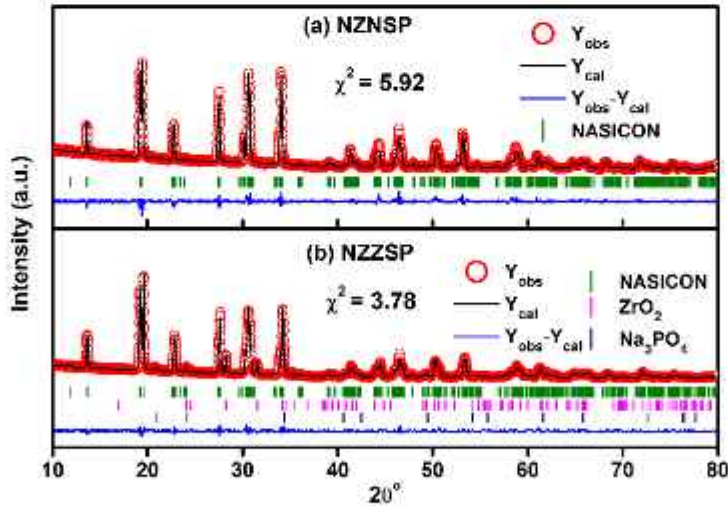


Figure 4.3: The Rietveld fit to the XRD pattern of (a) NZNSP and (b) NZZSP NASICON ceramic compositions

The room temperature XRD pattern of NZNSP ceramic powder was indexed to pure monoclinic $C2/c$ NASICON phase. In contrast, NZZSP ceramic powder ex-

hibited a predominant NASICON phase accompanied by minor secondary phases corresponding to ZrO₂ and Na₃PO₄. The phase purity achieved in NZNSP composition can be attributed to the SA-SSR method, wherein the use liquid medium during the precursor mixing promotes improved homogeneity.

The refined structural parameters for both NZZSP and NZNSP ceramic powders and the refined lattice parameters for the impurity phases are summarised in Tables 4.2–4.4

Table 4.2: Structural parameters of monoclinic $C2/c$ phase in nominal NZZSP composition obtained from Rietveld analysis of XRD data

Atom	Wyckoff position	x	y	z	Occupancy	U_{iso} ($\text{\AA}^2$)
Na1	4d	0.25	0.25	0.5	0.223(9)	0.006(3)
Na2	4e	0	0.396(3)	0.25	0.487(8)	0.006(3)
Na3	8f	0.325(7)	0.432(7)	0.329(4)	0.321(5)	0.006(3)
Na4	8f	0.190(4)	0.138(4)	0.566(7)	0.340(3)	0.006(3)
Na5	8f	0.700(8)	0.548(7)	0.807(8)	0.300	0.006(3)
Zr1	8f	0.100(2)	0.245(3)	0.057(3)	0.950	0.006(3)
Zn1	8f	0.100(2)	0.245(3)	0.057(3)	0.050	0.006(3)
Si1	4e	0	0.036(4)	0.25	0.224(2)	0.006(3)
P1	4e	0	0.036(4)	0.25	0.192(2)	0.006(3)
Si2	8f	0.355(4)	0.107(2)	0.259(1)	0.880(7)	0.006(3)
P2	8f	0.355(4)	0.107(2)	0.259(1)	0.212(2)	0.006(3)
O1	8f	0.148	0.432(9)	0.225(10)	1	0.006(3)
O2	8f	0.438	0.455(2)	0.089(6)	1	0.006(3)
O3	8f	0.249(9)	0.184(7)	0.217(7)	1	0.006(3)
O4	8f	0.378(5)	0.124(5)	0.097(1)	1	0.006(3)
O5	8f	0.552(1)	0.174(1)	0.0647(1)	1	0.006(3)
O6	8f	0.086(9)	0.141(8)	0.261(2)	1	0.006(3)
$a = 15.699(6) \text{ \AA}$, $b = 9.081(9) \text{ \AA}$, $c = 9.189(5) \text{ \AA}$, $\beta = 124.2^\circ$, $V = 1082.4 \text{ \AA}^3$						
Phase fraction of NZZSP:ZrO ₂ :Na ₃ PO ₄ = 91.53:4.08:4.38						

Table 4.3: Refined lattice parameters of impurity phases of ZrO₂ and Na₃PO₄ in NZZSP composition

Compositions	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	β ($^\circ$)	V ($\text{\AA}^3$)
ZrO ₂ ($P2_1/c$)	5.323(4)	5.202(5)	5.141(9)	80.7	140.3
Na ₃ PO ₄ ($Fm\bar{3}m$)	7.374(5)	7.374(5)	7.374(5)	-	401.0

Table 4.4: Structural parameters of pure monoclinic $C2/c$ phase in nominal NZNSP composition obtained from Rietveld analysis of XRD data

Atom	Wyckoff position	x	y	z	Occupancy	U_{iso} ($\text{\AA}^2$)
Na1	4d	0.25	0.25	0.5	0.307(3)	0.006(3)
Na2	4e	0	0.395(7)	0.25	0.480	0.006(3)
Na3	8f	0.331(7)	0.443(9)	0.303(2)	0.260(9)	0.006(3)
Na4	8f	0.182(7)	0.123(8)	0.617(2)	0.425(2)	0.006(3)
Na5	8f	0.699(5)	0.555(1)	0.821(2)	0.263	0.006(3)
Zr1	8f	0.100(6)	0.245(3)	0.056(9)	0.938(5)	0.006(3)
Nb1	8f	0.100(6)	0.245(3)	0.056(9)	0.049(7)	0.006(3)
Si1	4e	0	0.025(6)	0.25	0.290(5)	0.006(3)
P1	4e	0	0.025(6)	0.25	0.161(9)	0.006(3)
Si2	8f	0.353(5)	0.104(5)	0.264(1)	0.878(5)	0.006(3)
P2	8f	0.353(5)	0.104(5)	0.264(1)	0.213(5)	0.006(3)
O1	8f	0.145(9)	0.432(1)	0.253(1)	1	0.006(3)
O2	8f	0.441(6)	0.467(4)	0.091(8)	1	0.006(3)
O3	8f	0.257(2)	0.180(7)	0.219	1	0.006(3)
O4	8f	0.371(9)	0.131(9)	0.094(3)	1	0.006(3)
O5	8f	0.554(4)	0.183(5)	0.053(9)	1	0.006(3)
O6	8f	0.089(2)	0.155(5)	0.272(2)	1	0.006(3)
$a = 15.753(9) \text{ \AA}$, $b = 9.110(6) \text{ \AA}$, $c = 9.192(4) \text{ \AA}$, $\beta = 124.4^\circ$, $V = 1088.8 \text{ \AA}^3$						

4.3.1.2 Microstructural studies using SEM

Particle size of the filler plays a critical role in determining its dispersion, specific surface area, and overall interaction with the polymer matrix. These factors can strongly influence the ion transport properties of the composite films. Therefore, achieving an optimal filler particle size is essential for effective ceramic-polymer interaction.[19] To evaluate the particle size of the NASICON fillers, the sintered powders were manually ground for up to ~ 48 h to achieve uniform and fine particles, and SEM images were subsequently obtained on these powders. Figure 4.4(a, c, e) shows the SEM micrographs of the finely ground sintered powders of pristine NZZSP, NZNSP, and NZSSP samples, while in Figure 4.4(b, d, f) the corresponding particle size distributions are presented.

In NZZSP powder, the SEM micrograph revealed predominantly spherical grains with an average particle size of 219 nm. In contrast, the NZNSP sample exhibited

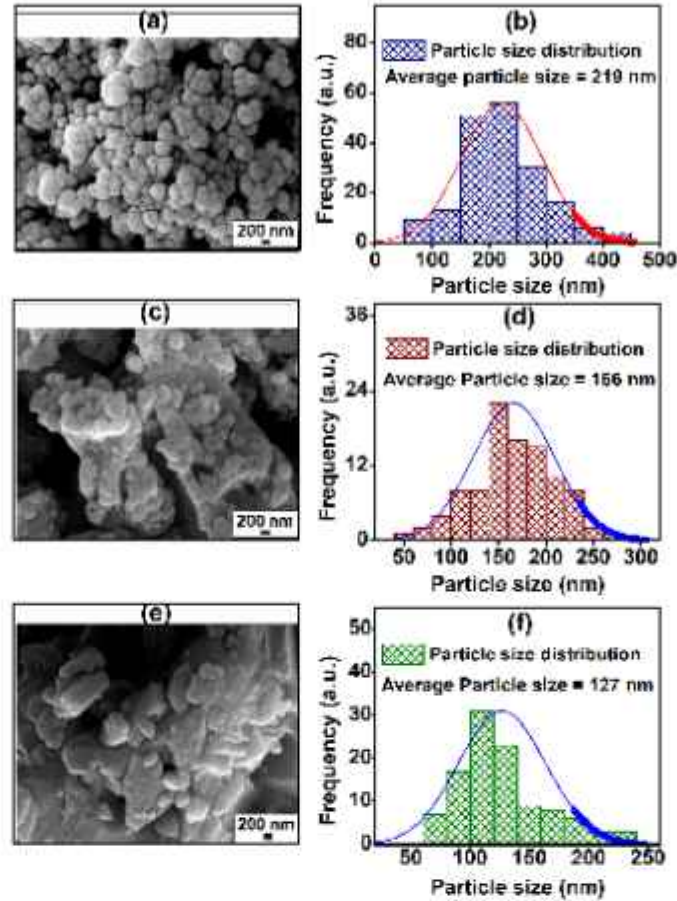


Figure 4.4: (a, c, e) The SEM images of NZZSP, NZNSP, and NZSSP sintered NASICON powder, and (b, d, f) corresponding particle size distribution

noticeable agglomeration, which became more pronounced in the NZSSP sample. The average particle sizes for NZNSP and NZSSP were determined to be 166 nm and 127 nm, respectively. These results indicated that different synthesis techniques (as mentioned in section 4.2.1.1–4.2.1.3) yielded NASICON fillers with distinct particle sizes, and that fillers with smaller particle sizes showed a greater tendency to agglomerate. This increased agglomeration behavior could be attributed to the increased surface area of the particles with reduced sizes.

4.3.1.3 Electric conductivity measurement using EIS and DC polarization study

Ionic conductivities of the sintered pellets were determined from impedance data measured in the temperature range of RT–120 °C. Figures 4.5(a, b) shows the

room temperature Nyquist plot for NZZSP and NZNSP compositions, obtained from the complex impedance data. In both cases, the Nyquist plot displays a small semicircle in the high-frequency region, followed by a low-frequency tail. To deconvolute the contributions of grain (R_g) and grain boundary resistances (R_{gb}) to the total conductivity, the impedance data were fitted using an equivalent circuit as shown in the insets. The black line represents the simulated fits derived from these equivalent circuit models.

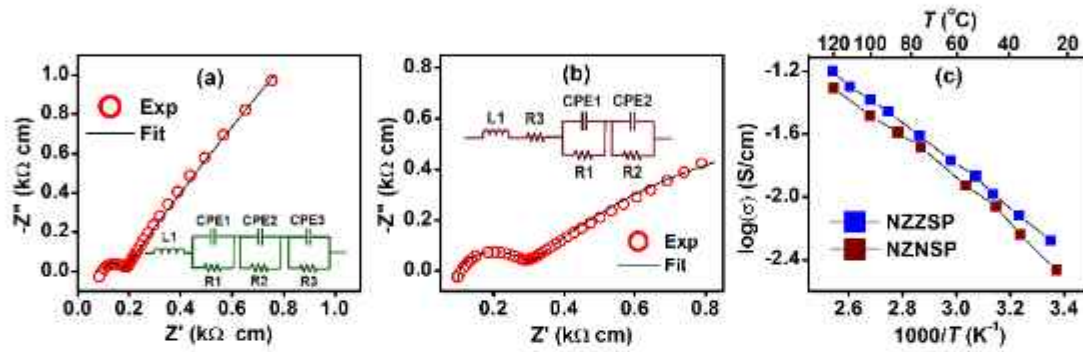


Figure 4.5: RT Nyquist plot for (a) NZZSP, (b) NZNSP, and (c) their corresponding Arrhenius plots

The estimated R_g , R_{gb} values, and RT conductivity shown by pristine NZZSP, NZNSP, and NZSSP samples are listed in Table 4.5.

Table 4.5: Simulated values of the grain, grain boundary resistances, and the conductivity values for NASICON ceramic filler compositions

Composition	R_g (Ω cm)	R_{gb} (Ω cm)	L (H)	σ_t (S cm^{-1})
$\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZZSP)	87.0	102	5.97×10^{-7}	5.27×10^{-3}
$\text{Na}_{3.4}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ (NZNSP)	98.7	193.1	8.54×10^{-7}	3.42×10^{-3}
$\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZSSP)	107.9	203.5	9.99×10^{-7}	3.19×10^{-3}

From Table 4.5, it was observed that the values of both R_g , R_{gb} were lower for the NZZSP sample, resulting in a high room temperature conductivity of 5.27 mS/cm, which is consistent with a value reported previously.[12] The NZNSP composition displayed an RT conductivity of 3.42 mS/cm, while NZSSP exhibited a conductivity of 3.19 mS/cm. Among these three compositions, the bulk conduc-

tivity was highest for NZZSP, followed by NZNSP and then NZSSP composition. Accordingly, dispersing active filler of higher bulk conductivity into the polymer matrix is expected to improve the ionic conductivity of the resulting composite film. This behavior is examined and discussed in further detail in section 4.3.2.5. The temperature dependence of conductivity for NZZSP and NZNSP compositions, presented in Figure 4.5(c), shows Arrhenius-type behaviour. The activation energies were estimated to be 0.26 eV for NZZSP composition and 0.27 eV for NZNSP composition.

DC polarisation measurement was performed to determine the ionic transference numbers using a symmetric $\text{Ag}|\text{electrolyte}|\text{Ag}$ configuration under an applied constant potential of 0.8 V. The variation of total current as a function of time is shown in Figure 4.6.

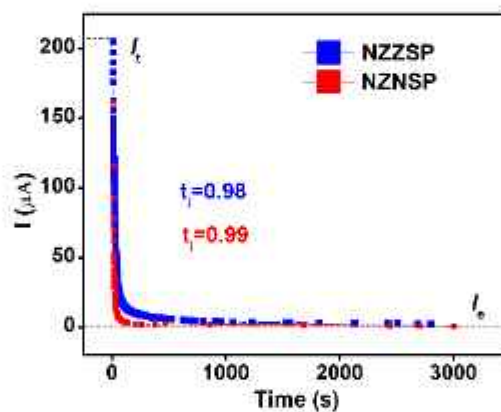


Figure 4.6: DC polarization response of $\text{Ag}|\text{NZZSP}|\text{Ag}$ (blue) and $\text{Ag}|\text{NZNSP}|\text{Ag}$ (red) cell

The calculated ionic transference numbers (t_i) for NZZSP and NZNSP were 0.98 and 0.99, respectively. These high values of (t_i) confirmed that the electronic contribution to the total conductivity was negligible for both NZZSP and NZNSP compositions.

4.3.1.4 Electrochemical performance study by CV and GCD

The interfacial stability of the NASICON compositions of NZZSP and NZNSP against sodium metal, along with their practical performance, was evaluated using

cyclic voltammetry (CV) and galvanostatic charge-discharge cycling (GCD). The cyclic voltammetry profile of $\text{Ag}|\text{NZZSP}|\text{Na}$ and $\text{Ag}|\text{NZNSP}|\text{Na}$ cells is displayed in Figure 4.7(a, c).

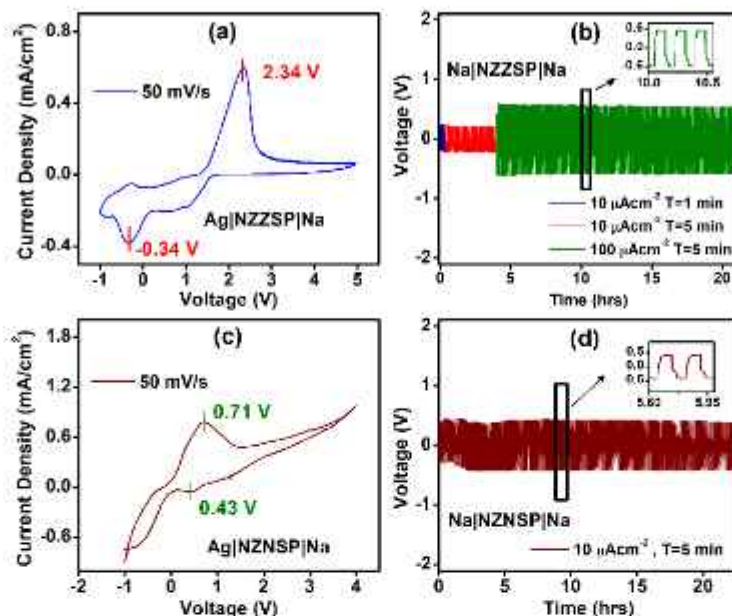


Figure 4.7: (a, c) Cyclic voltammetry profile of NZZSP and NZNSP, and (b, d) galvanostatic cycling behavior of NZZSP and NZNSP symmetric cell.

A pair of redox peaks is observed at 2.34 V and -0.34 V for NZZSP composition, corresponding to sodium plating and stripping processes. In contrast, the CV profile of NZNSP exhibited redox peaks at 0.71 V and 0.43 V, with a smaller peak separation (ΔE_p) of 0.28 V compared to 2.68 V in the NZZSP sample. In addition, unlike NZZSP, the CV tail of NZNSP composition did not attain a steady plateau region at higher voltages. The reduced peak separation and the absence of a steady CV tail at higher voltages are suspected to be associated with the multivalent nature of the Nb dopant, which acts as redox redox-active center and prevents the establishment of a steady response.

The galvanostatic cycling of the symmetric $\text{Na}|\text{NZZSP}|\text{Na}$ and $\text{Na}|\text{NZNSP}|\text{Na}$ cells is displayed in Figure 4.7(b, d). The GCD measurements were performed under a constant current density of $10 \mu\text{A}/\text{cm}^2$ for NZNSP and at both 10 and $100 \mu\text{A}/\text{cm}^2$ for NZZSP compositions. In both cases, the galvanostatic voltage profile demonstrated stable polarization voltage throughout the measurement du-

ration, indicating good interfacial stability and cyclability for NZZSP and NZNSP electrolytes.

4.3.2 Characterization of PEO- NaNO_3 -NASICON polymer composite

4.3.2.1 Phase identification and structure determination

The complexation of pure PEO with NaNO_3 and the dispersion of NASICON filler within the resulting PEO- NaNO_3 matrix were examined using X-ray diffraction. The stacked XRD pattern of PEO- NaNO_3 polymer electrolyte (PE), the NZZSP ceramic filler, and corresponding composite CE15Zn, CE30Zn, CE45Zn, CE60Zn, and CE75Zn electrolytes are presented in Figure 4.8.

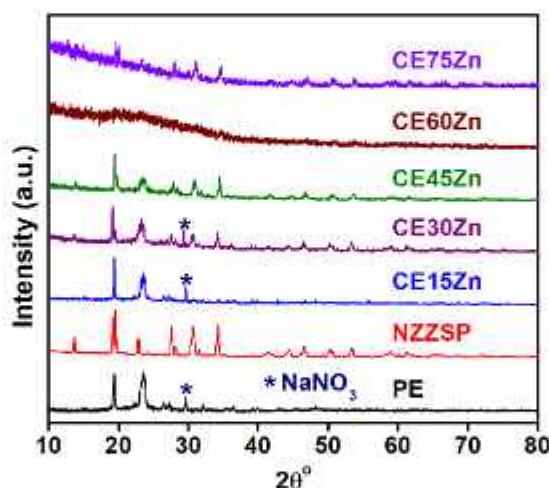


Figure 4.8: XRD stack plot of PE, NZZSP, and CE15/30/45/60/75Zn with varying NZZSP weight percentages (15-75 wt%).

The XRD spectrum of polymer electrolyte (PE) displays two prominent Bragg peaks at 19.2° and 23.3° , corresponding to the characteristic crystalline reflections of pure PEO.[20] These peaks originate from the ordering of polyether side chains in the PEO matrix, reflecting its semi-crystalline nature ($>60\%$). In the composite films, the persistence of these crystalline peaks indicates the coexistence of both crystalline and amorphous PEO phases. Additionally, a weak Bragg peak at $\sim 29.7^\circ$ (marked by *) attributed to NaNO_3 appears in PE, CE15Zn, and CE30Zn

composites. This suggested that a small fraction of salt may have remained uncomplexed despite continuous stirring during the film preparation.

With increasing NZZSP content, the intensity of PEO peaks gradually reduced, reaching a nearly amorphous pattern at 60 wt% loading (CE60Zn). This behavior indicated significant suppression of PEO crystallinity in CE60Zn composite. Correspondingly, NZZSP peaks were not detectable at a lower filler content of 15 wt%, but became visible at 30 and 45 wt%. On further addition, the increased amorphous fraction in CE60Zn resulted in a fully amorphous pattern. Subsequently, at a higher loading of 75 wt% (CE75Zn), a few NZZSP peaks reappeared on the amorphous background.

A small but gradual shift of NASICON peaks was also noticed with increasing ceramic content. This shifting could be due to internal stress generated by the differential thermal expansion of the polymer and ceramic. During the cooling phase of synthesis, the polymer matrix contracts faster than the ceramic particles, inducing a structural contraction leading to higher angle peak shifts. The absence of new peak(s) in the composite XRD pattern confirmed that the NASICON filler dispersed in the polymer matrix existed as an independent phase.

4.3.2.2 Crystallinity evaluation of polymer composites by DSC

The thermal properties of the composite electrolytes were investigated using differential scanning calorimetry (DSC). Figure 4.9(a) depicts the DSC thermograms recorded during the heating cycle from 30 °C–100 °C, while Figure 4.9(b) shows the thermogram corresponding to both heating and cooling cycles in PEO, PE, and CE60Zn samples.

The DSC thermogram of Pure PEO, PE, and all composite electrolytes (CEs), recorded during the heating cycle, shows an endothermic peak at ~ 67 °C. This endothermic peak corresponds to the melting of PEO and its transition from crystalline to a molten phase. The onset of melting for PEO was determined to be at ~ 62.5 °C. The residual crystallinity (χ_c) of the PE and CEs was estimated

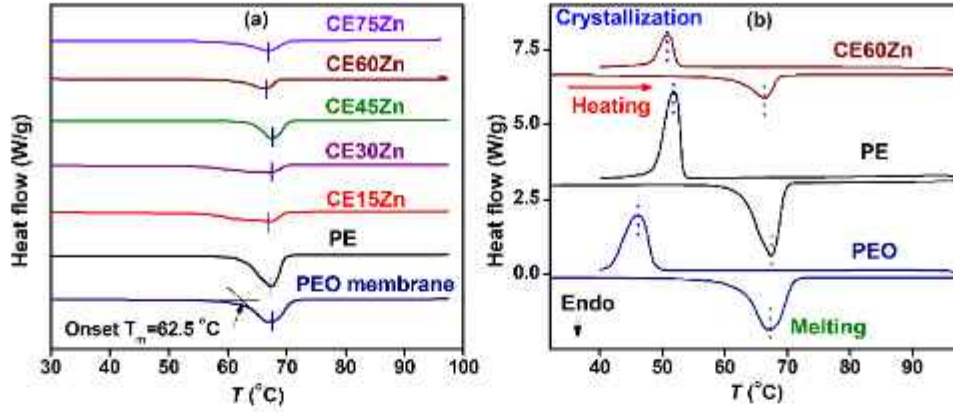


Figure 4.9: DSC thermograms of (a) heating cycle for pure PEO film, PE, and CE15/30/45/60/75Zn films and (b) heating and cooling cycle for pure PEO, PE, and CE60Zn.

from the melting peak area (ΔH_m) and normalized using the reference melting enthalpy of pure PEO ($\Delta H_m^0 = 213 \text{ J/g}$) following the equation[21],

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%$$

The crystallinity fractions and the associated melting/crystallization temperatures derived from the DSC analysis are listed in Table 4.6. Crystallinity fractions obtained from XRD analysis are also tabulated alongside and show close agreement with the DSC results. It was noted that, with increasing NZZSP ceramic content in CEs, the crystallinity of PEO gradually decreased, reaching a minimum in CE60Zn, followed by a slight increase in CE75Zn. This reduction in crystallinity fraction is attributed to the disruption of the ordered polyether side chains of PEO caused by the addition of NaNO₃ and NZZSP filler. Among all the CEs, CE60Zn exhibits the lowest crystallinity (22.3 % from DSC), indicating prominent amorphization of the polymer matrix. Furthermore, the intensity of the DSC curves for CE15Zn and CE30Zn composite electrolytes shows comparatively lower but broader endothermic features, indicating a wider distribution of melting temperatures for these composites. This broadening likely reflects the formation of PEO crystallites with varying sizes at lower ceramic loading; whereas, at higher ceramic content, the growth rate of these crystallites is largely suppressed.[22]

Table 4.6: Crystallization temperature, melting temperature, estimated crystallinity (XRD and DSC), and RT ionic conductivity of the PE and CEs.

Compositions	T_c (°C)	T_m (°C)	Crystallinity (%) from XRD	Crystallinity (%) from DSC
PEO:NaNO ₃ (PE)	51.9	67.4	57.4	61.9
85 wt% PE:15 wt% NZZSP (CE15Zn)	49.6	66.9	45.0	43.1
70 wt% PE:30 wt% NZZSP (CE30Zn)	49.6	67.0	34.9	33.0
55 wt% PE:45 wt% NZZSP (CE45Zn)	50.3	67.4	34.1	34.3
40 wt% PE:60 wt% NZZSP (CE60Zn)	50.9	66.3	25.6	22.3
25 wt% PE:75 wt% NZZSP (CE75Zn)	50.0	66.9	31.3	29.0

The melting and the crystallization peak for PEO, PE, and CE60Zn observed during the heating-cooling cycle are presented in Figure 4.9(b), illustrating the transition of the polymer between the partially crystalline and molten amorphous states.

4.3.2.3 Microstructural analysis using SEM and EDX

Figure 4.10 (a-f) illustrates the surface morphology of PE and composites containing varying weight ratios of NZZSP.

The SEM micrographs of these PEO-based membranes show complex morphology arising from the coexistence of the crystalline and amorphous phases. The vein-like bulk regions observed in the micrographs are believed to correspond to the crystalline domains (spherulites) and are surrounded by the amorphous matrix. The characteristic lamellar microstructure of these spherulites can be seen in the magnified view of Figure 4.10(g, h). The identification of the lamellae is consistent with the observations by Patla *et al.*[23]

On the introduction of the NZZSP into the polymer matrix, NZZSP crystallites were found to integrate within both the lamellae of the spherulites as well as the amorphous region, as highlighted in Figure 4.10(h). At 60 wt% of the NZZSP

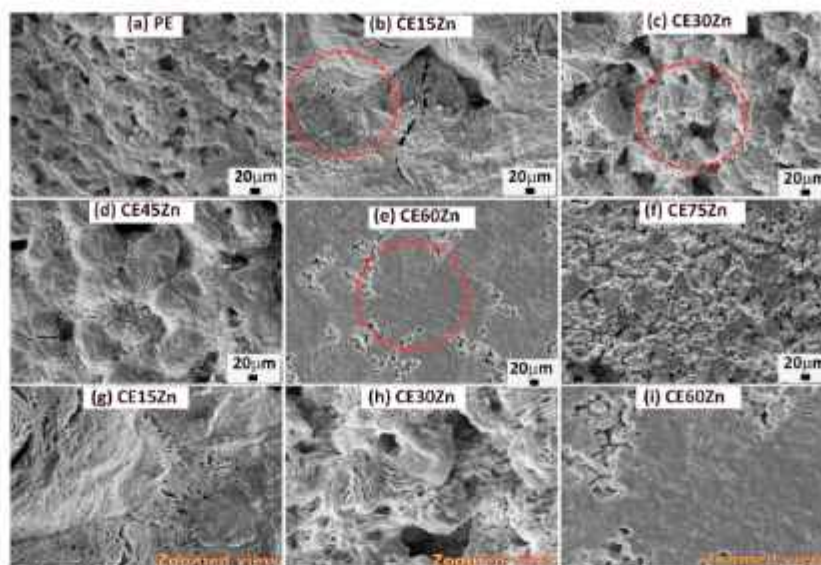


Figure 4.10: SEM images of PE film (a), CE15/30/45/60/75Zn composite films (b-f), and zoomed view of CE15/30/60Zn from the red circle region (g-i).

loading, the surface of the membrane appeared notably smoother, with minimal pores, indicating higher amorphous character in CE60Zn. This observation is also in agreement with its lowest crystallinity fraction as obtained from XRD and DSC analysis. Further increasing the NZZSP filler to 75 wt% resulted in phase separation within the composite. To further examine the distribution of the NZZSP filler within the polymer matrix, energy dispersive X-ray (EDX) mapping analysis was also conducted. The EDX elemental maps for CE45Zn and CE60Zn are displayed in Figures 4.11 and 4.12.

In the EDS mapping images for CE45Zn and CE60Zn, the elements specific to the NASICON filler, i.e., Zr, P, and Si, were probed and found to be uniformly distributed within the polymer matrix. This confirmed that the NZZSP NASICON filler was uniformly dispersed in the polymer matrix.

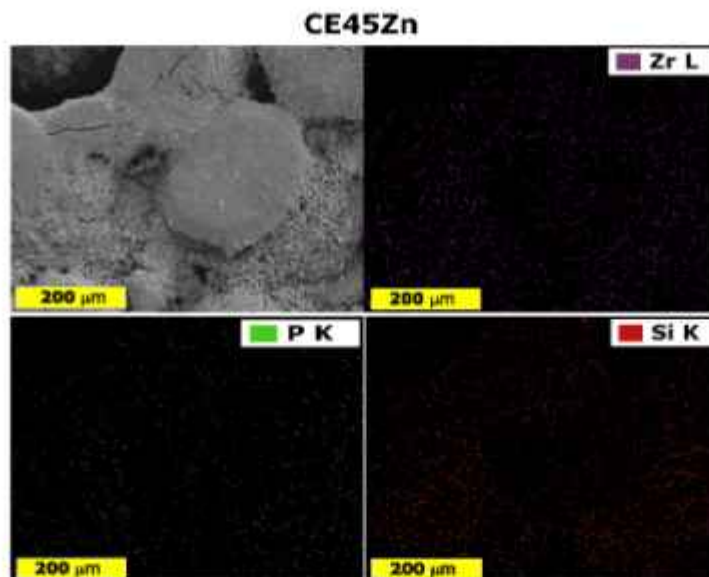


Figure 4.11: EDX mapping of Zr, P, and Si in CE45Zn composite film

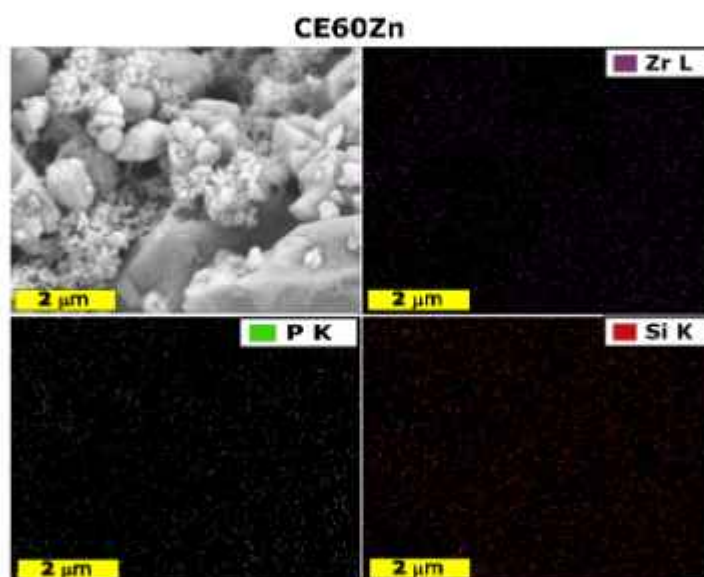


Figure 4.12: EDX mapping of Zr, P, and Si in CE60Zn composite film

4.3.2.4 ^{23}Na MAS-NMR spectrum and spin-lattice relaxation time measurement

Procuring detailed structural features of sodium ions in the polymer composite electrolytes is challenging using the conventional XRD technique, as sodium, being a lighter element, scatters weakly. Additionally, the integration of a polymer matrix with NASICON filler adds another layer of intricacy. In such a case, local

Na environment and its dynamics within the polymer and ceramic phases can be probed using ^{23}Na MAS NMR. ^{23}Na MAS NMR spectra of the pure NZZSP NASICON, NaNO_3 powder, and corresponding CEs are presented in Figure 4.13(a).

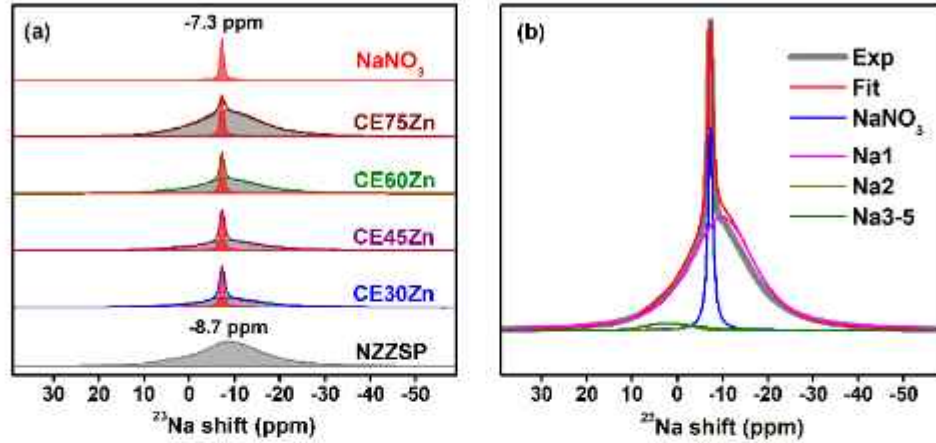


Figure 4.13: (a) ^{23}Na MAS NMR spectra of NZZSP, NaNO_3 powders, and CE30/45/60/75Zn electrolytes and ^{23}Na MAS NMR spectra of CE60Zn with four simulated Na site contributions.

The ^{23}Na NMR spectrum of NaNO_3 displays a narrow resonance at the peak position of -7.3 ppm, whereas NZZSP NASICON exhibits a broad signal centered at -8.7 ppm. The narrow resonance line observed for NaNO_3 arises from its very small chemical shift anisotropy and low quadrupolar coupling constant. On the other hand, the broad resonance signal in NASICON originates from the overlap of signals associated with multiple non-equivalent Na sites having high quadrupolar coupling constants. The spectrum of composite electrolytes (CEs) possesses structural features of both NaNO_3 and NZZSP, and a progressive increase in the relative intensity of NZZSP contribution is evident with increasing NASICON content. Figure 4.13(b) presents the deconvolution of the CE60Zn spectra performed using the DMfit program.[18] A satisfactory fit was achieved with four signal contributions corresponding to NaNO_3 and Na1, Na2, and Na3-5 sites of NZZSP ceramic. These Na sites were selected based on the crystallographic sites in monoclinic $C2/c$ NASICON structure and correspond to the Wyckoff positions of 6b, 4e, and 8f, respectively. The assignment of four signals was directed by the

Na site positions and previous ^{23}Na NMR reports.[24], [25]

In addition, the interaction between the $(\text{NO}_3)^-$ group and the NASICON grains was substantiated by comparing the experimental and calculated values of relative NaNO_3 intensity, as shown in Figure 4.14.

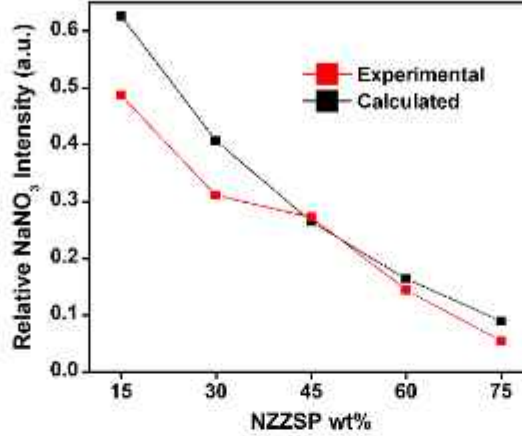


Figure 4.14: Relative NMR signal due to NaNO_3 of composite films.

It was observed that the experimental relative intensity of NaNO_3 NMR spectra was lower than the nominal NaNO_3 content in the composite. This deviation indicates an increased dissolution of the NaNO_3 salt by the ceramic particles, which suggests an electrostatic interaction between $(\text{NO}_3)^-$ groups and Na^+ ions located on the surface of the NASICON ceramic grains.

Spin lattice relaxation time (T_1) measurement is sensitive to localized Na^+ -ion jumping and dynamics and was therefore used to estimate the Na^+ -ion migration rates in polymer composites. [26], [27] In the current case, ^{23}Na spin-lattice relaxation time (T_1) for CE60Zn was measured by the inversion recovery method. Figure 4.15 displays the ^{23}Na nuclear spin moment recovery curve for different applied delays together with the corresponding fitting. A satisfactory fit to the experimental curve was attained using the following equation,

$$M(\tau) = M_s \left[A_1 \left(1 - 2e^{-\tau/T_1^C} \right) + (1 - A_1) \left(1 - 2e^{-\tau/T_1^P} \right) \right]$$

Where $M_s = 4.711$, $A_1 = 0.602$ are fitting constants, and T_1^C and T_1^P represent the relaxation times for ceramic and polymer phases, respectively.

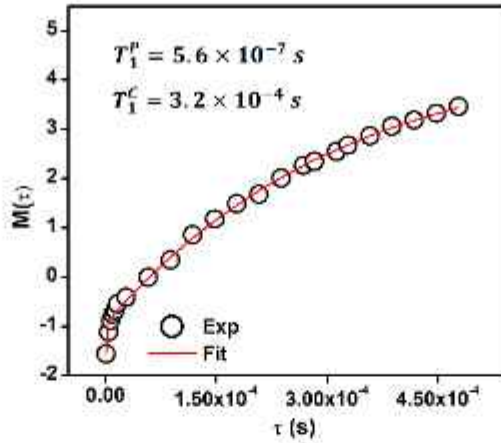


Figure 4.15: ^{23}Na spin-lattice relaxation measurement by the inversion recovery method.

This two-component model accounted for the contribution of Na^+ -ion migration in the polymer and ceramic phases of the composite electrolyte. The estimated spin-lattice relaxation rate for the polymer phase (SLR^P) was $0.18 \times 10^7 \text{ s}^{-1}$, whereas that for the ceramic phase (SLR^C) was $0.31 \times 10^4 \text{ s}^{-1}$. Since a higher relaxation rate (SLR) reflects faster ionic motion, the estimated relaxation times indicated that at room temperature, Na^+ -ion migration rate is much faster in the polymer phase than in the ceramic phase. However, the Na^+ ion's migration across the polymer-ceramic interface could not be identified by T_1 measurement.

4.3.2.5 Electrical conductivity measurement using EIS and DC polarization study

Ionic conductivities of the prepared polymer electrolyte and the composite electrolytes were evaluated using electrochemical impedance spectroscopy over a frequency range of 10 Hz to 8 MHz. The corresponding Nyquist plots, obtained from RT EIS data of the PE and all CEs containing different concentrations of NZZSP ceramic, are presented in Figure 4.16(a).

All the Nyquist plots exhibit a compressed semicircle in the high-frequency region, followed by an inclined spike at lower frequencies. The semicircle corresponds to the ionic conduction through the bulk of the polymer electrolyte, whereas the spike arises due to the blocking nature of silver electrodes (electrode polarization). As

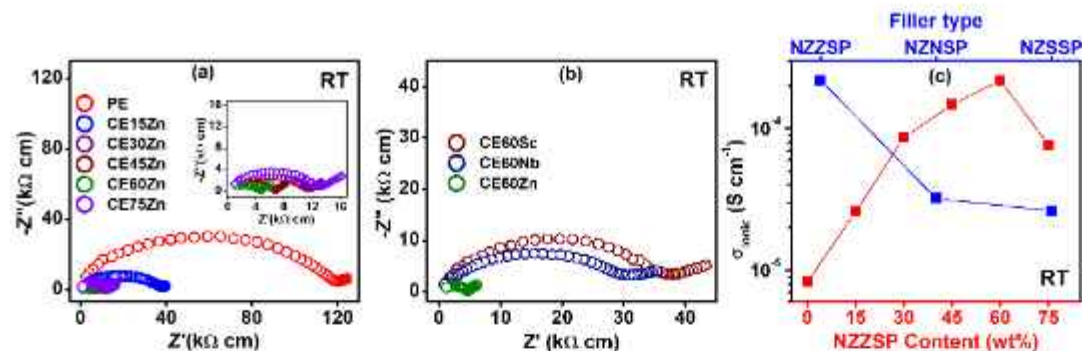


Figure 4.16: RT Nyquist plots of impedance data for (a) PE and CE15/30/45/60/75Zn. Impedance data at high frequencies are shown in the inset. (b) Comparison of RT Nyquist plot for CE60Zn/Nb/Sc composite electrolytes and (c) Comparison of RT ionic conductivity of composite electrolyte with varying NZZSP content and ceramic filler.

shown in the insets, the diameter of the semicircle gradually decreases with increasing NZZSP content, with the smallest semicircle observed for the CE60Zn composite. Similarly, Figure 4.16(b) compares the Nyquist plots of composite electrolytes containing 60 wt% of different NASICON compositions (NZZSP, NZNSP, and NZSSP). In this case, it was observed that the semicircles for CE60Nb and CE60Sc were significantly larger than that of CE60Zn, indicating comparatively higher resistance. Furthermore, the ionic conductivities derived from the impedance data are plotted in Figure 4.16(c), comparing CEs with varying NZZSP content (red data points) and those containing different NASICON compositions at 60 wt% loading (blue data points). The conductivity of the CE membrane increased with NZZSP content, attaining a maximum value of $2.2 \times 10^{-4} \text{ S cm}^{-1}$ in CE60Zn, before decreasing for CE75Zn. These results inferred that the optimal ceramic content for the PEO- NaNO_3 -NZZSP composite electrolyte is $\sim 60 \text{ wt\%}$. However, replacing the NASICON composition from NZZSP to NZNSP and NZSSP resulted in lower ionic conductivities of $3.2 \times 10^{-5} \text{ S cm}^{-1}$ and $2.6 \times 10^{-5} \text{ S cm}^{-1}$ for CE60Nb and CE60Sc, respectively.

Additionally, to reveal contributions influencing the overall conductivity, the Nyquist plots of PE, CE60Zn, CE60Nb, and CE60Sc were fitted using equivalent circuit models. The experimental Nyquist plots along with the simulated lines and corresponding equivalent circuit models are displayed in Figure 4.17(a-d).

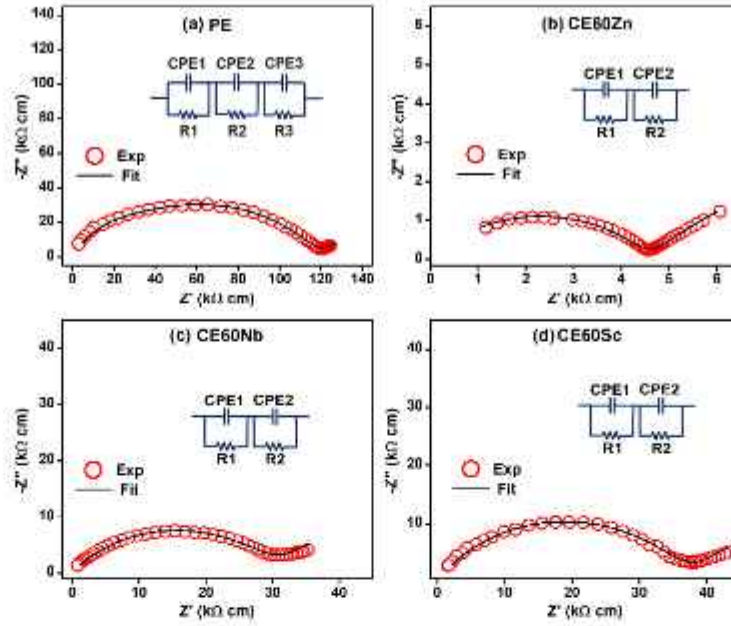


Figure 4.17: Nyquist plots for complex impedance data recorded at RT for (a) PE, (b) CE60Zn, (c) CE60Nb, and (d) CE60Sc with their equivalent circuit fitting in insets.

The high-frequency semicircle of the PE sample was fitted using two $R \parallel CPE$ (CPE: constant phase element) components, representing the contributions from the polymer bulk amorphous phase (with resistance R_A) and crystalline phase (with resistance R_C) of the electrolyte. In contrast, the Nyquist plots of CE60Zn/Nb/Sc were adequately fitted using only a single $R \parallel CPE$ component, attributing solely to ionic transport through the amorphous phase of the composite. This behavior indicates that at 60 wt% of NASICON loading, the dominant mode of ion transport was governed by the amorphous phase of the composite. This observation is consistent with XRD/DSC analysis, which revealed reduced crystallinity in the composite membrane, as well as ^{23}Na spin-lattice relaxation time (T_1) measurement that demonstrated faster migration within the polymer phase. The estimated RT conductivities and the equivalent circuit fitting parameters are listed in Table 4.7.

The ionic and electronic conductivity fractions of PE and all the CEs were evaluated employing direct current (DC) measurement, as shown in Figure 4.18. The DC polarization of NZZSP ceramic is also included in Figure 4.18 for reference.

Table 4.7: Simulated values of the amorphous and crystalline phase resistances, and the conductivity values for the PE and CEs

Composition	R_A (Ω cm)	R_C (Ω cm)	σ_t (S cm ⁻¹)
(PEO) ₁₅ NaNO ₃ (PE)	12007	1.06×10^5	8.29×10^{-6}
PEO-NaNO ₃ -60NZZSP (CE60Zn)	4593	-	2.20×10^{-4}
PEO-NaNO ₃ -60NZNSP (CE60Nb)	31057	-	3.22×10^{-5}
PEO-NaNO ₃ -60NZSSP (CE60Sc)	37879	-	2.64×10^{-5}

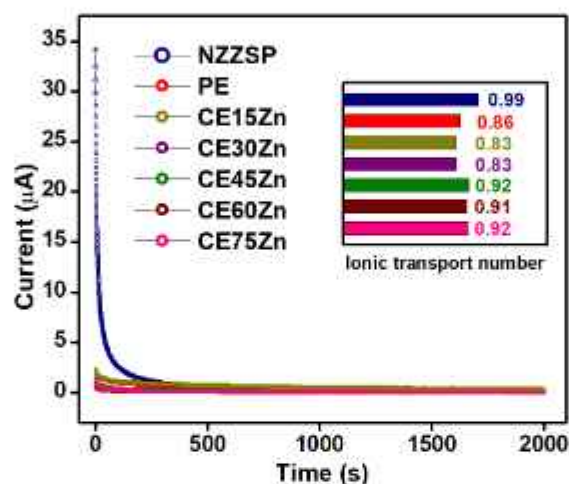


Figure 4.18: Potentiostatic polarization curves of the NZZSP filler, PE, and CEs (tested at room temperature under 0.8 V; Insets are the calculated ionic transference number)

As listed in Figure 4.18, the ionic transference number (t_i) of NZZSP ceramic is 0.99, and while that of CEs is in the range 0.83-0.92. These values confirm that overall conduction in NZZSP, PE, and CE membranes is ion-dominated.

4.3.2.6 Evaluation of free volume by PALS study

Free volume governed by chain dynamics of polymeric material plays a crucial role in the ion conduction process, as it facilitates the migration of ions through the matrix. Ion transport models further suggest that a critical free volume is required for effective ionic movement.[28], [29], [30] In this regard, positron annihilation lifetime spectroscopy (PALS) serves as a suitable means to probe the free volume

changes, since ortho-positronium ($o\text{-}P_s$) localizes within the free volume holes and its lifetime directly reflects their characteristics.[31], [32], [33]

PAL spectra were recorded at room temperature for PE as well as for all the polymer composite electrolyte (CEs) membranes. A representative PAL spectrum recorded for CE15Zn is shown in Figure 4.19.

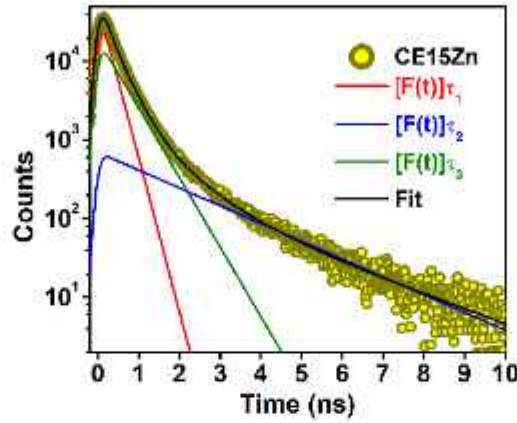


Figure 4.19: Experimental PALS spectrum recorded for CE15Zn composite electrolyte. Simulated spectrum with three components is shown with lines

The multi-exponential nature of the PAL spectra was examined by decomposing the lifetime spectrum, $F(t)$, into three exponential decaying components, as illustrated by the simulated lines in Figure 4.19. The spectra were analyzed using the relation, $F(t) = \sum_{i=1}^k \frac{I_i}{\tau_i} e^{-t/\tau_i}$ where $F(t)$ is the number of counts at time t , and τ_i is the lifetime of the i^{th} component having intensity of I_i . [34] The fitted values of the components τ_i and I_i ($i=1-3$) for PE and CEs are summarised in Table 4.8.

Based on the values of lifetime and intensity components listed in Table 4.8, component-1 (τ_1 and I_1) was attributed to the annihilation of para-positronium ($p\text{-}P_s$) and free-positron in the bulk while they diffused into the matrix during thermalization. Component-2 (τ_2 and I_2) was assigned to the annihilation of positrons that have not formed positronium; instead were trapped by the polar groups or free volume defects present in the polymer.[32] Component-3 (τ_3 and I_3) was associated with the pick-off annihilation of $o\text{-}P_s$ in the free volume present in the matrix. The trapped positron lifetime (τ_2) in polymer-based materials is typically observed in the range of 0.4-0.5 ns, with its intensity dependent on the

Table 4.8: Positron annihilation lifetimes and intensity at RT

Composition	Component-1		Component-2		Component-3	
	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)
PE	0.184 ± 0.003	60.08 ± 1.39	0.451 ± 0.010	32.76 ± 1.26	1.79 ± 0.026	7.16 ± 0.19
CE15Zn	0.222 ± 0.003	49.61 ± 1.48	0.492 ± 0.008	44.02 ± 1.38	1.92 ± 0.02	6.34 ± 0.14
CE30Zn	0.246 ± 0.004	60.58 ± 2.16	0.528 ± 0.016	33.03 ± 1.96	1.85 ± 0.04	6.38 ± 0.27
CE45Zn	0.249 ± 0.005	58.39 ± 2.55	0.509 ± 0.015	35.82 ± 2.37	1.88 ± 0.039	5.79 ± 0.24
CE60Zn	0.269 ± 0.004	64.93 ± 2.73	0.524 ± 0.017	32.39 ± 2.60	2.08 ± 0.08	2.68 ± 0.18
CE75Zn	0.256 ± 0.005	48.06 ± 2.51	0.492 ± 0.009	48.82 ± 2.41	1.93 ± 0.04	3.12 ± 0.14

fraction of positrons annihilating through these states.[35] In the present case, among the three components, component-3 is of particular significance.

The positronium (P_s), a bound state of a positron and electron, may exist in two spin states depending on the relative spin orientation of electron and positron: the spin-triplet state or ortho- P_s ($o-P_s$), which annihilates into a three-photon mode with an average lifetime of 142 ns in vacuum, and the spin-singlet state or para- P_s ($p-P_s$), which annihilates into a two-photon mode with a short average lifetime of 0.125 ns in vacuum.[32] In a molecular medium, $o-P_s$ energetically prefers to localize in the pre-existing free volume and gets trapped in it.[36] As a result, its lifetime is shortened to 1-10 ns due to pick-off quenching, where it interacts with an oppositely spinned electron from the inner surface of the free-volume wall and annihilates into two two-photon modes. Thus, the $o-P_s$ pick-off quenching rate is strongly related to the size and the surface properties of the free volume in the medium. The Tao-Eldrup [37], [38] equation provides a well-established semi-empirical relationship between the $o-P_s$ pick-off lifetime and the radius of the spherical free volume cavity (r_h), expressed as:

$$\tau_{\text{pick-off}} = \frac{1}{2} \left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi} \sin\left(\frac{2\pi r_h}{r_h + \delta r}\right) \right]^{-1}$$

Where $\delta r=0.1656$ nm is an empirical parameter.[31] The volume corresponding to

the free volume cavity (assumed to be spherical) can then be calculated using the equation,

$$V = \frac{4}{3}\pi r_h^3$$

This calculated hole volume should be interpreted as a mean value, as it represents an overall average of hole size and shape distribution. The variation of τ_3 and the corresponding estimated free volume sizes across composite compositions is shown in Figure 4.20.

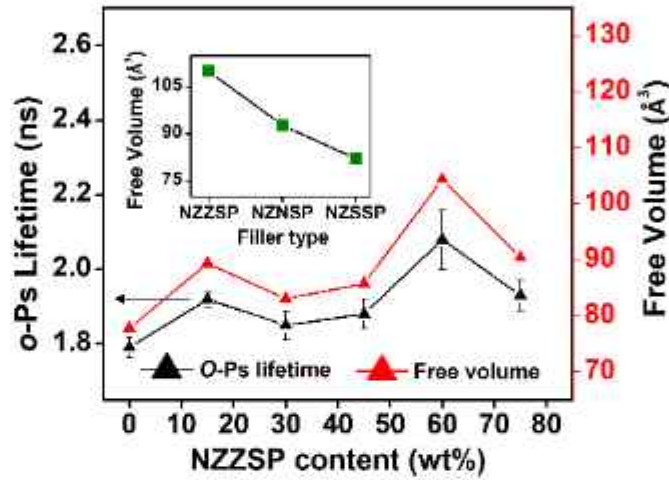


Figure 4.20: The variation of *o*- P_s lifetime and free volume with NZZSP ceramic wt%. The free volume estimated for CE60Zn, CE60Nb, and CE60Sc is shown in the inset.

It was observed that the *o*- P_s pick-off lifetime (τ_3) for CE membranes was slightly higher than that of PE, indicating an increase in free volume size upon filler incorporation. Among the composite electrolytes, CE60Zn exhibited maximum free volume size, whereas CE60Nb and CE60Sc displayed comparatively lower values (as shown in the insets of Figure 4.20) compared to CE60Zn. Notably, the trend of free volume size correlates well with the variation in ionic conductivity, both with increasing NZZSP content and across different NASICON compositions at fixed filler loading of 60 wt%.

4.3.2.7 Electrochemical performance study by LSV, CV, and GCD

The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) test of the optimized composition of CE60Zn was carried out to evaluate its electrochemical stability window (ESW). The room temperature LSV result for CE60Zn obtained using the blocking electrode configuration of SS|CE60Zn|SS is presented in Figure 4.21(a). The voltage was scanned from -1 to 5 V at a scan rate of 10 mV s^{-1} to record the corresponding data.

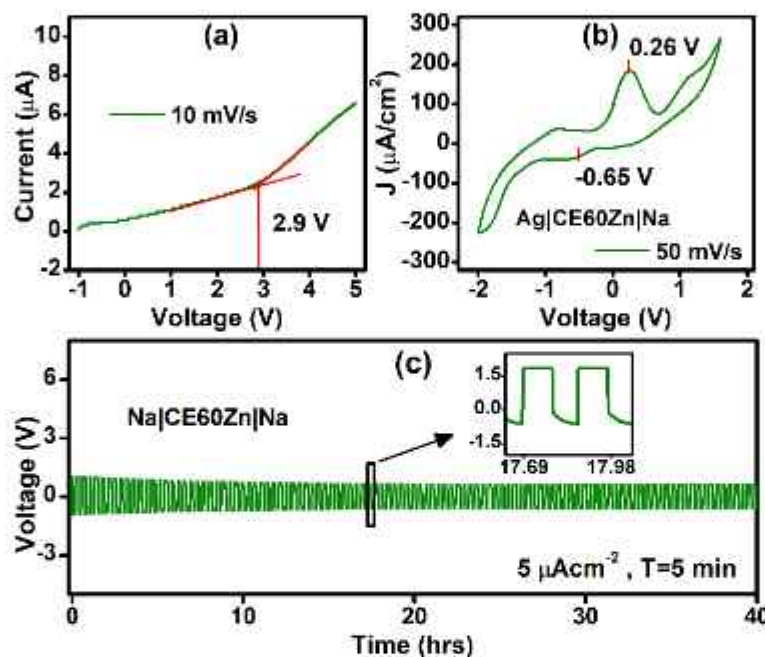


Figure 4.21: (a) Linear sweep voltammetry in the range -1 to 5 V for CE60Zn electrolyte sandwiched between stainless steel (SS) blocking electrodes. (b) Cyclic voltammograms for the Ag|CE60Zn|Na cell at a scan rate of 50 mV s^{-1} . (c) Galvanostatic cycling of Na|CE60Zn|Na symmetric cells under a constant current density of $5.0 \mu\text{A cm}^{-2}$.

From the LSV curve, the current was found to remain stable up to 2.9 V, beyond which a rapid increase in current was detected. This indicates that CE60Zn possesses an electrochemical stability window of $\sim 2.9 \text{ V}$. Such stability can be considered reasonable at room temperature, where achieving strong interfacial adhesion in polymer electrolytes is inherently challenging. Moreover, this stability limit is also in close agreement with that reported for the PEO- NaCF_3SO_3 - $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ composite studied by Dalvi *et al.*[39], measured under comparable conditions.

To further investigate the redox behavior, cyclic voltammetry (CV) was performed on the Ag|CE60Zn|Na cell as shown in Figure 4.21(b). The CV profile displays a pair of redox peaks at 0.26 and -0.65 V, corresponding to oxidation and reduction vs. Na/Na⁺. The resulting peak separation of $\Delta E=0.91$ V is comparably smaller than 2.68 V obtained for Ag|NZZSP|Na cell (section 4.3.1.4). This reduced separation indicates improved electrochemical reversibility and relatively low polarization, likely arising from the intimate interface between the CE60Zn electrolyte and sodium metal.

Besides LSV and CV tests, the electrochemical cycling performance was assessed using a symmetrical Na|CE60Zn|Na Swagelok cell, subjected to a constant current density of $5 \mu\text{A cm}^{-2}$ at room temperature. A lower current density value was selected to probe the intrinsic interfacial stability of the electrolyte-Na interface, while minimizing polarization and parasitic reactions that could mask baseline behavior. As shown in Figure 4.21(c), the Na|CE60Zn|Na symmetrical cell delivered a stable voltage profile curve with no significant fluctuation throughout the experimental duration of 40 h, confirming reversible sodium plating and stripping. These results collectively demonstrated favorable dynamic stability and good electrochemical compatibility between the CE60Zn and the sodium metal electrode. For comparison, similar electrochemical measurements were also conducted in the CE60Nb composite electrolyte. The corresponding results are presented in Figure 4.22(a-c).

As illustrated in Figure 4.22(a), the LSV of the SS|CE60Nb|SS cell displayed nearly steady current up to 0.87 V, which is much lower than the stability limit observed for the SS|CE60Zn|SS cell. This reduced electrochemical stability window may stem from the multivalent nature of Nb, which can undergo redox activity or surface reduction at comparatively lower potentials, leading to earlier current onset in LSV. This behavior is also consistent with the CV characteristics of NZNSP ceramic (discussed earlier in section 4.3.1.4), and a similar observation was reported by Patra *et al.*[40] for NASICON-Nb₂(PO₄)₃.

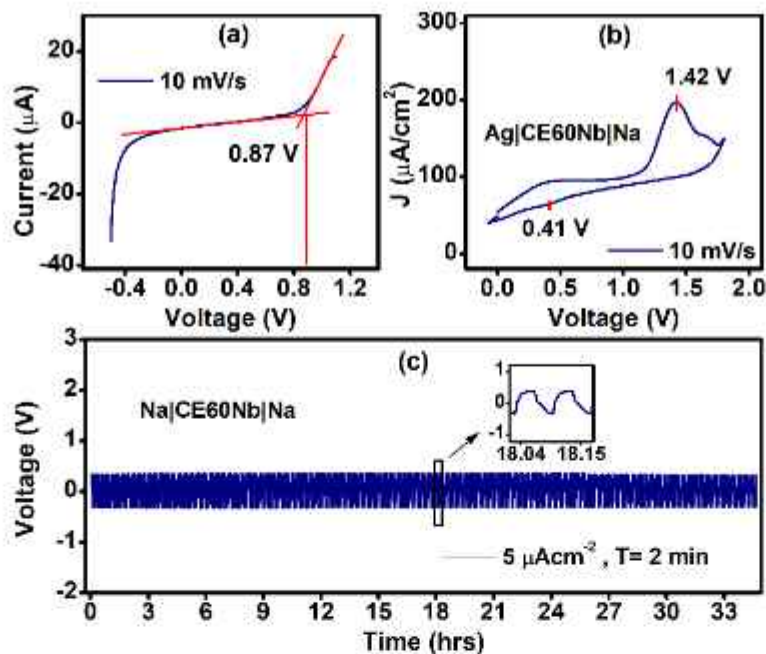


Figure 4.22: (a) Linear sweep voltammetry in the range -0.5 to 1.3 V for the SS|CE60Nb|SS cell. (b) Cyclic voltammograms for the Ag|CE60Nb|Na cell at a scan rate of 10 mV s^{-1} . (c) Galvanostatic charging and discharging cycles of Na|CE60Nb|Na symmetric cells under a constant current density of $5.0 \mu\text{A cm}^{-2}$.

The CV profile of Ag|CE60Nb|Na cell exhibited redox peaks at ~ 1.24 and ~ 0.41 V with peak separation of $\Delta E = 0.83$ V, as depicted in Figure 4.22(b). This ΔE value is comparable to that obtained for the CE60Zn composite. Furthermore, the GCD cycling of Na|CE60Nb|Na symmetric cell demonstrated stable performance at a current density of $5 \mu\text{A cm}^{-2}$, as displayed in Figure 4.22(c).

Overall, these results suggest that CE60Zn exhibits more favorable electrochemical behavior, including good interfacial stability with Na metal and sufficient electrochemical stability of nearly 3 V, making it a suitable candidate for room temperature sodium ion battery application. In contrast, although CE60Nb shows good ionic transport, its low ESW (~ 0.87 V) restricts its applicability to lower potential sodium systems.

4.4 Understanding the Composition-Property relationship in PEO-NaNO₃-NASICON composites

The solid composite electrolyte integrates a polymer matrix with ceramic filler, and at an optimized balance between these components, enables enhanced ionic conductivity. In the ceramic phase, ion transport proceeds through vacancies/interstitial ion hopping, whereas in the polymer matrix, migration of ions occurs between the complexation sites, assisted by local segmental motions of polymer chains in the amorphous regions. Within the composite electrolyte, both these mechanisms can operate, yielding ionic conductivity higher than that of the polymer matrix alone.[41]

In the present study, it is noticed that the introduction of NASICON ceramic increased the amorphous phase fraction and thus improved the mobility of Na⁺-ion through the polymer phase of the composite. Furthermore, the strong affinity of the acidic (NO₃)⁻ group towards the NASICON surface promoted the dissociation of NaNO₃, [41] thereby increasing the concentration of mobile Na⁺-ions. This behavior is confirmed by ²³Na MAS NMR results presented in section 4.3.2.4 (Figure 4.14). As a consequence, ionic conductivity progressively increased with NASICON content, exhibiting the highest conductivity of $2.2 \times 10^{-4} \text{ S cm}^{-1} \text{ S/cm}$ for CE60Zn. The subsequent decrease in the conductivity observed for CE75Zn is attributed to its lower amorphous phase fraction.

It is also well established that the ionic conductivity increases with the free volume hole size of the polymer phase.[33] The result of the PALS study in the current case showed that the composite electrolytes had higher free volume compared to that of polymer electrolytes, with CE60Zn exhibiting the highest free volume, consistent with its ionic conductivity.

In evaluating the effect of NASICON fillers on ionic conductivity of the compos-

ites, two factors were identified as critical: (1) particle size and (2) intrinsic bulk conductivity. Due to variation in the synthesis route, the NASICON fillers exhibited different average particle sizes, viz. 219 nm (NZZSP), 166 nm (NZNSP), and 127 nm (NZSSP). SEM analysis of these compositions revealed that fillers of smaller particles (NZNSP and NZSSP) were more susceptible to agglomeration. This agglomeration weakens filler-polymer interactions, limiting the disruption of polymer crystallinity, thereby reducing the free volume. Consequently, CE60Nb and CE60Sc showed lower ionic conductivities.

With regards to intrinsic bulk conductivity, all three NASICON compositions were prepared with Na content/formula unit of 3.4, corresponding to the optimal Na vacancy-to-occupancy ratio for maximizing bulk conductivity. From the impedance fitting, NZZSP exhibited bulk (grain) conductivity of 11.5 mS cm^{-1} , while NZNSP and NZSSP showed slightly lower values of 10.0 and 9.27 mS cm^{-1} , respectively. The effects of varying particle size and bulk conductivity led to different ionic conductivities of 2.2×10^{-4} , 3.2×10^{-5} , and $2.6 \times 10^{-5} \text{ S cm}^{-1}$ at RT for CE60Zn, CE60Nb, and CE60Sc, respectively. However, based on the free volume analysis, it is evident that particle size plays the major role in enhancing the conductivity of these composites. The conductivity achieved for CE60Zn surpasses several previously reported values for the NASICON filler-based composite system.[42], [43], [44], [45]

4.5 Identification of conduction pathways in PEO- NaNO_3 -NASICON composites

As discussed in the previous section, Na^+ -ion transport in the composite electrolyte proceeds through three primary pathways: polymer phase, ceramic bulk phase, and the interfacial region between polymer and ceramic. The relative contribution of each of these pathways is strongly influenced by the type, content, and morphology of the ceramic filler.[41]

In the present system of PEO- NaNO_3 -NASICON, it is understood that ion conduction is predominantly supported by the NASICON-modified amorphous phase of the polymer matrix. To determine whether electrochemical cycling induces any change in the ion distribution across these pathways, ^{23}Na MAS NMR measurements were repeated in the GCD cycled CE60Zn and CE60Nb compositions. Figure 4.23(a) displays the ^{23}Na MAS NMR spectra of pristine and cycled CE60Zn and CE60Nb electrolytes.

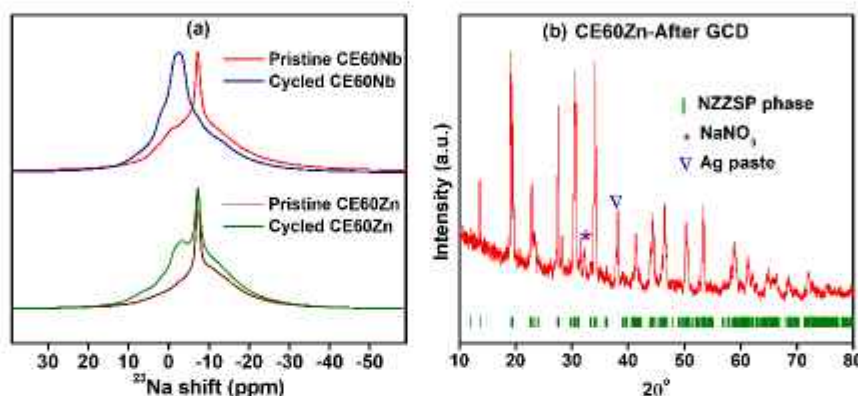


Figure 4.23: (a) ^{23}Na MAS NMR spectrum of CE60Nb and CE60Zn electrolyte before and after GCD, and (b) XRD pattern of GCD cycled CE60Zn electrolyte.

From Figure 4.23(a), noticeable changes were observed in the NMR spectra. In order to verify whether these changes arise from any structural modification, XRD was performed on the CE60Zn composite post cycling. As shown in Figure 4.23(b), the XRD pattern of cycled CE60Zn did not exhibit new crystalline phase(s), ruling out the possibility of new NMR signals. Therefore, to further investigate the spectral changes observed after cycling, the CE60Zn NMR spectrum (before and after GCD) was analyzed using the DMfit program as presented in Figure 4.24. The fitting model used for this analysis was the same as that employed for ^{23}Na NMR spectra of CE60Zn prior to cycling. As discussed earlier, the four signals used in the model correspond to NaNO_3 and Na sites (Na1, Na2, Na3-5) in the NASICON crystal structure. The analysis of the cycled NMR spectrum revealed a prominent decrease in the relative intensity of the NaNO_3 signal, accompanied by a significant increase in Na2, Na3-5 signals. These observations suggest that during GCD

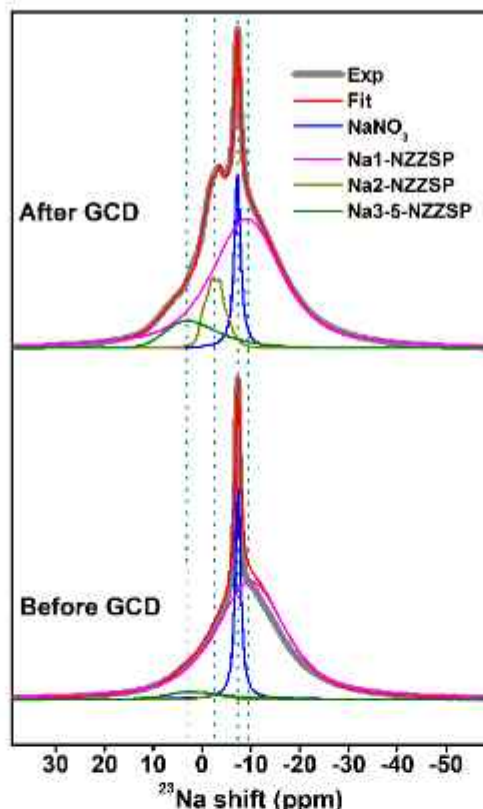


Figure 4.24: ^{23}Na MAS NMR spectrum recorded in CE60Zn before and after galvanostatic charging-discharging (GCD) cycles. The experimental spectra were fitted with four different signal contributions.

cycling, Na^+ ions diffuse from the polymer phase to the ceramic phase. Thus, the increase in the NASICON-related signal intensities can be interpreted as higher time-averaged occupancy of Na2, Na3-5 site within NMR timescale, as a result of additional Na^+ diffusion. Such Na^+ ion transfer from the polymer to the ceramic phase, therefore, supports the existence of additional pathways through ceramic and ceramic-polymer interfacial phases.

In the best conducting composition, CE60Zn, the high ceramic loading of 60 wt% enables the formation of continuous ion conduction pathways. Nevertheless, in T_1 relaxation measurement of CE60Zn, the ^{23}Na moment recovery curve was fitted using two components, corresponding to the Na^+ ion transport through polymer as well as ceramic phases. Therefore, in PEO- NaNO_3 -60 wt% NZZSP composite, ion transport is mostly through the polymer, ceramic, and also possibly through their interface. The pathways are schematically depicted in Figure 4.25.

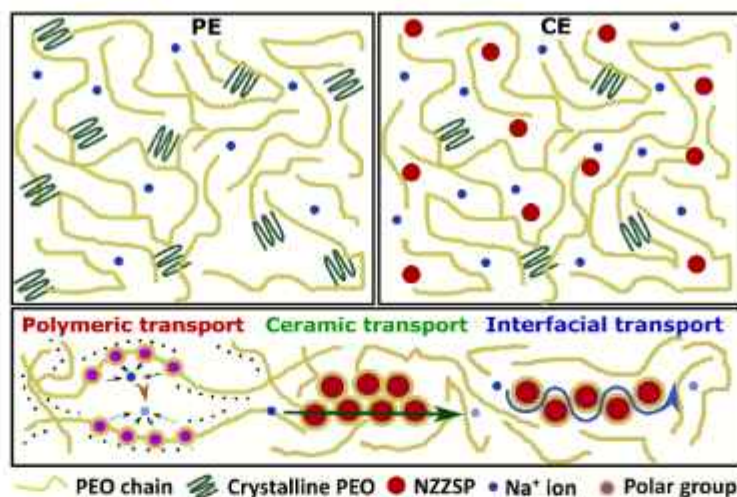


Figure 4.25: Possible ion migration pathways in PE (top left panel) and CE (top right panel).

4.6 Conclusion

In the present work, we synthesized polymer-ceramic composite electrolytes by dispersing NZZSP fillers into a PEO- NaNO_3 matrix. High RT conductivity of $\sigma > 1 \times 10^{-4} \text{ S cm}^{-1}$ were achieved for both PEO- NaNO_3 -45/60 wt% NZZSP (CE45Zn, CE60Zn). This enhanced conductivity is attributed to their increased amorphous phase content as supported by XRD/DSC, ^{23}Na MAS NMR, and PALS results. The LSV analysis of CE60Zn indicated a high electrochemical stability window of $\sim 3 \text{ V}$, while the GCD of its symmetric cell with Na metal demonstrated good cyclability. Composite electrolytes incorporated with Nb and Sc (CE60Nb and CE60Sc) showed comparatively low ionic conductivities. These low conductivities were due to their lower bulk conductivity and the smaller particle size of the incorporated fillers. Nevertheless, the symmetric Na|CE60Nb|Na cell demonstrated long-term interfacial stability. The combination of high conductivity, ionic transference number, and interfacial stability signifies CE60Zn and CE60Nb as potential electrolytes for application in sodium ion batteries. Overall, the findings of this work offer valuable guidelines for designing next-generation composite electrolytes for room temperature applications. Extended cycling and estimation of rate capability can be undertaken in the full battery assembly as future work.

References

- [1] Z. Zhang et al., *Energy Environ. Sci.*, vol. 11, pp. 1945–1976, 8 2018. DOI: 10.1039/C8EE01053F.
- [2] A. Chakraborty, R. Thirupathi, S. Bhattacharyya, K. Singh, and S. Omar, *Journal of Power Sources*, vol. 572, p. 233 092, 2023, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2023.233092>.
- [3] F. Gebert, J. Knott, R. Gorkin, S.-L. Chou, and S.-X. Dou, *Energy Storage Materials*, vol. 36, pp. 10–30, 2021, ISSN: 2405–8297. DOI: <https://doi.org/10.1016/j.ensm.2020.11.030>.
- [4] A. Boschini and P. Johansson, *Electrochimica Acta*, vol. 175, pp. 124–133, 2015, ISSN: 0013-4686. DOI: <https://doi.org/10.1016/j.electacta.2015.03.228>.
- [5] J. Serra Moreno, M. Armand, M. Berman, S. Greenbaum, B. Scrosati, and S. Pancro, *Journal of Power Sources*, vol. 248, pp. 695–702, 2014, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2013.09.137>.
- [6] A. A. Shindrov, K. V. Mishchenko, O. A. Podgornova, A. A. Shapovalova, and N. V. Kosova, *Solid State Ionics*, vol. 406, p. 116 485, 2024, ISSN: 0167–2738. DOI: <https://doi.org/10.1016/j.ssi.2024.116485>.
- [7] X. Yu, L. Xue, J. B. Goodenough, and A. Manthiram, *ACS Materials Lett.*, vol. 1, no. 1, pp. 132–138, Jul. 2019.
- [8] Y. L. Ni'mah, M.-Y. Cheng, J. H. Cheng, J. Rick, and B.-J. Hwang, *Journal of Power Sources*, vol. 278, pp. 375–381, 2015, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2014.11.047>.
- [9] S. Han et al., *Electrochimica Acta*, vol. 441, p. 141 795, 2023, ISSN: 0013–4686. DOI: <https://doi.org/10.1016/j.electacta.2022.141795>.
- [10] K. Hiraoka, M. Kato, T. Kobayashi, and S. Seki, *J. Phys. Chem. C*, vol. 124, no. 40, pp. 21 948–21 956, Oct. 2020.

- [11] A. Tiwari and R. Kumar Singh, *ChemPhysChem*, vol. 25, no. 24, e202400620, Dec. 2024.
- [12] J. Yang et al., *ACS Energy Lett.*, vol. 5, no. 9, pp. 2835–2841, Sep. 2020.
- [13] Y. Liu et al., *Journal of Power Sources*, vol. 518, p. 230765, 2022. DOI: 10.1016/j.jpowsour.2021.230765.
- [14] O. Arcelus et al., *Journal of Applied Crystallography*, vol. 57, no. 5, pp. 1676–1690, Oct. 2024. DOI: 10.1107/S1600576724006885.
- [15] A. S. Bondarenko and G. A. Ragoisha, in *Progress in Chemometrics Research*, A. L. Pomerantsev, Ed., Program available at <http://www.abc.chemistry.bsu.by/vi/analyser/>, New York: Nova Science Publishers, 2005, pp. 89–102.
- [16] C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, *Nature Methods*, vol. 9, no. 7, pp. 671–675, Jul. 2012.
- [17] J. V. Olsen, P. Kirkgaard, and M. Eldrup, Department of Energy Conversion and Storage, Technical University of Denmark, Tech. Rep., 2022, Version 3.251.
- [18] D. Massiot et al., *Magnetic Resonance in Chemistry*, vol. 40, no. 1, pp. 70–76, Jan. 2002.
- [19] X. Yang et al., *Nano-Micro Letters*, vol. 15, no. 1, p. 74, Mar. 2023.
- [20] B. Jinisha, K. M. Anilkumar, M. Manoj, A. Abhilash, V. S. Pradeep, and Jayalekshmi, *Ionics*, vol. 24, no. 6, pp. 1675–1683, Jun. 2018.
- [21] Q. Zhang et al., *Journal of The Electrochemical Society*, vol. 167, no. 7, p. 070523, Feb. 2020. DOI: 10.1149/1945-7111/ab741b.
- [22] J. Xi, X. Qiu, J. Wang, Y. Bai, W. Zhu, and L. Chen, *Journal of Power Sources*, vol. 158, no. 1, pp. 627–634, 2006, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2005.10.010>.

- [23] S. K. Patla, R. Ray, K. Asokan, and S. Karmakar, *Journal of Applied Physics*, vol. 123, no. 12, p. 125 102, Mar. 2018, ISSN: 0021-8979. DOI: 10.1063/1.5022050.
- [24] B. Santhoshkumar et al., *Chemical Physics Letters*, vol. 776, p. 138 706, 2021, ISSN: 0009-2614. DOI: <https://doi.org/10.1016/j.cplett.2021.138706>.
- [25] E. R. Losilla et al., *Chem. Mater.*, vol. 12, no. 8, pp. 2134–2142, Aug. 2000.
- [26] S. H. Chung, K. R. Jeffrey, and J. R. Stevens, *The Journal of Chemical Physics*, vol. 108, no. 8, pp. 3360–3372, Feb. 1998.
- [27] X. Li et al., *J. Am. Chem. Soc.*, vol. 145, no. 21, pp. 11 701–11 709, May 2023.
- [28] T. Miyamoto and K. Shibayama, *Journal of Applied Physics*, vol. 44, no. 12, pp. 5372–5376, Dec. 1973.
- [29] D. Bamford et al., *The Journal of Chemical Physics*, vol. 115, no. 15, pp. 7260–7270, Oct. 2001.
- [30] D. Bamford, A. Reiche, G. Dlubek, F. Alloin, J.-Y. Sanchez, and M. A. Alam, *The Journal of Chemical Physics*, vol. 118, no. 20, pp. 9420–9432, May 2003.
- [31] P. Utpalla, S. K. Sharma, K. Sudarshan, S. K. Deshpande, M. Sahu, and P. K. Pujari, *J. Phys. Chem. C*, vol. 124, no. 8, pp. 4489–4501, Feb. 2020.
- [32] Y. Kobayashi, *Defect and Diffusion Forum*, vol. 331, pp. 253–274, Dec. 2012. DOI: 10.4028/www.scientific.net/DDF.331.253.
- [33] P. Utpalla, S. K. Sharma, K. Sudarshan, S. K. Deshpande, M. Sahu, and P. K. Pujari, *J. Phys. Chem. C*, vol. 124, no. 8, pp. 4489–4501, Feb. 2020.
- [34] G. Dlubek, C. Hübner, and S. Eichler, *physica status solidi (a)*, vol. 172, no. 2, pp. 303–315, Apr. 1999.

- [35] W. Salgueiro, A. Somoza, S. Goyanes, G. Rubiolo, A. Marzocca, and G. Consolati, *physica status solidi (a)*, vol. 186, no. 1, R16–R18, Jul. 2001.
- [36] Y. Jean, *Microchemical Journal*, vol. 42, no. 1, pp. 72–102, 1990, ISSN: 0026-265X. DOI: [https://doi.org/10.1016/0026-265X\(90\)90027-3](https://doi.org/10.1016/0026-265X(90)90027-3).
- [37] S. J. Tao, *The Journal of Chemical Physics*, vol. 74, no. 8, pp. 4754–4754, Apr. 1981, ISSN: 0021-9606. DOI: 10.1063/1.441776.
- [38] M. Eldrup, D. Lightbody, and J. Sherwood, *Chemical Physics*, vol. 63, no. 1, pp. 51–58, 1981, ISSN: 0301-0104. DOI: [https://doi.org/10.1016/0301-0104\(81\)80307-2](https://doi.org/10.1016/0301-0104(81)80307-2).
- [39] Neha and A. Dalvi, *Materials Science and Engineering:B*, vol. 289, p. 116252, 2023, ISSN: 0921-5107. DOI: <https://doi.org/10.1016/j.mseb.2022.116252>.
- [40] B. Patra, K. Kumar, D. Deb, S. Ghosh, G. S. Gautam, and P. Senguttuvan, *J. Mater. Chem. A*, vol. 11, no. 15, pp. 8173–8183, 2023.
- [41] S. Li et al., *Advanced Science*, vol. 7, no. 5, p. 1903088, Mar. 2020.
- [42] Z. Zhang et al., *J. Mater. Chem. A*, vol. 4, no. 41, pp. 15823–15828, 2016.
- [43] L. Shen, S. Deng, R. Jiang, G. Liu, J. Yang, and X. Yao, *Energy Storage Materials*, vol. 46, pp. 175–181, 2022, ISSN: 2405-8297. DOI: <https://doi.org/10.1016/j.ensm.2022.01.010>.
- [44] X. Yu, L. Xue, J. B. Goodenough, and A. Manthiram, *Advanced Functional Materials*, vol. 31, no. 2, p. 2002144, Jan. 2021.
- [45] X. Yu, L. Xue, J. B. Goodenough, and A. Manthiram, *Advanced Energy and Sustainability Research*, vol. 2, no. 1, p. 2000061, Jan. 2021.

CHAPTER 5

V and Sr/Ca co-doped Bi₂O₃ ceramics

5.1 Introduction

Bismuth oxide in its fluorite-type face-centered cubic (*fcc*) structure (δ -Bi₂O₃) exhibits the highest conductivity among known oxide-ion conductors, with a reported value of $\sim 2.0 \text{ S cm}^{-1}$ at 800 °C.[1], [2], [3] This exceptionally high conductivity arises from the highly disordered oxygen sublattice of δ -Bi₂O₃, which intrinsically contains two oxygen vacancies per unit cell.[4] In addition, the high polarizability of Bi³⁺ ions, together with the weak Bi-O bonding, promotes the formation of vacant oxygen sites and thereby enables high oxide-ion mobility within the crystal structure. Owing to these favorable attributes, the δ -Bi₂O₃ phase has been widely regarded as a promising candidate for solid oxide fuel cells, gas sensors, and ferroelectric applications.[5], [6] However, despite these advantages, the δ -Bi₂O₃ phase is thermodynamically stable only within a narrow temperature range of 730 °C–825 °C.[3], [4] On cooling below 730 °C, the δ -Bi₂O₃ phase undergoes a phase transformation from fluorite-type *fcc* phase to the monoclinic phase (α -Bi₂O₃) via intermediate β or γ phases. This structural transformation leads to a drastic decrease in oxide ion conductivity by nearly four orders of magnitude.[3], [4] Thus, for intermediate temperature device applications, it is essential to stabilize the higher conducting *fcc* phase well below its thermodynamic stability limit ($< 730^\circ\text{C}$). To achieve this, several studies have explored cation substitution

as an effective strategy to stabilize the *fcc* structure using a range of isovalent (Ln³⁺: Lanthanide ions)[7], [8], [9], [10], [11], [12] or aliovalent (Nb⁵⁺)[13], [14], [15], (Ta⁵⁺)[16], [17], (P⁵⁺)[18], (W⁶⁺) dopants.[2], [7], [8] However, substitution with cations of relatively larger ionic radii has been found to stabilize the rhombohedral phase instead.[3], [19], [20] Both of these stabilized phases (*fcc* and rhombohedral) exhibit high oxide-ion conductivity at elevated temperatures; however, their conductivities are typically an order of magnitude lower than that of the δ -Bi₂O₃ phase. Moreover, these phases also undergo reversible, time-dependent aging effects at temperatures below 600 °C accompanied by significant degradation of conductivity.[10]

Recent reports have shown that improved phase stability and conductivity can be achieved more effectively in co-doped Bi₂O₃ systems (Y-Ln [21], [22], [23], [24], Te-Ln[25], Re-Ln[26], etc.) as compared to single-ion-doped compositions. Nevertheless, prior studies indicated that the phase and structural stability of stabilized Bi₂O₃ compounds are highly complex, with aging effects further complicating their structural behavior. Consequently, while Ln-doped Bi₂O₃ systems have been investigated extensively, comparatively less attention has been spared to alkaline-earth and transition metal co-doped Bi₂O₃ systems. Notably, a transition metal-doped composition, Bi_{0.913}V_{0.087}O_{1.587}, has been reported to exhibit oxide ion conductivity of $\sigma = 3.9 \times 10^{-2} \text{ S cm}^{-1}$ at 500 °C, which is at par with the best performing lanthanide-based co-doped system, Bi_{12.5}La_{1.5}ReO_{24.5}. [26], [27] Motivated by these recent results, the present work explores the vanadium (V) in combination with Sr/Ca as co-dopants in the Bi₂O₃ system.

In the present study, a systematic investigation of phase stability and oxide ion conductivity of Bi_{1-x}V_xO_{1.5+x} ($x = 0.084, 0.087, 0.090, 0.100$, and 0.148) has been carried out to identify the optimal composition. As it was reported, Bi_{1-x}V_xO_{1.5+x} with $x=0.087$ displayed the highest conductivity. Based on this evaluation, Sr and Ca were subsequently introduced as co-dopants into the optimized composition ($x=0.087$), yielding Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} and Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577}. The ionic

radii of Sr²⁺ and Ca²⁺ ($r_{\text{Sr}^{2+}} = 1.18 \text{ \AA}$, $r_{\text{Ca}^{2+}} = 1.00 \text{ \AA}$)[28], being slightly higher than or close to that of Bi³⁺ ($r_{\text{Bi}^{3+}} = 1.03 \text{ \AA}$), were expected to maintain the local disordered structure, thereby sustaining high oxide-ion conductivity.

In order to evaluate the aging behavior, Bi_{0.913}V_{0.087}O_{1.587} (BV_{0.087}O), Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} (BS_{0.02}V_{0.087}O), Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577} (BC_{0.02}V_{0.087}O), and Bi_{0.852}V_{0.148}O_{1.648} (BV_{0.148}O) compositions were annealed at two different temperatures (400 °C and 600 °C) for 100 hours, after which their phase and conductivity were characterized. Moreover, the effect of Sr concentration (at 4 and 6 mole %) on the properties of as-sintered and annealed BV_{0.087}O composition has also been investigated. Finally, the phase stability of Bi_{0.913}V_{0.087}O_{1.587}, Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577}, and Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577} compositions was verified under reducing conditions.

The objectives of the present investigation are thus:

- Synthesis and characterization of Bi_{1-x}V_xO_{1.5+x} ($x = 0.084, 0.087, 0.090, 0.100, \text{ and } 0.148$) and Sr/Ca co-doped compositions (Bi_{0.893}M_{0.02}V_{0.087}O_{1.577}, with M=Sr/Ca)
- Investigating the effect of prolonged temperature exposure on the phase stability and ionic conductivity of the synthesized compositions.
- Investigating the role of dopant substitution, annealing conditions, and temperature on the local structure of the compositions.
- Evaluating the influence of Sr concentration on phase evolution and conductivity in both as-sintered and annealed compositions.
- Verifying the phase stability under reducing conditions.
- Understanding the ion migration pathway in the proposed system.

5.2 Methods and experimental design

5.2.1 Synthesis of V- and Sr/Ca co-doped compositions

Nominal polycrystalline Bi_{1-x}V_xO_{1.5+x} (BV_xO: $x=0.084-0.148$) and co-doped, Bi_{0.893}M_{0.02}V_{0.087}O_{1.577} (BM_{0.02}V_{0.087}O with M = Sr²⁺, Ca²⁺) compositions, were prepared by the solid-state reaction method. Stoichiometric amounts of Bi₂O₃ (Alfa Aesar, 99.0 %), V₂O₅ (Alfa Aesar, 99.2 %), SrCO₃ (Alfa Aesar, 99.0 %), and CaCO₃ (Alfa Aesar, 99.95 %) were weighed accurately and mixed thoroughly. The mixture was subsequently ground using isopropanol to obtain a homogeneous mixture in an agate mortar and pestle. Following this initial mixing, the compound was calcined at 700, 750, 800, and 825 °C for 12 hours, with intermittent grinding after each heating step. Later, the samples were furnace cooled to room temperature with an approximate pass time of 3 h. The resulting product was reground and pressed to form pellets of 10 mm diameter and ~ 2 mm thickness, applying a pressure of 250 MPa for 2 min. Finally, the pellets were sintered at 825 °C for 12 h. The heating scheme employed in this work is similar to that reported by Kuang *et al.*[29]

The chemical reaction of the synthesized composition of Bi_{1-x}V_xO_{1.5+x} is as follows:



To confirm the stability of the phase under operating conditions, four representative compositions of BV_xO ($x=0.087$ and 0.148) and BM_{0.02}V_{0.087}O (M = Sr²⁺, Ca²⁺) were subjected to prolonged high-temperature exposure. This was accomplished by annealing the samples at 400 °C/100 h and 600 °C/100 h in air, followed by furnace cooling to room temperature. The annealing temperatures were selected to fall within the intermediate working temperature range while also being close to the reported aging temperature (~ 600 °C) for the phase-stabilized Bi₂O₃ system. Furthermore, to probe the effect of higher Sr concentrations, com-

positions with Sr contents of 4 and 6 mol% were synthesized using the same preparation route (as-sintered samples). The effect of annealing treatment was also systematically investigated in these samples (aged samples). Finally, phase stability under reducing conditions was evaluated for the selected compositions of Bi_{0.913}V_{0.087}O_{1.587}, Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} and Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577} by heating at 400 °C for 5 hours in 25 % H₂ - 75 % N₂ atmosphere.

The abbreviations used for the synthesized compositions are listed in Table 5.1 and will be used throughout the remainder of this chapter.

Table 5.1: List of abbreviations for synthesized V and Sr/Ca- co-doped compositions

Thermal treatment	Compositions	Abbreviations
As-sintered	Bi _{0.916} V _{0.084} O _{1.584}	BV _{0.084} O
	Bi _{0.913} V _{0.087} O _{1.587}	BV _{0.087} O
	Bi _{0.910} V _{0.090} O _{1.590}	BV _{0.090} O
	Bi _{0.900} V _{0.100} O _{1.600}	BV _{0.100} O
	Bi _{0.852} V _{0.148} O _{1.648}	BV _{0.148} O
	Bi _{0.893} Sr _{0.02} V _{0.087} O _{1.577}	BS _{0.02} V _{0.087} O
	Bi _{0.893} Ca _{0.02} V _{0.087} O _{1.577}	BC _{0.02} V _{0.087} O
	Bi _{0.873} Sr _{0.04} V _{0.087} O _{1.567}	BS _{0.04} V _{0.087} O
	Bi _{0.853} Sr _{0.06} V _{0.087} O _{1.557}	BS _{0.06} V _{0.087} O
Annealed at 400 °C/100 h	Bi _{0.913} V _{0.087} O _{1.587}	BV _{0.087} O 400 °C/100 h
	Bi _{0.852} V _{0.148} O _{1.648}	BV _{0.148} O 400 °C/100 h
	Bi _{0.893} Sr _{0.02} V _{0.087} O _{1.577}	BS _{0.02} V _{0.087} O 400 °C/100 h
	Bi _{0.893} Ca _{0.02} V _{0.087} O _{1.577}	BC _{0.02} V _{0.087} O 400 °C/100 h
	Bi _{0.873} Sr _{0.04} V _{0.087} O _{1.567}	BS _{0.04} V _{0.087} O 400 °C/100 h
	Bi _{0.853} Sr _{0.06} V _{0.087} O _{1.557}	BS _{0.06} V _{0.087} O 400 °C/100 h
Annealed at 600 °C/100 h	Bi _{0.913} V _{0.087} O _{1.587}	BV _{0.087} O 600 °C/100 h
	Bi _{0.852} V _{0.148} O _{1.648}	BV _{0.148} O 600 °C/100 h
	Bi _{0.893} Sr _{0.02} V _{0.087} O _{1.577}	BS _{0.02} V _{0.087} O 600 °C/100 h
	Bi _{0.893} Ca _{0.02} V _{0.087} O _{1.577}	BC _{0.02} V _{0.087} O 600 °C/100 h
	Bi _{0.873} Sr _{0.04} V _{0.087} O _{1.567}	BS _{0.04} V _{0.087} O 600 °C/100 h
	Bi _{0.853} Sr _{0.06} V _{0.087} O _{1.557}	BS _{0.06} V _{0.087} O 600 °C/100 h

5.2.2 X-ray and Neutron powder diffraction study

The X-ray diffraction (XRD) measurements of the powder samples were performed on a Rigaku diffractometer, using Cu K_α radiation at room temperature. Diffrac-

tion data were collected in a 2θ range of 20° - 80° with a step size of 0.02° .

Room and high-temperature neutron powder diffraction (NPD) measurements were performed using the neutron powder diffractometer (PD-2) at Dhruva Research Reactor, Bhabha Atomic Research Centre (BARC), Mumbai, India. For these measurements, the powder samples were loaded in a cylindrical vanadium container (~ 8 mm diameter) and attached to a high-temperature furnace. All the NPD data were recorded during the heating cycle starting from room temperature, with samples thermalized for ~ 30 minutes at each temperature before acquiring the data.

Phase identification and structural refinements for XRD/NPD data were carried out using the Rietveld method in the Full Prof Suite software.[30] In the refinements, a pseudo-Voigt function was used to model the diffraction peak profile. In the initial stages, scale factors, background coefficients, 2θ zero positions, line widths, and peak shapes were refined, followed by refinement of positional parameters and site occupancies. For compositions exhibiting multiple intermediate phases, the Le Bail method was used for reliable phase identification.

In addition, soft bond valence sum (BVS) analysis was carried out using the NPD data to determine the ionic conduction pathways. The BVS calculations were performed using the Bond_STR program, an inbuilt package within the Full Prof Suite software.[31] The calculated conduction pathways within the unit cell were subsequently visualized using VESTA software.[32]

5.2.3 Impedance spectroscopy (EIS) and scanning electron microscopy (SEM) study

Electrical conductivity measurements were performed using electrochemical impedance spectroscopy (EIS) with an impedance analyzer (PSM1735 NumetriQ, UK) in the frequency range of 1 Hz to 10 MHz. Before the EIS measurement, the samples were coated with silver paste on both parallel surfaces, followed by firing at 500°C for 2 h to ensure good electrical contact. The acquired impedance data

were analyzed using equivalent circuit fitting using EISSA software.

The microstructural characterization of the samples was conducted using a Carl Zeiss scanning electron microscope (SEM). In order to create a thin conducting layer on the surface of the non-conducting sample, pellets were sputtered with gold before SEM analysis. The elementary composition of the polycrystalline samples was determined by the Energy Dispersive X-ray (EDX) spectroscopy technique attached to the SEM instrument.

5.2.4 Differential Scanning Calorimetry

Thermal analysis of the BV_xO compositions was carried out using Differential Scanning Calorimetry (DSC) measurement performed in a Shimadzu DSC-60 thermal analyzer. The measurements were carried out over the temperature range from RT to 500 °C at a heating rate of 5 ° min⁻¹. A sample weighing ~ 8-10 mg was sealed in the aluminum pan and used for measurement.

5.2.5 X-ray Absorption Fine Structure Spectroscopy (XANES/EXAFS)

X-ray absorption fine structure (XAFS) spectroscopy was employed to investigate the local structural environment of the prepared compositions. For room temperature XAFS measurement, finely powdered samples were meticulously spread onto the scotch tape to achieve a layer of uniform thickness. A suitable number of these layers was then stacked to achieve an absorption edge jump, $\Delta\mu t \leq 1$.

For a high-temperature XAFS experiment conducted in the range of 100-500 °C, the samples were thoroughly mixed with boron nitride (BN) powder in an appropriate ratio and pressed into pellets of 13 mm diameter. Extended X-ray absorption fine structure (EXAFS) measurements at the Bi L₃-edge were performed in transmission mode over an energy range of 13118-14300 eV, while X-ray absorption near-edge structure (XANES) measurements at the V K-edge were conducted in fluorescence mode. All the measurements were performed at the XAFS beam

line of Elettra synchrotron, Trieste, Italy.[33] The acquired XAFS data were processed and analyzed using the Demeter suite software following well-established procedures.[34]

5.3 Results

5.3.1 Characterization of As-sintered V- and Sr/Ca co-doped Bi₂O₃ ceramics

In this section, the results for as-sintered (as-prepared) BV_xO ($x=0.084, 0.087, 0.090, 0.100, 0.148$) and BM_{0.02}V_{0.087}O (M= Sr, Ca) compositions are presented.

5.3.1.1 Phase identification and structure determination

Phase analysis of the as-sintered Bi_{1-x}V_xO_{1.5+x} with $x=0.084-0.148$ (BV_xO), Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} (BS_{0.02}V_{0.087}O), and Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577} (BC_{0.02}V_{0.087}O) samples was investigated using X-ray powder diffraction. Room temperature XRD pattern of as-sintered V-doped compositions is compared in Figure 5.1(a), and that of Sr/Ca co-doped compositions is presented in 5.1(b).

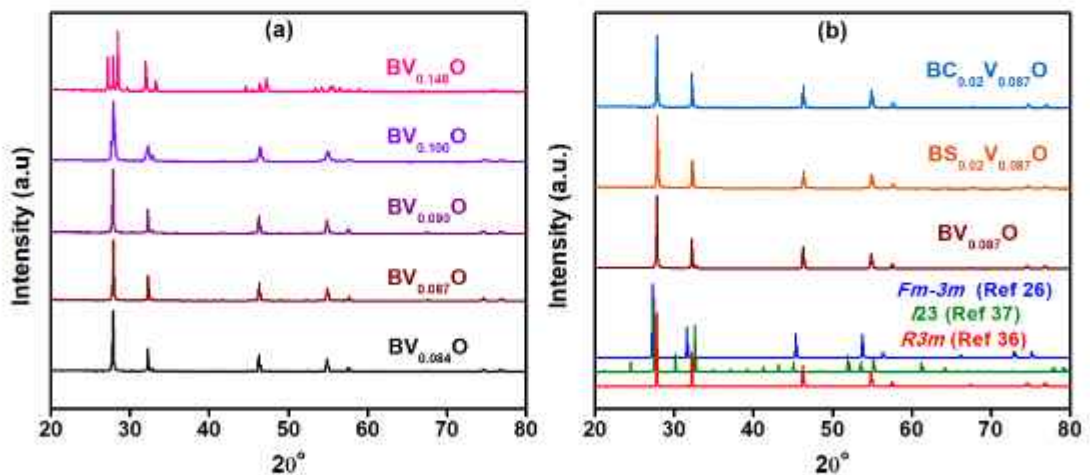


Figure 5.1: (a) XRD pattern of the as-sintered samples of BV_xO ($x= 0.084, 0.087, 0.090, 0.100$, and 0.148) and (b) Stack plot of XRD patterns of BV_{0.087}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O samples with reference patterns of *Fm-3m*, *R3m*, and *I23* structures

From Figure 5.1(a), it was observed that varying V content from $x = 0.084$ to 0.100 resulted in an identical XRD pattern, indicating no structural change in low V-doped compositions. However, a distinct phase change was observed at $x=0.148$. The Sr and Ca co-doped $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions, shown in Figure 5.1(b), also displayed XRD patterns identical to that of $\text{BV}_{0.087}\text{O}$. The reference patterns of $Fm\bar{3}m$, $R3m$, and $I23$ structures displayed in Figure 5.1(b) revealed that the diffraction features of $R3m$ and $Fm\bar{3}m$ phases were very similar. Therefore, to reliably determine the actual crystal structure, Rietveld refinement was performed in $\text{BV}_{0.087}\text{O}$ composition using both $R3m$ and $Fm\bar{3}m$ models, as shown in Figure 5.2.

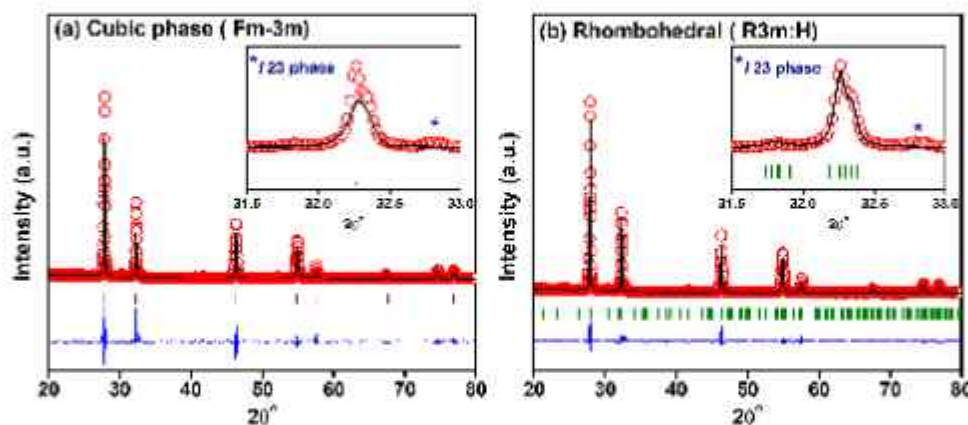


Figure 5.2: A comparison of Rietveld refinement of as-sintered $\text{BV}_{0.087}\text{O}$ using (a) the cubic $Fm\bar{3}m$ model and with (b) the rhombohedral $R3m$ model. A peak, marked by * in the inset, represents the $I23$ phase.

From the zoomed-in view (Bragg peaks $\sim 31.5^\circ$ – 33.0°) of the first XRD peak fitting shown in the insets of Figure 5.2, it was observed that the $Fm\bar{3}m$ model did not satisfactorily fit the experimental diffraction pattern. In contrast, the same pattern was fitted well using the $R3m$ space group, with the $I23$ space group (corresponding to the γ phase of Bi_2O_3) as a secondary phase. Based on this observation, the $R3m + I23$ model was adopted for subsequent Rietveld fittings of lower V-doped compositions. Figure 5.3(a-f) displays the Rietveld refined XRD patterns of BV_xO ($x=0.084, 0.087, 0.090, 0.100$, and 0.148) and $\text{BM}_{0.02}\text{V}_{0.087}\text{O}$ ($M=\text{Sr}, \text{Ca}$) compositions.

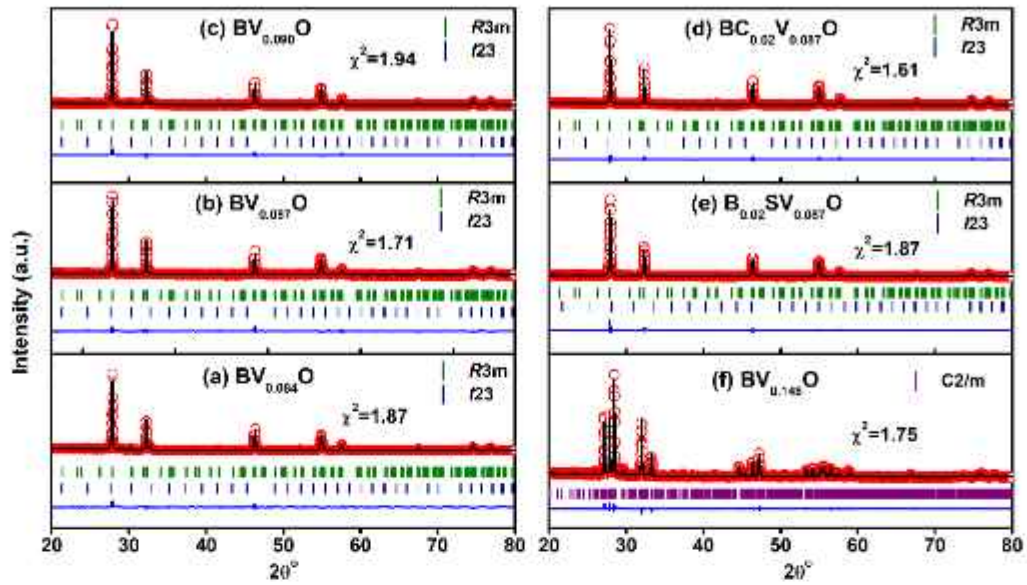


Figure 5.3: (a-f) Room temperature XRD patterns with Rietveld refinement fit of as-sintered samples.

The results of Rietveld refinement confirmed that the XRD patterns of the low V-doped compositions, as well as Sr/Ca co-doped compositions, could be indexed using rhombohedral $R3m$ and cubic $I23$ symmetries. Whereas, the highest V-doped composition, $BV_{0.148}O$, was indexed exclusively with monoclinic $C2/m$ symmetry. For intermediate composition of $BV_{0.100}O$, formation of multiple phases was evident, and thus, fitting was carried out using Le-bail refinement, as shown in Figure 5.4.

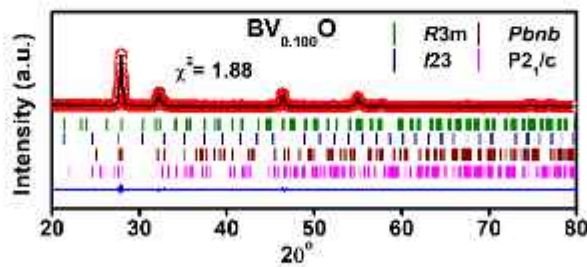


Figure 5.4: Rietveld refinement of XRD data of $BV_{0.100}O$ was analyzed by the Le-Bail method

The fitting of $BV_{0.100}O$ revealed intermediate phases of ϵ -Bi₂O₃ ($Pbnb$), β -Bi₂O₃ ($P2_1/c$), together with γ -Bi₂O₃ ($I23$) and $R3m$ phases. The lattice parameters of the $BV_{0.100}O$ phase are listed in Table 5.2

Table 5.2: Refined lattice parameters of phases for BV_{0.100}O XRD data

Lattice parameters			
<i>R3m</i>	<i>I23</i> (γ -Bi ₂ O ₃)	<i>Pbnb</i> (ϵ -Bi ₂ O ₃)	<i>P2₁/c</i> (β -Bi ₂ O ₃)
$a = b = 11.736(6) \text{ \AA}$, $c = 28.826(8) \text{ \AA}$	$a = b = c$ $= 10.206(5) \text{ \AA}$	$a = 4.927(8) \text{ \AA}$, $b = 5.584(4) \text{ \AA}$, $c = 12.761(7) \text{ \AA}$	$a = 5.748(7) \text{ \AA}$, $b = 8.088(5) \text{ \AA}$, $c = 7.498(8) \text{ \AA}$, $\beta = 66.8^\circ$

For the Rietveld refinements, the initial crystallographic parameters were taken from the reported *R3m* [35], [36], *I23* [37] and *C2/m* [38] structural models, followed by stepwise refinement of the lattice parameters, atomic parameters and occupancy parameters. The final refined structural parameters for BV_{0.087}O (*R3m* and *I23* phases) and BV_{0.148}O (*C2/m*) are presented in Tables 5.3–5.5.

Table 5.3: Structural parameters of *R3m* phase in nominal BV_{0.087}O obtained from Rietveld analysis of XRD

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
O1	3a	0	0	0.715	0.166(7)	0.09
O2	3a	0	0	0.059	0.166(7)	0.047
O3	3a	0	0	0.255	0.166(7)	0.08
O4	9b	0.541	0.459	0.168	0.5	0.04(1)
O5	9b	0.412(3)	0.587(7)	0.306(7)	0.5	0.10(9)
O6	9b	0.462(7)	0.537(3)	0.113(3)	0.5	0.12
O7	9b	0.803(3)	0.196(7)	0.296(7)	0.5	0.06
O8	9b	0.545(7)	0.454(3)	0.518(3)	0.5	0.13(1)
O9	9b	0.111(7)	0.888(3)	0.291(3)	0.5	0.12
O10	9b	0.233(7)	0.766(3)	0.0293(3)	0.50	0.10(9)
O11	9b	0.756(7)	0.243(3)	0.122(3)	0.5	0.06
O12	9b	0.264(3)	0.735(7)	0.145(7)	0.5	0.08
O13	18c	0.330(3)	0.024(7)	0.050(7)	1	0.09(1)
O14	18c	0.053(3)	0.372(7)	0.232(7)	1	0.10(9)
O15	3a	0	0	0.374	0.166(7)	0.07(1)
V1	3a	0	0	0.633(9)	0.166(7)	0.05

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
V2	3a	0	0	0	0.014(5)	0.09
Bi2	3a	0	0	0	0.152(2)	0.09
V3	3a	0	0	0.314(4)	0.014(5)	0.09
Bi3	3a	0	0	0.314(4)	0.152(2)	0.09
Bi4	9b	0.555(8)	0.444(2)	0.419(9)	0.5	0.02(7)
Bi5	9b	0.112(4)	0.887(6)	0.195(9)	0.5	0.10
Bi6	9b	0.557(7)	0.442(2)	0.086(9)	0.5	0.01
Bi7	9b	0.443(9)	0.556(1)	0.197(7)	0.5	0.01
Bi8	9b	0.776(5)	0.223(5)	0.192(3)	0.5	0.01
Bi9	9b	0.213(5)	0.786(4)	0.078(7)	0.5	0.01
Bi10	18c	0.343	0.002(1)	0.308(6)	1	0.01
$a = b = 11.749(7) \text{\AA}$, $c = 28.890(5) \text{\AA}$, $\gamma = 120^\circ$, $V = 3454.11 \text{\AA}^3$						

Table 5.4: Rietveld refined structural parameters of $I23$ phase (Space group: $I23$) in $\text{BV}_{0.087}\text{O}$

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Bi1	24f	0.169(9)	0.323(1)	0.019(6)	1	0.5
Bi2	2a	0	0	0	0.076	0.5
O1	24f	0.136(5)	0.247(6)	0.503(8)	1	0.5
O2	8c	0.187(4)	0.187(4)	0.187(4)	0.33(3)	0.5
O3	8c	0.888(5)	0.888(5)	0.888(5)	0.33(3)	0.5
V1	2a	0	0	0	0.001	0.5
$a = b = c = 10.215(3) \text{\AA}$, $V = 1066 \text{\AA}^3$						

Table 5.5: Rietveld refined crystallographic data of monoclinic $C2/m$ phase, determined from XRD data of $\text{BV}_{0.148}\text{O}$ at room temperature

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Bi1	4i	0.076(4)	0.500	-0.264(3)	0.5	0.03(6)
Bi2	8j	0.405(9)	0.169(1)	-0.259(6)	1	0.03(6)
Bi3	8j	0.190(1)	0.662(6)	-0.088(5)	1	0.03(6)

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Bi4	8j	0.258(4)	0.675(5)	-0.223(8)	1	0.03(6)
Bi5	4i	0.029(5)	0	-0.574(9)	0.5	0.03(6)
Bi6	4i	0.266(7)	0.5	0.246(1)	0.5	0.03(6)
Bi7	8j	0.358(2)	0.839(7)	-0.079(7)	1	0.03(6)
Bi8	8j	0.067(7)	0.182(3)	-0.256(5)	1	0.03(6)
Bi9	4i	0.327(3)	0.5	0.092(6)	0.5	0.03(6)
Bi10	8j	0.300(6)	0.338(9)	-0.422(9)	1	0.03(6)
Bi11	8j	0.139(1)	0.846(3)	-0.403(5)	1	0.03(6)
Bi12	8j	-0.035(4)	0.322(1)	-0.425(1)	1	0.03(6)
Bi13	8j	0.022(6)	0.836(1)	-0.095(4)	1	0.03(6)
Bi14	4i	0.095(6)	0	0.265(4)	0.5	0.03(6)
O13	8j	-0.091(8)	0.160(2)	-0.445(8)	1	0.04(7)
O14	8j	0.134(8)	0.185(3)	-0.103(3)	1	0.04(7)
O15	4i	0.349(2)	0.5	-0.379(4)	0.5	0.04(7)
O16	4i	0.522(5)	0.5	-0.283(6)	0.5	0.04(7)
O17	8j	0.005(8)	0.808(9)	-0.395(3)	1	0.04(7)
O18	4i	0.296(8)	0	-0.102(5)	0.5	0.04(7)
O19	4i	0.134(6)	0	-0.199(4)	0.5	0.04(7)
O20	4i	0.048(1)	0	-0.460(3)	0.5	0.04(7)
O21	8j	0.469(1)	0.674(7)	0.204(3)	1	0.04(7)
O22	8j	0.201(9)	0.184(4)	-0.269(4)	1	0.04(7)
O23	8j	0.354(1)	0.679(2)	-0.298(7)	1	0.04(7)
O24	4i	0.048(1)	0	-0.122(6)	0.5	0.04(7)
O25	4i	0.144(9)	0	-0.337(7)	0.5	0.04(7)
O26	8j	-0.008(7)	0.666(7)	-0.295(7)	1	0.04(7)
O27	8j	0.139(3)	0.360(9)	-0.206(6)	1	0.04(7)
O28	8j	0.257(3)	0.792(8)	-0.022(6)	1	0.04(7)
O29	8j	0.325(3)	0.203(7)	-0.185(4)	1	0.04(7)
O30	8j	0.255(1)	0.244(8)	-0.131(1)	1	0.04(7)
V1	4i	0.374(3)	0.5	-0.068(9)	0.5	0.03(6)

Atom	Wyckoff position	x	y	z	Occupancy	U_{iso} ($\text{\AA}^2$)
V2	4i	0.144(5)	0.5	-0.400(2)	0.5	0.03(6)
V3	4i	0.024(3)	0.5	-0.102(3)	0.5	0.03(6)
V4	4i	0.300(4)	0	-0.412(2)	0.5	0.03(6)
O1	4i	0.282(6)	0.5	-0.109(2)	0.5	0.07(8)
O2	8j	0.400(2)	0.621(1)	-0.019	1	0.07(8)
O3	4i	0.414(1)	0.5	-0.128(6)	0.5	0.07(8)
O4	8j	0.096(8)	0.621(1)	-0.437(6)	1	0.07(8)
O5	4i	0.225(6)	0.5	-0.410(8)	0.5	0.07(8)
O6	4i	0.158(6)	0.5	-0.314(9)	0.5	0.07(8)
O7	4i	-0.058(6)	0.5	-0.095(4)	0.5	0.07(8)
O8	4i	0.014(1)	0.5	-0.186(8)	0.5	0.07(8)
O9	8j	0.070(9)	0.621(1)	-0.063(6)	1	0.07(8)
O10	8j	0.349(6)	0.121(1)	-0.413	1	0.07(8)
O11	4i	0.279(5)	0	-0.340(1)	0.5	0.07(8)
O12	4i	0.222(6)	0	-0.482(8)	0.5	0.07(8)
$a = 19.986(1) \text{ \AA}$, $b = 11.573(9) \text{ \AA}$, $c = 21.138(2) \text{ \AA}$, $\beta = 111.302^\circ$, $V = 4555.56 \text{ \AA}^3$						

The relative ratio of $R3m : I23$ phases were also determined and are tabulated in Table 5.6 along with the refined lattice parameters.

It was observed from Table 5.6 that, among the low V-doped compositions, the highest $R3m$ phase fraction was obtained for BV_{0.087}O ($R3m:I23 = 0.93:0.07$). Further higher $R3m$ phase fraction was achieved for BS_{0.02}V_{0.087}O and BC_{0.02}V_{0.087}O samples. This implied that BV_{0.087}O possessed optimal stoichiometry among the lower V-doped compositions, and Sr/Ca co-doping further suppressed the phase conversion from $R3m$ to $I23$. Kuang *et al.*[29] previously reported that low vanadium (V) doping stabilizes the rhombohedral phase instead of the fluorite-type δ -Bi₂O₃ phase. However, unlike the present study, their BV_{0.087}O sample showed only $R3m$ phase, while the samples with $x=0.074$ -0.083 contained simultaneous presence of both $R3m$ and $I23$ phases.

Table 5.6: Rietveld refined lattice parameters and phase percentages, determined from XRD data

Samples	Lattice parameters			<i>R3m:I23</i> (%)
	<i>R3m</i>	<i>I23</i>	<i>C2/m</i>	
BV _{0.084} O	$a = b = 11.750(6) \text{ \AA}$ $c = 28.887(1) \text{ \AA}$	$a = b = c$ $= 10.214(3) \text{ \AA}$	-	88.5:11.5
BV _{0.087} O	$a = b = 11.749(7) \text{ \AA}$ $c = 28.890(5) \text{ \AA}$	$a = b = c$ $= 10.215(3) \text{ \AA}$	-	92.9:7.3
BV _{0.090} O	$a = b = 11.750(7) \text{ \AA}$ $c = 28.887(1) \text{ \AA}$	$a = b = c$ $= 10.213(6) \text{ \AA}$	-	88.3:11.7
BV _{0.148} O	-	-	$a = 19.986(1) \text{ \AA}$ $b = 11.573(9) \text{ \AA}$ $c = 21.138(2) \text{ \AA}$	-
BS _{0.02} V _{0.087} O	$a = b = 11.749(2) \text{ \AA}$ $c = 28.877(4) \text{ \AA}$	$a = b = c$ $= 10.187(4) \text{ \AA}$	-	97.9:2.1
BC _{0.02} V _{0.087} O	$a = b = 11.731(8) \text{ \AA}$ $c = 28.861(8) \text{ \AA}$	$a = b = c$ $= 10.198(6) \text{ \AA}$	-	98.5:1.5

The specific structure of the Bi₂O₃:V₂O₅=9:1 systems was also investigated previously by Zhou[39] and Kashida *et al.*[36] Zhou *et al.* reported a 3×3×3 cubic superstructure derived from the fluorite lattice with the *Fm3m* space group.[39] In contrast, Kashida *et al.* identified a 3×3×3 fluorite-type superstructure with the *R3m* space group for the same composition.[36] This discrepancy in reported symmetries was attributed to the difference in their cooling protocols employed during the sample synthesis. In Zhou's [39] study, the specimens were quenched directly to RT after preparation, whereas Kashida *et al.*[36] cooled the specimens from 850 to 600 °C at the rate of 6 ° h⁻¹, followed by rapid cooling to room temperature.

The present results are consistent with those reported by Kashida *et al.*[36] and the presence of the γ phase of Bi₂O₃ (*I23*) can be explained by the results of Harwig *et al.*[4] who demonstrated the persistence of the γ phase of Bi₂O₃ (*I23*) to RT in slow cooling conditions. Therefore, the observation of co-existence of *R3m* and *I23* symmetries in the present study is well supported by prior reports.

5.3.1.2 Electrical conductivity measurement using EIS

Electrochemical impedance spectroscopy (EIS) was employed to investigate the ionic conductivity and to distinguish its underlying contributions. The impedance

measurement was recorded in the temperature range of 150-500 °C and in the frequency range of 1 Hz to 10 MHz. Figure 5.5(a-d) shows the complex impedance (Nyquist) plot of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BV}_{0.148}\text{O}$ compositions recorded at 200 °C.

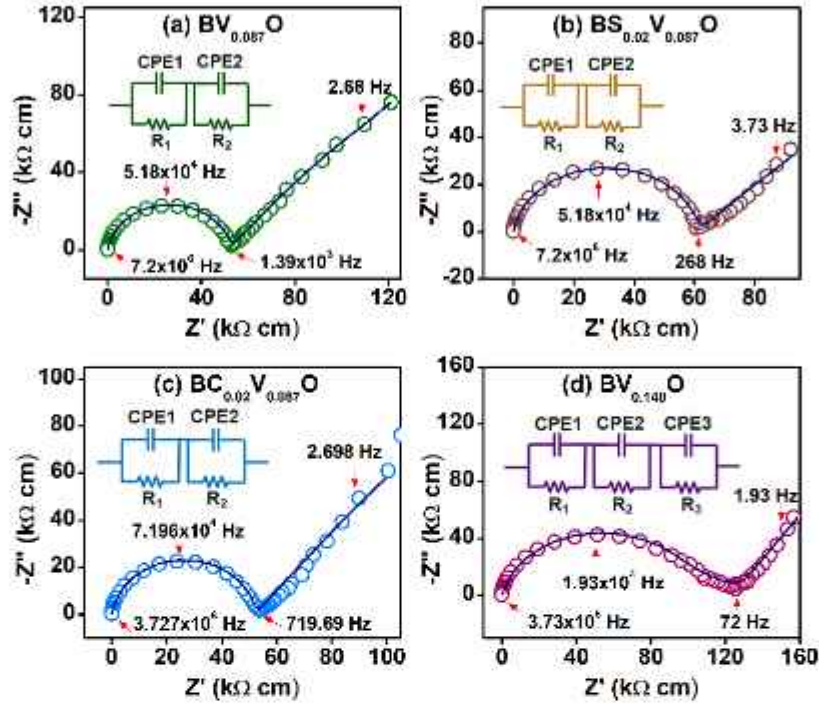


Figure 5.5: Nyquist plots of complex impedance data of as-sintered (a) $\text{BV}_{0.087}\text{O}$, (b) $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, (c) $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$, and (d) $\text{BV}_{0.148}\text{O}$ samples.

The representative complex impedance plots of $\text{BV}_{0.087}\text{O}$, $\text{BV}_{0.148}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ samples exhibited a single semicircle at high-frequency region, followed by a spike at low-frequency values. In order to deconvolute the underlying contributions, the impedance spectra were fitted with an equivalent circuit model, comprising a constant phase element (CPE) and resistance. For lower V-doped/Sr, Ca co-doped compositions, two $R||CPE$ elements were sufficient, representing the contributions from bulk (grain) and sample electrode interface. In contrast, the $\text{BV}_{0.148}\text{O}$ composition required three $R||CPE$ elements for a satisfactory fit, accounting for the bulk and grain boundary contribution associated with the semicircle, and charge build up at sample electrode interface responsible for the low frequency spike.

The presence of grain boundary resistance in BV_{0.148}O composition is further supported by its SEM microstructure, as shown in Figure 5.8. The bulk and the grain boundary conductivities were evaluated using, $\sigma_b = 1/R_b$ and $\sigma_{gb} = 1/R_{gb}$ respectively, while the total conductivity was calculated as $\sigma_t = 1/(R_b + R_{gb})$. The estimated conductivity values at 400 and 500 °C are listed in Table 5.7. The fitted values of R_b , R_{gb} , and the total conductivities at 200 °C are listed in Table 5.8.

Table 5.7: Conductivity values of the as-sintered compositions at 400 and 500 °C

Samples	$\sigma_{400^\circ\text{C}}$ (S/cm)	$\sigma_{500^\circ\text{C}}$ (S/cm)
BV _{0.084} O	2.87×10^{-2}	1.11×10^{-1}
BV _{0.087} O	3.05×10^{-2}	1.15×10^{-1}
BV _{0.090} O	3.17×10^{-2}	1.22×10^{-1}
BV _{0.100} O	3.45×10^{-3}	1.69×10^{-2}
BV _{0.148} O	2.69×10^{-3}	1.96×10^{-2}
BS _{0.02} V _{0.087} O	3.31×10^{-2}	1.06×10^{-1}
BC _{0.02} V _{0.087} O	3.04×10^{-2}	0.97×10^{-1}

Table 5.8: Simulated values of bulk and grain boundary resistance (R_b and R_{gb}) and capacitance (C_b and C_{gb}) values determined from the fitting of impedance data at 200 °C for as-sintered samples.

Samples	R_b (k Ω cm)	C_b (F cm ⁻¹)	R_{gb} (k Ω cm)	C_{gb} (F cm ⁻¹)
BV _{0.087} O	52.1	6.9×10^{-11}	—	—
BV _{0.148} O	96.2	8.4×10^{-11}	31.1	6.1×10^{-9}
BS _{0.02} V _{0.087} O	61.1	7.5×10^{-11}	—	—
BC _{0.02} V _{0.087} O	52.1	5.0×10^{-11}	—	—

The as-sintered compositions of BV_{0.087}O, BS_{0.02}V_{0.087}O and BC_{0.02}V_{0.087}O exhibited high ionic conductivity values of the order $\sim 10^{-3}$ S/cm at 300 °C, increasing to $\sim 10^{-2}$ S/cm at 400 °C and further to $\sim 10^{-1}$ S/cm at 500 °C. In comparison, BV_{0.084}O and BV_{0.090}O compositions showed only a marginal change, whereas a significant reduction was observed for BV_{0.100}O and BV_{0.148}O compositions. The highest V-doped BV_{0.148}O composition exhibited conductivity of $\sim 10^{-2}$ S/cm at 500 °C, nevertheless, this value still remains comparable to the conductivity reported for yttria-stabilized zirconia (Zr_{0.84}Y_{0.16}O_{1.92}) at 730 °C.[6], [40] The reduced conductivity in BV_{0.148}O is attributed to the growth of grain boundary

resistance (R_{gb}), which was negligible in other compositions, as shown by the impedance analysis in Figure 5.5(d) and corresponding fitting parameters in Table 5.8.

The temperature-dependent total ionic conductivity of as-sintered compositions from 150-500 °C is presented in Figure 5.6(a, b). Each data point in Figure 5.6 was extracted from the corresponding Nyquist plots.

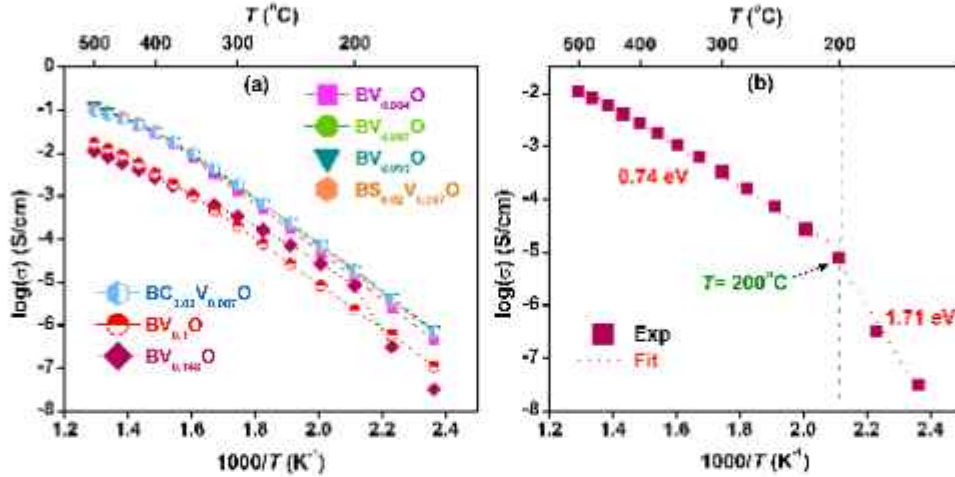


Figure 5.6: (a) Arrhenius plot of total conductivity (σ) of the as-sintered samples of BV_xO ($x = 0.087, 0.09, 0.100$, and 0.148), $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions and (b) Linear fitted $\text{BV}_{0.148}\text{O}$ sample

For all the low V-doped and Sr/Ca co-doped compositions, the conductivity curves displayed a gradual change in slope (or activation energy). In contrast, the $\text{BV}_{0.148}\text{O}$ composition showed a significant change in slope at around 180 °C, with the activation energy decreasing from 1.71 eV to 0.74 eV. This abrupt change in slope is likely due to an order-disorder transition. The presence of this transition is also observed from the differential scanning calorimetry (DSC) curve presented in section 5.3.1.4. However, the corresponding high-temperature XRD pattern of this composition remains unchanged, as shown in Figure 5.7, indicating an absence of any long-range structural phase transformation.

The conductivity values determined for $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions in the current results are slightly higher than those reported by Kuang *et al.*[29] for similar compositions, as well as those of the best-known co-doped Bi_2O_3 -based system of $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$. [26] Moreover, these

conductivity values at 500 °C also significantly exceed the value corresponding to the conventional SOFC electrolyte of yttria-stabilized zirconia (Zr_{0.84}Y_{0.16}O_{1.92}) at 730 °C.[6], [40]

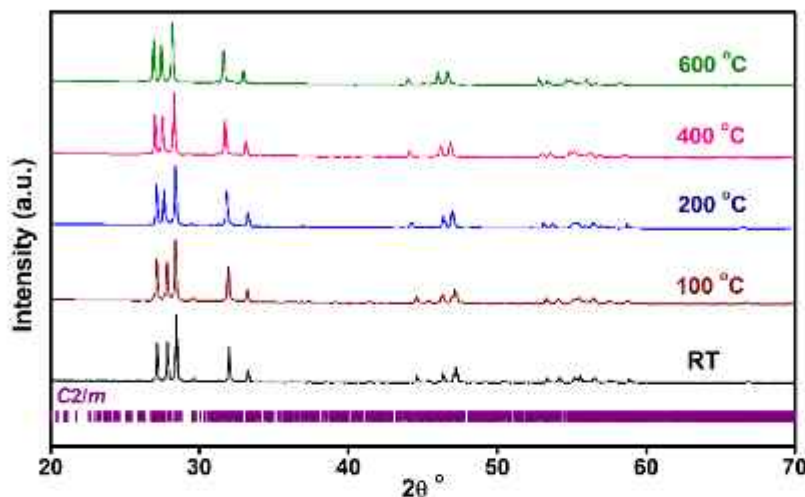


Figure 5.7: The high temperature XRD of BV_{0.148}O composition in the temperature range of RT-600 °C.

Previously, several mixed oxide systems in Bi₂O₃-M_xO_y (M= Ca, Sr, Ba, La, W, Y, Gd, Mo, Nb, V, etc.) have been widely reported as oxygen ion conductors.[1], [2], [8], [19], [41], [42], [43], [44], [45] In particular, Sr²⁺ doped Scheelite structured composition Bi_{0.9}Sr_{0.1}VO_{3.93}, which possesses a fluorite-related phase, has recently been identified as an oxygen ion conductor through electromotive force (EMF) measurement.[43] Furthermore, nuclear magnetic resonance and quasi-elastic neutron scattering studies on BV_xO ceramics have demonstrated that the dominant charge transport mechanism in such systems arises from diffusion of oxygen ions.[46], [47], [48] Thus, based on the prior literature reports, total conductivity in the present study is attributed to the conduction of oxygen ions. Accordingly, the BV_xO, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O compositions are inferred to be predominantly oxygen-ion conducting. In addition, as shown by Huggins,[49] the lower frequency spike observed in the impedance spectra of the compositions is further supportive of this interpretation.

5.3.1.3 Microstructural studies using SEM

The microstructure of the as-sintered compositions was investigated using scanning electron microscopy (SEM). Figure 5.8 presents representative SEM micrographs of the as-sintered $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BV}_{0.148}\text{O}$ samples.

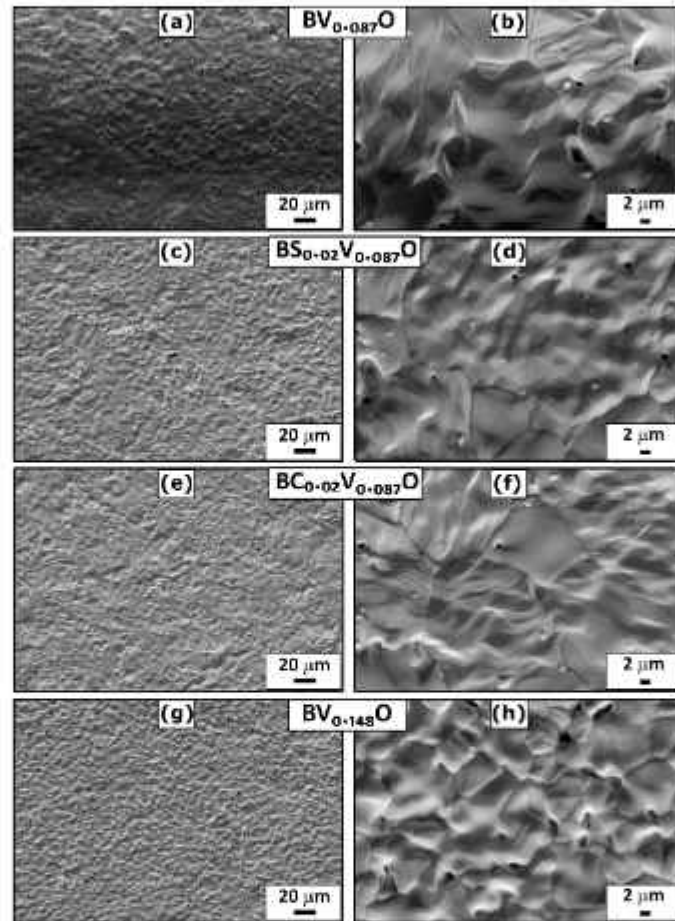


Figure 5.8: Microstructure of as-sintered (a, b) $\text{BV}_{0.087}\text{O}$, (c, d) $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, (e, f) $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$, and (g, h) $\text{BV}_{0.148}\text{O}$ samples. The left panels (a, c, e, g) show SEM micrographs with lower magnification, and the right panels (b, d, f, h) with higher magnification.

The SEM images of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions revealed large grains with an average size of $\sim 26\text{ }\mu\text{m}$, along with the presence of the melt-like phase within the grains. In these compositions, only a few isolated micropores and grain boundaries were observed, indicating a highly dense microstructure. Such microstructural features were consistent with the observation of negligible grain boundary resistance in $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$.

On the other hand, the $\text{BV}_{0.148}\text{O}$ composition exhibited a large number of grain boundaries, micropores, and a reduced average grain size ($\sim 8\text{ }\mu\text{m}$) in the microstructure. This noticeable grain boundary is also reflected by the requirement of an additional semicircle for fitting the Nyquist plot of $\text{BV}_{0.148}\text{O}$ (Figure 5.5(d)) and provided an explanation for the reduced oxide ion conductivity in the $\text{BV}_{0.148}\text{O}$ composition. The development of micropores and grain boundaries in $\text{BV}_{0.148}\text{O}$ could arise due to the anisotropic thermal shrinkage during the cooling following the sintering process. The present microstructure analysis thus indicated that 2 mole% of Sr/Ca and 8.7 mole% V substitutions for Bi are ideal for minimizing the grain boundary resistance contribution and achieving dense microstructure.

Additionally, the melt-like phase, observed in the SEM images of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ specimens, suggested the possible presence of a substantial amount of amorphous phase in the specimens. However, quantitative analysis of the XRD patterns of the $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ sample with the internal standard method (as shown in Figure 5.9) revealed that the amorphous phase content is limited to 8-9 % only. This result implied that the melt-like phase is confined to the surface of the sintered pellet of the specimen rather than its bulk.

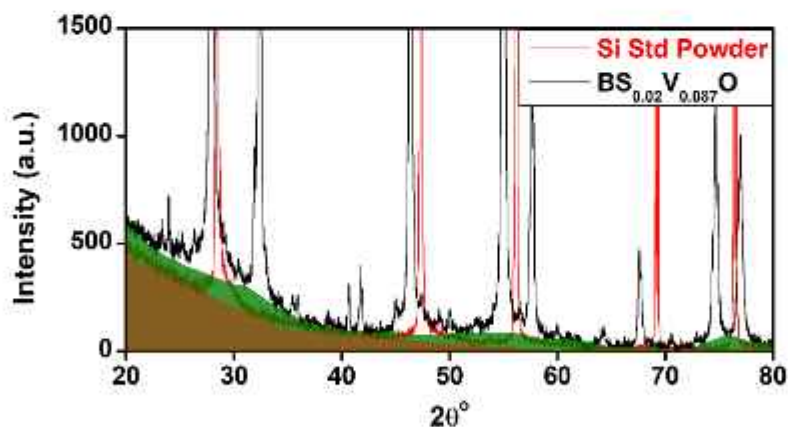


Figure 5.9: XRD pattern (zoomed around background) of $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and Si standard samples.

The EDX analysis was carried to determine the elemental compositions in the V and Sr/Ca co-doped compositions. A comparison of the EDX-determined and nominal compositions is presented in Table 5.9.

Table 5.9: EDX analyzed compositions

Nominal composition	EDX analyzed composition
Bi _{0.893} Sr _{0.02} V _{0.087} O _{1.577}	Bi _{0.82(9)} Sr _{0.02(1)} V _{0.08(1)} O _{1.64(9)}
Bi _{0.893} Ca _{0.02} V _{0.087} O _{1.577}	Bi _{0.86(9)} Ca _{0.02(1)} V _{0.07(1)} O _{1.63(9)}

5.3.1.4 Thermal analysis using DSC study

The thermal properties of the as-sintered compositions were investigated using differential scanning calorimetry (DSC). Figure 5.10 depicts the DSC thermograms recorded for BV_{0.087}O and BV_{0.148}O compositions during the heating and cooling cycle.

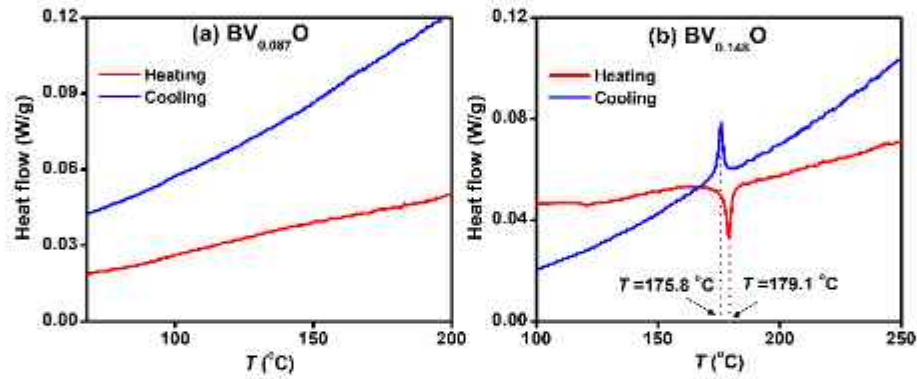


Figure 5.10: DSC thermogram of as-sintered (a) BV_{0.087}O and (b) BV_{0.148}O sample

The DSC thermogram of BV_{0.148}O composition exhibited a peak at $\sim 179.1^\circ\text{C}$ during the heating cycle and at $\sim 175.8^\circ\text{C}$ during the cooling cycle. These peaks were reversible, and the temperature at which they occurred roughly coincided with the temperature corresponding to the slope change observed in the Arrhenius plot for the same composition. In contrast, the other BV_xO and Sr/Ca co-doped compositions did not show any thermal transition within this temperature range.

5.3.2 Characterization of Aged V- and Ca/Sr co-doped compositions

In this section, the results for annealed (aged) compositions of BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O, and BV_{0.148}O are presented.

5.3.2.1 Phase identification and structure determination

Figures 5.11(a-d) display the comparison of XRD patterns of 400 °C/100 h and 600 °C/100 h annealed (aged) compositions of $\text{BV}_{0.087}\text{O}$, $\text{BV}_{0.148}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ with their as-sintered counterpart.

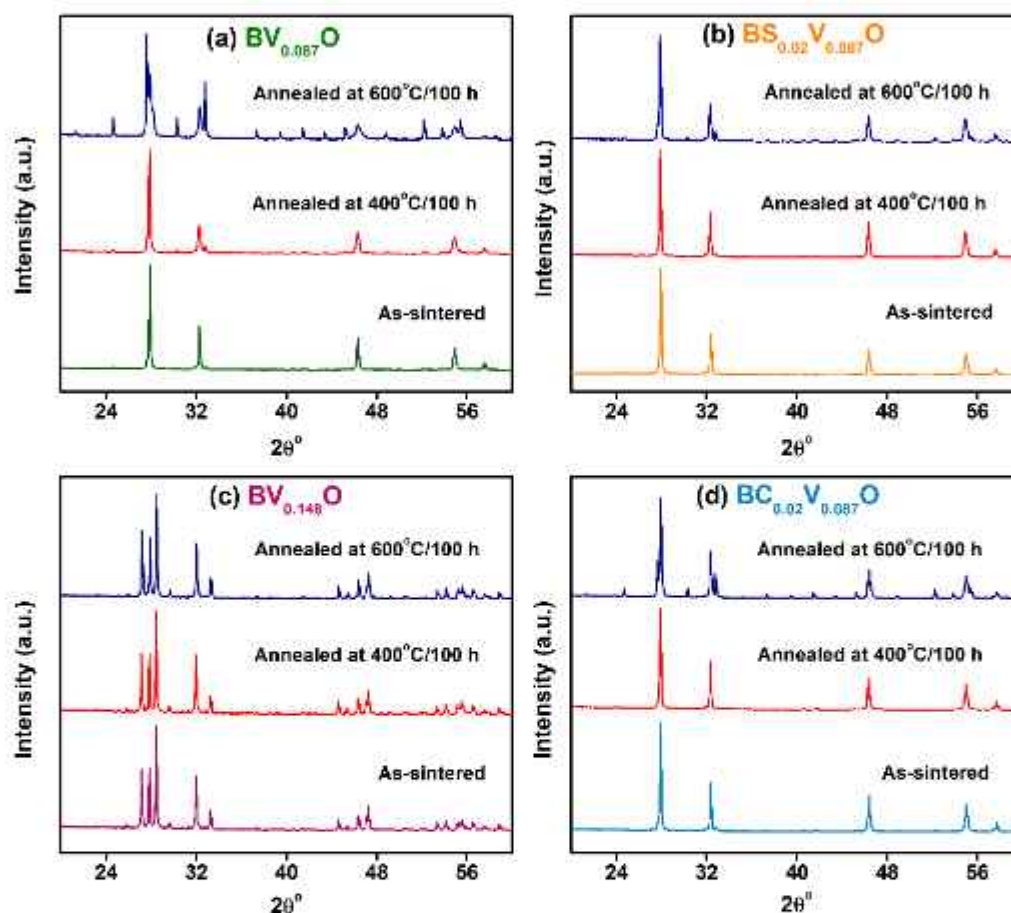


Figure 5.11: (a-d) XRD pattern of as-sintered and annealed samples of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, $\text{BV}_{0.148}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$, respectively

Figure 5.11(a-d) shows that all four 400 °C/100 h annealed compositions displayed XRD patterns similar to those of their as-sintered counterparts. In contrast, additional Bragg peaks were observed in $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions after annealing at 600 °C/100 h, indicating a structural transformation from the $R3m$ phase to a new phase(s). It was also noted that the conversion rate of the stabilized $R3m$ phase in $\text{BV}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions was significantly faster than that of the $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ sample. Conversely, the 600 °C/100 h annealed $\text{BV}_{0.148}\text{O}$ sample did not show any additional Bragg peaks,

confirming the preservation of the monoclinic $C2/m$ phase in this composition. In order to identify the additional phases formed in annealed $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions, Rietveld refinement of their XRD patterns was carried out. The refinement results of $\text{BV}_{0.087}\text{O}$ and $\text{BV}_{0.148}\text{O}$ samples are presented in Figures 5.12, while those of $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ are shown in Figure 5.13.

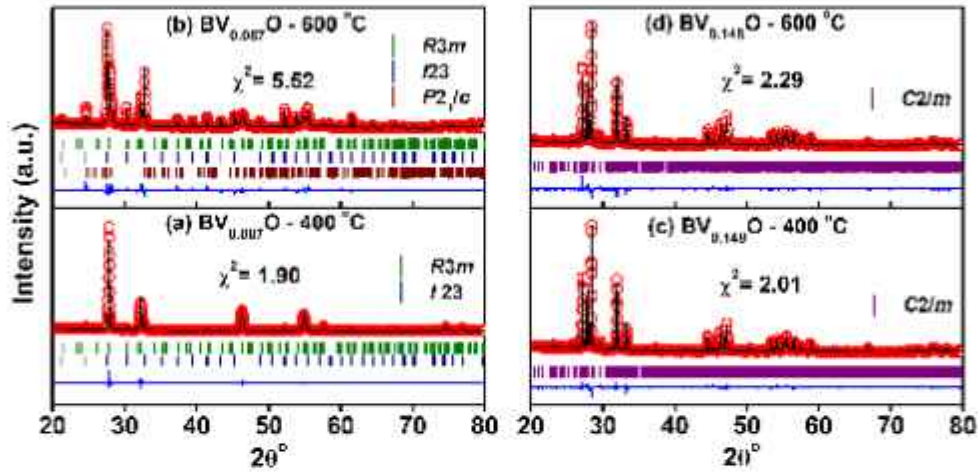


Figure 5.12: Room temperature XRD patterns with Rietveld refined fit of (a, c) 400 °C/100 h and (b, d) 600 °C/100 h annealed $\text{BV}_{0.087}\text{O}$ and $\text{BV}_{0.148}\text{O}$ compositions

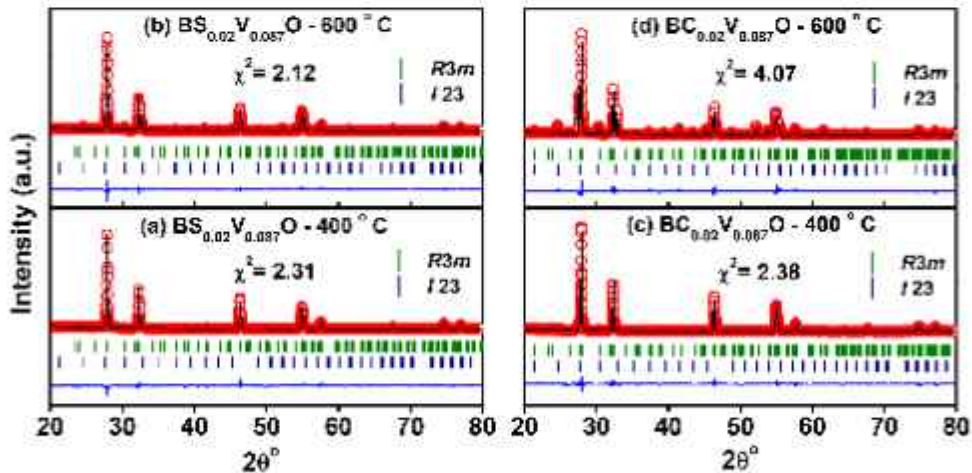


Figure 5.13: Room temperature XRD patterns with Rietveld refined fit of (a, c) 400 °C/100 h and (b, d) 600 °C/100 h annealed $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions

The refinement results were well fitted using the $R3m + I23$ structural model for both the 400 °C and 600 °C annealed $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ composi-

tions. In contrast, the 600 °C annealed BV_{0.087}O sample required an additional α -phase to achieve a satisfactory fit. From the Rietveld fitting, the additional Bragg peaks observed for BV_{0.087}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O compositions after annealing at 600 °C/100 h were attributed to the conversion of the *R3m* phase to the *I23* phase. The extent of phase conversion in 400 °C/100 h annealed samples was marginal; however, it increased significantly upon annealing at 600 °C/100 h, reaching 37% for BV_{0.087}O, 12% for BS_{0.02}V_{0.087}O, and 26% for BC_{0.02}V_{0.087}O. The corresponding phase fractions and lattice parameters are listed in Table 5.10.

Table 5.10: Rietveld refined lattice parameters and phase percentages of annealed (aged) compositions, determined from XRD data.

Samples	Lattice parameters			<i>R3m</i> : <i>I23</i> (%)
	<i>R3m</i>	<i>I23</i>	<i>P2₁/c</i>	
BV _{0.087} O 400 °C/100 h	$a - b = 11.757(2) \text{ \AA}$ $c = 28.864(1) \text{ \AA}$	$a - b - c$ $= 10.217(5) \text{ \AA}$	-	88.6:11.4
BV _{0.087} O 600 °C/100 h	$a - b = 11.731(4) \text{ \AA}$ $c = 28.914(8) \text{ \AA}$	$a - b - c$ $= 10.215(5) \text{ \AA}$	$a = 5.819(4) \text{ \AA}$ $b = 8.129(6) \text{ \AA}$ $c = 7.451(4) \text{ \AA}$ $\beta = 67.3^\circ$	60.8:37.4
BS _{0.02} V _{0.087} O 400 °C/100 h	$a - b = 11.746(7) \text{ \AA}$ $c = 28.842(7) \text{ \AA}$	$a - b - c$ $= 10.209(2) \text{ \AA}$	-	97.2:2.8
BS _{0.02} V _{0.087} O 600 °C/100 h	$a - b = 11.745(4) \text{ \AA}$ $c = 28.848(7) \text{ \AA}$	$a - b - c$ $= 10.213(4) \text{ \AA}$	-	88:12
BC _{0.02} V _{0.087} O 400 °C/100 h	$a - b = 11.728(8) \text{ \AA}$ $c = 28.836(8) \text{ \AA}$	$a - b - c$ $= 10.193(8) \text{ \AA}$	-	90.9:9.1
BC _{0.02} V _{0.087} O 600 °C/100 h	$a - b = 11.724(9) \text{ \AA}$ $c = 28.854(1) \text{ \AA}$	$a - b - c$ $= 10.212(7) \text{ \AA}$	-	73.9:26.1

Therefore, the present refinement results suggested that Sr and V co-doping suppresses the phase conversion from *R3m* to *I23* phase. In addition, comparatively faster phase conversion, noted in BC_{0.02}V_{0.087}O, is consistent with an earlier report on a 2 mole% CaO-doped 78% Bi₂O₃-20% Er₂O₃ system.[50]

5.3.2.2 Electrical conductivity of the aged compositions

Figure 5.14(a-d) shows the complex impedance plane (Nyquist) plot of 400 °C annealed BV_{0.087}O, BV_{0.148}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O compositions recorded at 200 °C.

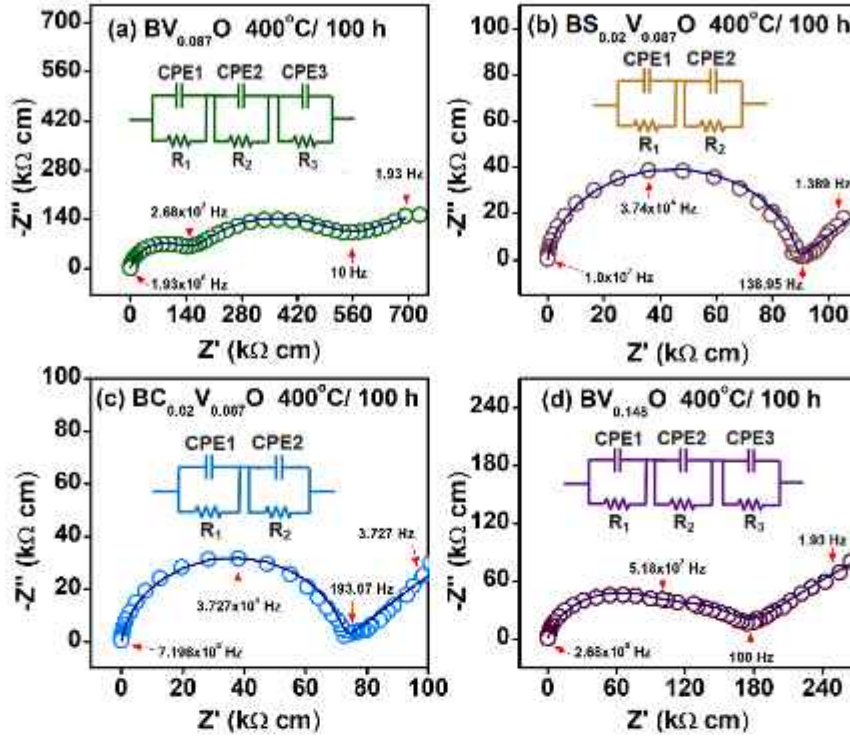


Figure 5.14: Nyquist plots of complex impedance data at $T = 200\text{ }^{\circ}\text{C}$ for $\text{BV}_{0.087}\text{O}$ (a), $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ (b), $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ (c), and $\text{BV}_{0.148}\text{O}$ (d) samples annealed at $400\text{ }^{\circ}\text{C}/100\text{ h}$.

The complex impedance plots of $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions, annealed at $400\text{ }^{\circ}\text{C}/100\text{ h}$, exhibited a single semicircle followed by a low-frequency spike. This semicircular region in these plots was fitted satisfactorily using a single $R||C$ element corresponding to the grain (bulk) resistance. However, in purely V-doped compositions of $\text{BV}_{0.087}\text{O}$ and $\text{BV}_{0.148}\text{O}$, an additional $R||C$ element was required to achieve a satisfactory fit, after $400\text{ }^{\circ}\text{C}/100\text{ h}$ annealing. This additional $R||C$ element was attributed to the growth of grain boundary resistance induced by the annealing treatment. On the other hand, the high frequency (semicircular) region in $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions was adequately fitted using single $R||C$ element, even after annealing at $600\text{ }^{\circ}\text{C}/100\text{ h}$, as shown in Figure 5.15 (a, b). The suitability of a single $R||C$ element in these compositions confirmed the dominance of bulk conduction even after prolonged annealing. This indicated that Sr/Ca co-doping could effectively suppress the conductivity degradation arising from increased grain-boundary resistance compared to purely V-doped compositions.

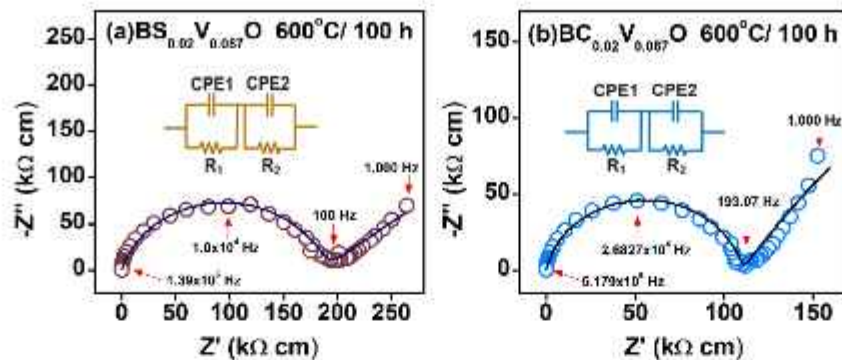


Figure 5.15: (a-b) Nyquist plots of complex impedance data at $T = 200\text{ }^{\circ}\text{C}$ of $600\text{ }^{\circ}\text{C}/100\text{ h}$ annealed $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ samples

The fitted values corresponding to the R_b , R_{gb} , and experimentally determined total conductivities at $400\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$ are listed in Table 5.11–5.12, respectively.

Table 5.11: Simulated values of bulk and grain boundary resistance (R_b and R_{gb}) and capacitance (C_b and C_{gb}) values determined from the fitting of impedance data at $200\text{ }^{\circ}\text{C}$ for annealed samples.

Samples	R_b ($\text{k}\Omega\text{ cm}$)	C_b (F cm^{-1})	R_{gb} ($\text{k}\Omega\text{ cm}$)	C_{gb} (F cm^{-1})
$\text{BV}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	140.0	7.5×10^{-11}	408.0	3.2×10^{-9}
$\text{BV}_{0.148}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	96.2	8.2×10^{-11}	73.1	1.9×10^{-9}
$\text{BS}_{0.02}\text{V}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	68.6	6.1×10^{-11}	–	–
$\text{BC}_{0.02}\text{V}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	61.9	5.6×10^{-11}	–	–
$\text{BS}_{0.02}\text{V}_{0.087}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	186.6	7.8×10^{-11}	–	–
$\text{BC}_{0.02}\text{V}_{0.087}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	110.0	5.9×10^{-11}	–	–

Table 5.12: Conductivity values of the annealed compositions at 400 and $500\text{ }^{\circ}\text{C}$

Samples	$\sigma_{400\text{ }^{\circ}\text{C}}$ (S/cm)	$\sigma_{500\text{ }^{\circ}\text{C}}$ (S/cm)
$\text{BV}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	5.88×10^{-3}	3.04×10^{-2}
$\text{BV}_{0.087}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	2.01×10^{-3}	1.26×10^{-2}
$\text{BS}_{0.02}\text{V}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	2.50×10^{-2}	1.09×10^{-1}
$\text{BS}_{0.02}\text{V}_{0.087}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	9.98×10^{-3}	5.60×10^{-2}
$\text{BC}_{0.02}\text{V}_{0.087}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	2.24×10^{-2}	0.89×10^{-2}
$\text{BC}_{0.02}\text{V}_{0.087}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	1.57×10^{-2}	6.78×10^{-2}
$\text{BV}_{0.148}\text{O } 400\text{ }^{\circ}\text{C}/100\text{ h}$	2.39×10^{-3}	1.02×10^{-2}
$\text{BV}_{0.148}\text{O } 600\text{ }^{\circ}\text{C}/100\text{ h}$	2.42×10^{-3}	1.04×10^{-2}

For further clarity, the temperature-dependent conductivity of as-sintered, $400\text{ }^{\circ}\text{C}/100\text{ h}$, and $600\text{ }^{\circ}\text{C}/100\text{ h}$ annealed (aged) compositions of $\text{BV}_{0.087}\text{O}$,

BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O and BV_{0.148}O are compared in Figure 5.16 (a-d).

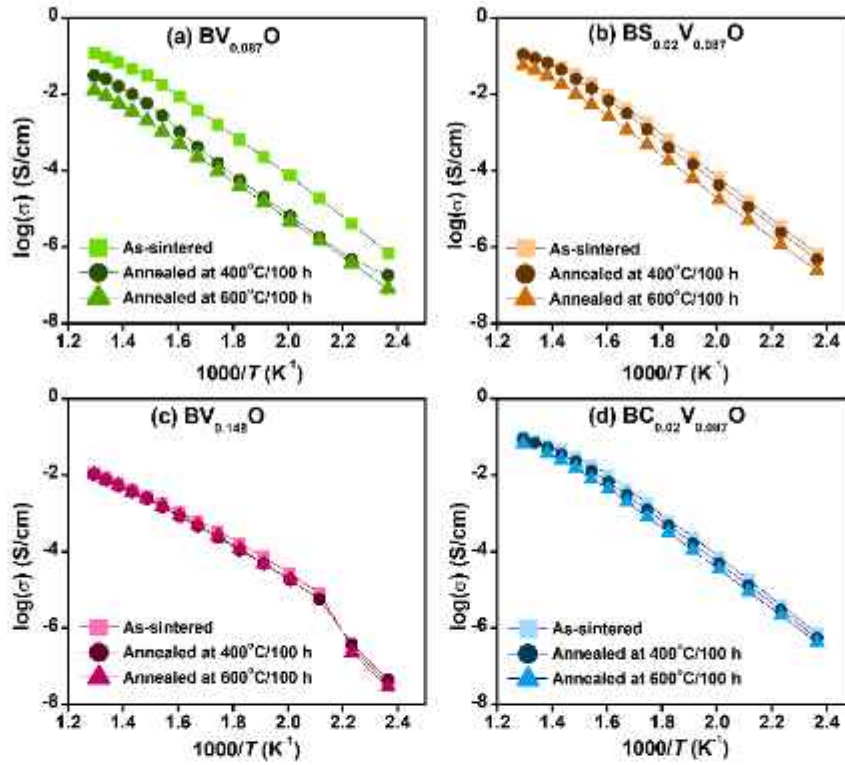


Figure 5.16: (a-d) Comparison of total conductivity of as-sintered and annealed samples of BV_{0.087}O, BS_{0.02}V_{0.087}O, BV_{0.148}O, and BC_{0.02}V_{0.087}O, respectively.

As shown in Figure 5.16, the conductivity of the BV_{0.087}O sample shows noticeable reduction upon annealing at 400 °C/100 h and 600 °C/100 h relative to its conductivity at the as-sintered condition. In contrast, only a marginal decrease was observed for BS_{0.02}V_{0.087}O (Figure 5.16 b), BV_{0.148}O (Figure 5.16 c), and BC_{0.02}V_{0.087}O (Figure 5.16 d) compositions upon annealing under similar conditions. Although the XRD pattern of as-sintered and 400 °C/100 h annealed BV_{0.087}O composition (Figure 5.11 (a)) did not reveal any noticeable structural difference, a significant conductivity reduction was evident. This behavior was previously reported in other doped-Bi₂O₃ systems and was commonly described as an aging phenomenon.[10], [51], [52] Unlike conventional crystallographic phase transformation, this phenomenon is associated with ordering of the oxygen sublattice and is accompanied by degradation in conductivity.[10], [51], [52] In the present study, the conductivity degradation related to the aging phenomenon was strongly

suppressed in BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O, and BV_{0.148}O compositions. This suppression is possibly governed by the Bi content and the ionic radius ratio (r_{cat}/r_{ani}) of these compositions. Moreover, Rietveld refinement of the XRD patterns of 600 °C/100 h annealed BV_{0.087}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O samples indicated a partial conversion of the *R3m* phase to the *I23* phase. However, this conversion is not expected to adversely affect the conduction property, as both γ -Bi₂O₃ and V-doped γ -Bi₂O₃ are intrinsically oxide ion-conducting phases.[4], [42] In addition, as shown in Figure 5.14 and Table 5.11, a distinct grain boundary contribution has emerged in 400 °C/100 h annealed BV_{0.087}O sample, whereas no such contribution was observed in similarly annealed BS_{0.02}V_{0.087}O and BC_{0.02}V_{0.087}O compositions. Therefore, the emergence of this additional grain boundary resistance also contributed to the overall reduction in total conductivity of the annealed BV_{0.087}O samples.

5.3.2.3 Phase analysis of BS_{0.02}V_{0.087}O composition using Neutron powder diffraction (NPD)

Neutron powder diffraction (NPD) was employed in addition to X-ray diffraction to accurately determine the crystal structure and constituent phase fractions, owing to its higher sensitivity to light atoms and lattice disorders. In the present study, variable temperature NPD measurements were carried out on the as-sintered BS_{0.02}V_{0.087}O composition over the temperature range of 40-600 °C. This composition was specifically chosen to evaluate its phase stability across the investigated temperature range. Figure 5.17 (a) displays the Rietveld analyzed NPD pattern of BS_{0.02}V_{0.087}O as-sintered composition at $T = 40$ °C, while Figure 5.17 (b) presents the corresponding Rietveld fits analyzed over the temperature range of 40-600 °C.

Consistent with the XRD Rietveld fitting of the same composition, the NPD pattern of BS_{0.02}V_{0.087}O composition at 40 °C was also refined using *R3m* + *I23* structural model, as shown in Figure 5.17 (a).

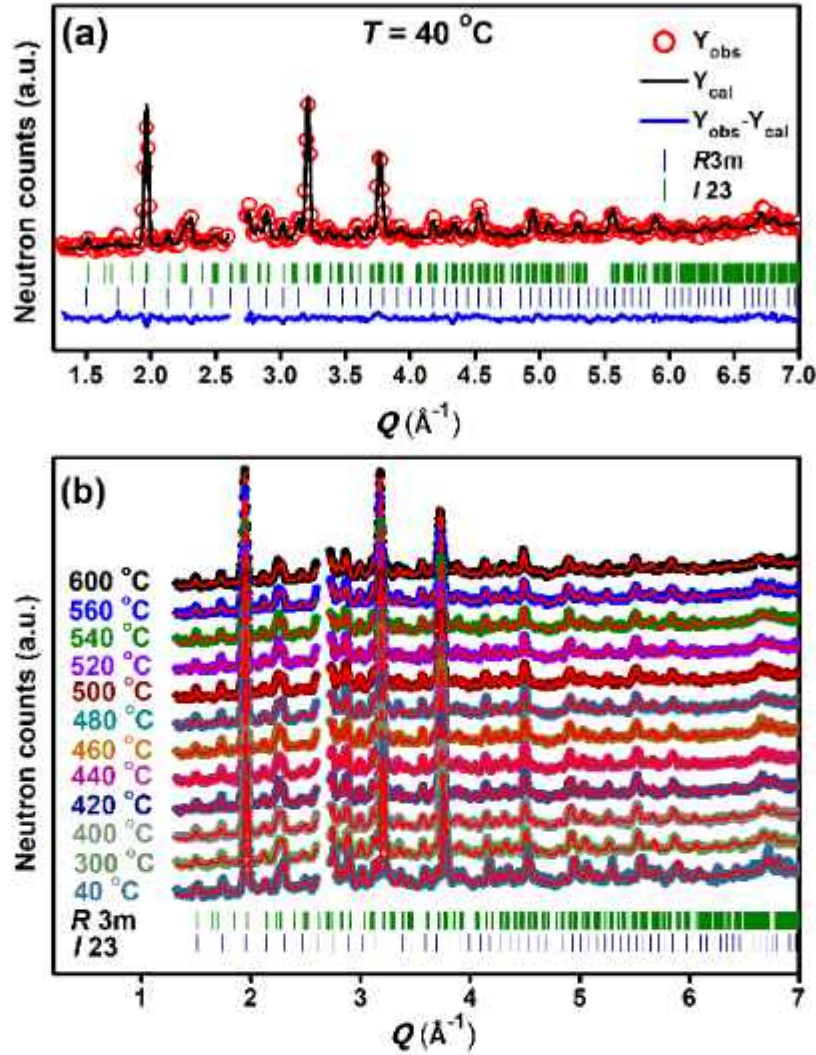


Figure 5.17: (a) The neutron powder diffraction pattern recorded for the as-sintered BS_{0.02}V_{0.087}O sample at 40 °C and (b) Neutron powder diffraction patterns and Rietveld fit in the temperature range of 40-600 °C.

During the refinement, the positions and occupancies of the V site were kept fixed to the values determined from XRD analysis, due to its smaller coherent scattering cross section for thermal neutrons. To ensure reliable fitting, the Q range of 2.9-2.95 Å⁻¹ was excluded from the analysis to avoid the contribution from the sample environment detected during the experiment.

The Rietveld refinement yielded the phase fractions of 0.72 and 0.28 for the $R3m$ and $I23$ phases, respectively, with the $R3m$ phase refining to a composition of Bi_{0.893}Sr_{0.0195}V_{0.062}O_{1.55}. This refined composition matched well with the composition obtained from EDX-analysis (as shown in Table 5.9). Furthermore, the

same structural model was employed to refine the temperature-dependent NPD patterns. As shown in Figure 5.17 (b), all the high-temperature NPD patterns were well fitted by using the same space groups and the same $R3m:I23$ ratio as determined for 40 °C data. This indicated the absence of structural phase transition in BS_{0.02}V_{0.087}O composition up to 600 °C, at least over the total experimental period (~ 4 days). These results, together with the XRD observations for the annealed samples, confirmed the phase stability of the BS_{0.02}V_{0.087}O composition under long-term thermal exposure and associated aging effect. The Rietveld refined lattice parameters, atomic parameters, occupancy parameters, and atomic displacement factors for $R3m$ and $I23$ phases of NPD data are presented in Table 5.13 and Table 5.14, respectively.

Table 5.13: Rietveld refined crystallographic data of rhombohedral $R3m$ phase, determined from NPD data of BS_{0.02}V_{0.087}O at 40 °C

Atom	Wyckoff position	x	y	z	Occupancy	U_{iso} (Å ²)
O1	3a	0	0	0.720(7)	0.166(6)	1.17(7)
O2	3a	0	0	0.041(7)	0.166(6)	0.08(9)
O3	3a	0	0	0.096(1)	0.166(6)	0.97(9)
O4	9b	0.529(3)	0.470(6)	0.169(7)	0.5	1.50(5)
O5	9b	0.443	0.557	0.311(9)	0.5	1.81(2)
O6	9b	0.520(9)	0.479	0.110(2)	0.5	1.37(9)
O7	9b	0.772(5)	0.227(5)	0.316(7)	0.5	1.64(1)
O8	9b	0.546(3)	0.453(7)	0.515(2)	0.5	1.50(5)
O9	9b	0.113(5)	0.886(5)	0.298(1)	0.5	0.01(2)
O10	9b	0.259(3)	0.740(7)	0.017(3)	0.5	1.38(2)
O11	9b	0.753(7)	0.246(3)	0.117(1)	0.5	1.19(3)
O12	9b	0.232(4)	0.767(6)	0.166(9)	0.5	1.85(1)
O13	18c	0.337(5)	-0.006(4)	0.057(4)	1.0	1.47(1)
O14	18c	0.038(4)	0.368(4)	0.226(1)	1.0	1.62(4)
O15	3a	0	0	0.418	0.166(6)	0.39(7)
Bi1	3a	0	0	0.175(5)	0.166(6)	0.06(7)

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
V2	3a	0	0	0	0.038(3)	0.84(6)
Bi2	3a	0	0	0	0.038(3)	0.84(6)
Sr2	3a	0	0	0	0.090(2)	0.84(6)
V3	3a	0	0	0.303(9)	0.083(4)	0.99(1)
Bi3	3a	0	0	0.303(9)	0.083(4)	0.99(1)
Bi4	9b	0.553(2)	0.446(8)	0.424(5)	0.5	0.47(7)
Bi5	9b	0.107(3)	0.892(7)	0.199(9)	0.5	0.15(9)
Bi6	9b	0.557(2)	0.442(8)	0.088(8)	0.5	0.61(2)
Bi7	9b	0.439(8)	0.560(2)	0.202(1)	0.5	0.43(7)
Bi8	9b	0.774(1)	0.225(9)	0.198(1)	0.5	1.33(5)
Bi9	9b	0.220(8)	0.779(1)	0.099(1)	0.5	0.63(2)
Bi10	18c	0.326(9)	0.011(1)	0.317(4)	1.0	1.34(9)

Table 5.14: Rietveld refined crystallographic data of cubic $I23$ phase, determined from NPD data of BS_{0.02}V_{0.087}O at 40 °C

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Bi1	24f	0.179(6)	0.323(4)	0.022(3)	1.0	1.70(3)
Bi2	2a	0	0	0	0.076(1)	0.44(4)
O1	24f	0.136(6)	0.253(8)	0.490(8)	1.0	1.76(5)
O2	8c	0.199(8)	0.199(8)	0.199(8)	0.333(3)	0.92(3)
O3	8c	0.891(3)	0.891(3)	0.891(3)	0.333(3)	1.72(2)
V2	2a	0	0	0	0.007(3)	0.32(1)
Sr2	2a	0	0	0	0.001(7)	0.32(8)

The unit cell volume of the $R3m$ phase was also obtained from the refinement across the measured temperature range, and its variation with temperature is shown in Figure 5.18. The unit cell volume of the rhombohedral $R3m$ phase was observed to vary almost linearly with temperature, without any anomalies. This behavior further supports the absence of a structural phase transition during the high-temperature NPD measurement of BS_{0.02}V_{0.087}O composition. The NPD refined crystal structure for the $R3m$ phase is presented in Figure 5.19.

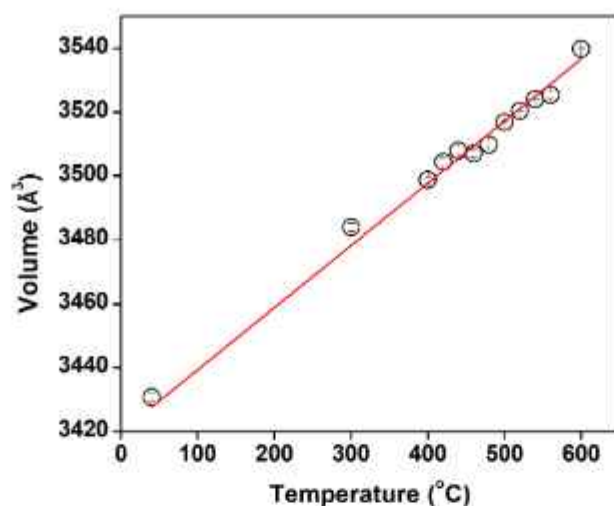


Figure 5.18: The temperature dependence of unit cell volume of the rhombohedral $R3m$ phase. The line passing through the data points are guide to the eyes

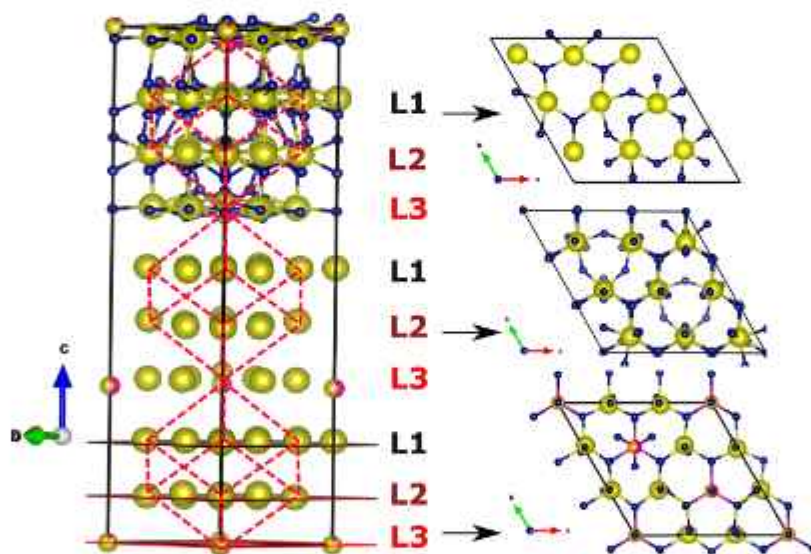


Figure 5.19: The final Rietveld refined crystal structure of the rhombohedral phase (in a hexagonal setting) in $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$.

As evident from the structural model of the rhombohedral $R3m$ phase (Table 5.13), the cation sites (Bi, Sr, and V- ions) occupy multiple Wyckoff positions. The crystal structure illustrated in the figure highlights the cationic planes of the $R3m$ phase, with yellow, blue, red, and pink spheres representing bismuth, oxygen, strontium, and vanadium ions, respectively. In order to maintain clarity, the oxygen ion positions are displayed only in the top slab of the rhombohedral unit

cell.

The rhombohedral structure of the $R3m$ phase was composed of a stacking of three distinct cationic layers, denoted as L1, L2, and L3 along the c-axis, as depicted in Figure 5.19. The L1 and L2 layers were found to be occupied purely by Bi ions, whereas Sr and V ions were confined to the L3 layers. In the L3 plane, the z-positions of Sr ($z=0.666(8)$) and V ($z=0.637(2)$) ions deviated from that of the Bi-ion layer ($z=0.650(7)$), leading to the formation of a quasi-two-dimensional (2D) layer. In addition, the smaller ionic radius of V compared to Bi led to smaller V-O bond distances, and consequently larger O-O separations in the L3 plane. In contrast, L1 and L2 layers, being composed exclusively of Bi-ions, remained structurally unaltered. Therefore, although V and Sr/Ca co-doping stabilized the high conducting $R3m$ phase, it may have hindered long-range oxygen ion transport, specifically in the substituted planes, thereby constraining the overall conductivity to approximately an order of magnitude lower than that of the δ -phase. The substitution of V ion, particularly in the L3 plane, was also earlier reported by Kashida et al.[36]

The structural relationship between the $R3m$ and the δ -phase ($Fm\bar{3}m$) unit cell was interpreted by comparing the orientation of their cationic layers, as illustrated by the red dotted unit cell in Figure 5.19. The cationic layers of the rhombohedral unit cell exhibited a repetitive sequence of L1, L2, L3/L1, L2, L3/L1, L2, L3/L1, which closely resembled the layer sequence of the cubic phase when its cationic layers were oriented along the (111) direction. Consequently, the $R3m$ phase can be regarded as a fluorite-type superstructure comprising $3\times 3\times 3$ subcells. A comparable structural relationship was also observed between cubic γ -Bi₂O₃ ($I23$) and cubic δ -Bi₂O₃ ($Fm\bar{3}m$). The γ -Bi₂O₃ phase contained multiple crystallographic sites for Bi³⁺ (24f and 2a) and O²⁻ (24f, 8c, and 8c), with the 8c site being partially occupied, analogous to the partial occupancy of O²⁻ at the 8c and 32f sites in cubic δ -phase. Thus, partial average occupancy of oxygen sites appeared to be the common structural feature connecting the δ -Bi₂O₃, $R3m$ and cubic γ -Bi₂O₃

(*I23*) phases and facilitating easier hopping of O^{2-} ions between the occupied and neighboring vacant sites.

5.3.2.4 Soft bond valence sum (BVS) analysis of NPD for determining the conduction pathways

Soft bond valence analysis (BVS) is employed as an efficient technique to identify the accessible sites for mobile ions by evaluating the bond valence mismatch ($\Delta\nu$) of the moving ions. The most probable paths are considered to be those connecting the accessible sites along which the valence mismatch remains sufficiently low. Accordingly, the iso surfaces of constant $|\Delta\nu|$ for a given mobile ion may be interpreted as a region accessible to that mobile ion within a certain activation energy.[53], [54] Thus, this approach can help to elucidate ion conduction pathways and has been successfully applied earlier to a variety of ion-conducting systems.[55], [56] In the present study, the soft bond valence sum analysis was performed on refined neutron diffraction data of $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ composition and analyzed using the Bond_STR program available in the Fullprof suite. The RT oxide ion conducting pathways determined using the crystal structural parameters of *R3m* phase of the $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ sample are illustrated in Figure 5.20.

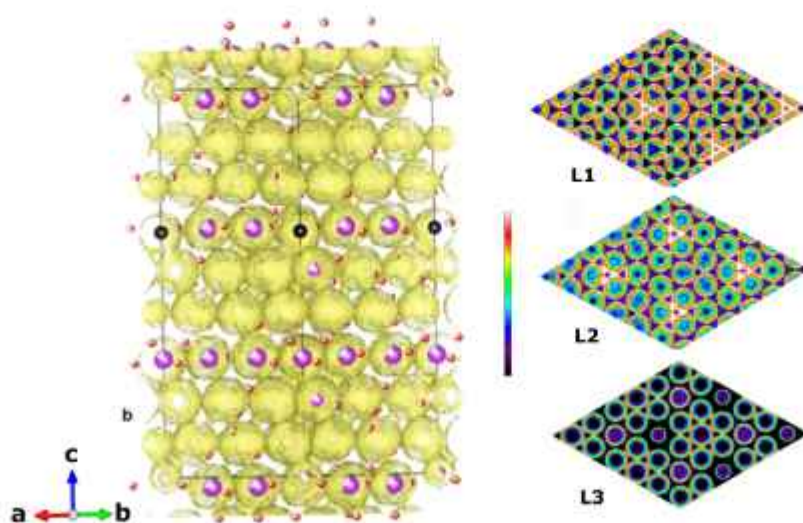


Figure 5.20: (Left) Effective oxygen ion conduction pathways, calculated from the soft-BVS analysis and (Right) the iso-surface BVS maps for individual L1, L2, and L3 layers for the rhombohedral phase

In the figure, the left panel shows the effective oxygen ion conduction pathways (isosurface) as calculated from the BVS, while the right panel focuses on the isosurface maps of the individual layers of the $R3m$ phase (L1, L2, L3 layers). The color bar represents the depth profile of the conduction pathways.

From the analysis, the available volume for oxygen ion conduction within the $R3m$ phase unit cell is determined to be $\sim 19.9\%$. The area of the isosurface (conduction pathway) for the L3 layer is significantly smaller than that for the L1 and L2 layers. This observation indicates that the incorporation of Sr and V atoms as dopants has disrupted the conduction pathways, leading to a reduced ionic conduction in the L3 layer. As a consequence, the diminished oxygen ion conductivity of V- substituted Bi₂O₃ relative to its δ -phase can be attributed to the disruption of conduction in L3 layers.

As the γ -Bi₂O₃ was identified as a secondary phase in the refinements of the prepared compositions, its BVS was also evaluated. Figure 5.21 presents the $I23$ crystal structure and its effective conduction pathways (iso-surface maps), including those of the (100) plane.

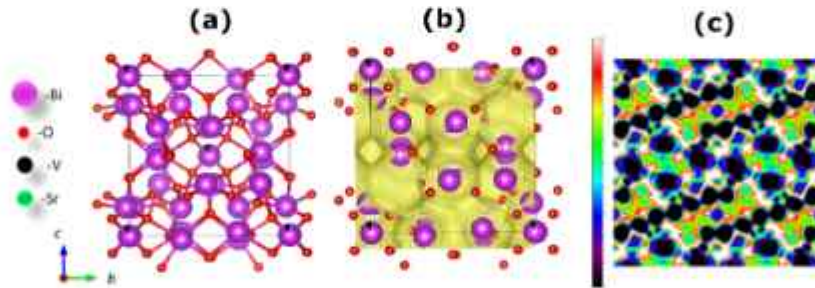


Figure 5.21: (a) Crystal structure of the $I23$ phase. (b) Effective oxygen ion conduction pathways calculated from the BVS analysis for $\Delta\nu = 0.3$ (as considered for $R3m$ phase). (c) The isosurface BVS maps for the (100) plane for the present compound.

As observed from the figure, the isosurfaces surrounding the BiO_n polyhedra in $I23$ phase are connected in all directions. This three-dimensional connectivity indicates that the oxygen ions can undergo long-range transport along all three crystallographic directions, which is a signature of a high ionic conductivity in the cubic $I23$ phase.[3], [4] In addition, the available volume for oxygen ion conduction

within the cubic $I23$ unit cell is estimated ~ 16.5 %. Accordingly, the present analysis reveals that significant amounts of volumes are available for the oxygen ionic conduction within the unit cells of both $R3m$ and $I23$ phases.

5.3.3 Local structural investigation using EXAFS and XANES

To understand the role of local structure in transport properties of synthesized compositions, Bi L₃-edge EXAFS measurements were performed in the temperature range of RT-500 °C. The superimposed plots of RT k^2 -weighted Bi L₃-edge EXAFS data ($k^2\chi(k)$) for as-sintered BV_{*x*}O ($x=0.084$ -0.100) and BV_{0.087}O, BV_{0.148}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O compositions are presented in Figure 5.22(a, c). The corresponding magnitudes of the Fourier transforms of ($k^2\chi(k)$) signal ($|\chi(R)|$) are also displayed alongside in Figure 5.22(b, d) for comparison.

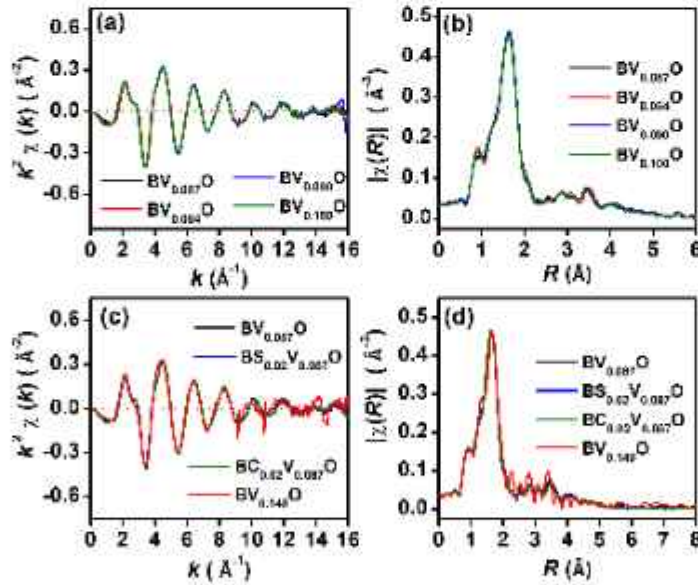


Figure 5.22: (a, c) $k^2\chi(k)$ versus k from the RT Bi L₃-edge of as-sintered samples of low V doping ($x=0.084, 0.087, 0.09, 0.100$) and BV_{0.087}O, BV_{0.148}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O. (b, d) The magnitude of the Fourier transform (FT) of the data in (a, c), $|\chi(R)|$.

The experimental $k^2\chi(k)$ and $|\chi(R)|$ plots of BV_{*x*}O compositions containing 8.4-10.0 mole % V₂O₅, together with those of BV_{0.087}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O (all with 8.7 mole % of V₂O₅) compositions, exhibited nearly iden-

tical spectra. The BV_{0.148}O composition with the highest V₂O₅ mole% showed a slight deviation in $k^2\chi(k)$ and $|\chi(R)|$ signals at higher k and R values. This suggested that the local Bi-O environment in the as-sintered BV_{0.148}O differed from the low V-doped compositions. Furthermore, to examine the influence of annealing conditions on the local Bi-O environment, $|\chi(R)|$ plots of as-sintered and annealed BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O and BV_{0.148}O compositions are compared in Figure 5.23.

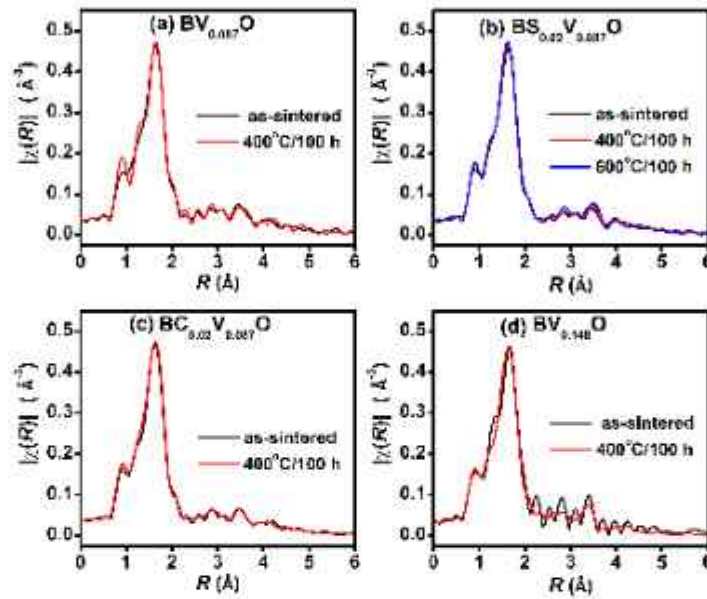


Figure 5.23: (a-d): Plot of $|\chi(R)|$ vs. R (Å) for BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O and BV_{0.148}O as-sintered and annealed samples

Consistent with their as-sintered counterparts, the annealed compositions of BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O and BV_{0.148}O also did not exhibit any significant variation in their local structure. This behavior implies that either the applied annealing condition did not alter the local structure surrounding the Bi³⁺ ion, or that the changed structure was not reflected in the current EXAFS measurement. In addition, no prominent correlation peaks beyond the first Bi-O coordination shell were observed, indicating that contributions from a possible second Bi-O shell or first Bi-Bi shell could not be detected. This suggests that Bi³⁺ ions possessed a heavily disordered local environment beyond the first Bi-O shell, as EXAFS in a well-ordered crystalline system is typically sensitive to local

correlations extending up to $\sim 4 \text{ \AA}$ from the absorbing atom.

Similar behavior has been previously reported for δ -Bi₂O₃ phase stabilized in (90%)Bi₂O₃-(10%)Ta₂O₅ system.[57] In several other EXAFS studies on Bi₂O₃-M₂O₃ (M=Y, Er, Yb) systems, characteristics of disordered local structure were also observed; however, correlations corresponding to the second Bi-O shell and first Bi-Bi/M were still detectable.[58] In comparison with these reported systems, the present system was inferred to exhibit a substantially higher degree of local structural disorder. Moreover, comparison of the EXAFS spectra of the highest V-doped compositions, BV_{0.148}O (monoclinic $C2/m$), with a similar phase reported by Saito *et al.*[57] i.e., α -Bi₂O₃ (monoclinic $P2_1/c$), suggested this sample also possessed a high degree of local disorder. Despite the significant local disorder, the XRD/NPD results on both the as-sintered and annealed compositions did not show any indication of a glass-like phase. Instead, the samples were found to crystallize in the $R3m + I23$ phase.

In order to probe the extent of local disorder and verify the presence of any structural contribution beyond the first Bi-O correlation, the back-transformed EXAFS signal ($\chi(q)$) obtained from two R ranges, 1-2.3 $\text{\AA}$ and 2.3-5 $\text{\AA}$, were compared with the experimental EXAFS data ($\chi(k)$) as shown in Figure 5.24.

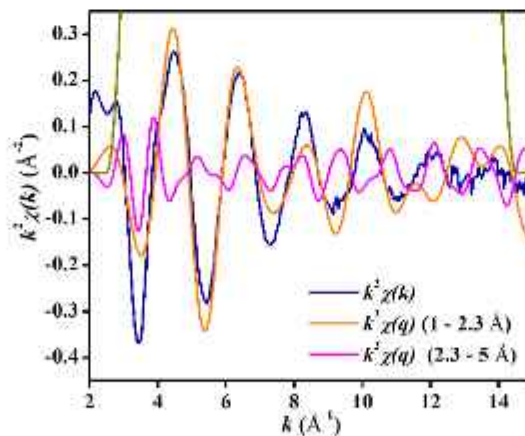


Figure 5.24: Experimental $k^2\chi(k)$ vs. k (blue line) plotted with back FT $k^2\chi(q)$ in 1-2.3 $\text{\AA}$ (orange line) and 2.3-5 $\text{\AA}$ (magenta line) for the BV_{0.087}O sintered sample.

In this comparison, $\chi(q)$ in R range of 1-2.3 $\text{\AA}$ (orange line) was obtained by fit-

ting the first shell contribution and subsequently back transforming it to q space. This $\chi(q)$ signal was then subtracted from the raw experimental data (blue line). Following the subtraction, a weak residual signal (magenta line) was observed, indicating the presence of a weak contribution in the R range of 2.3-5 Å. The structural models of both $R3m$ and $I23$ phases contained several Bi-O and Bi-Bi scattering correlations that contribute within this R -range. Therefore, as an initial step to obtain the average bond distance (R_j), the mean square disorder (MSD) in the bond distance (σ^2), and the average coordination number (N_j), the first correlation peak in the $|\chi(R)|$ spectra were fitted using first shell fitting approach. The results of this fitting for the as-sintered compositions are presented in Figure 5.25-5.26, while those for the annealed composition are shown in Figure 5.27.

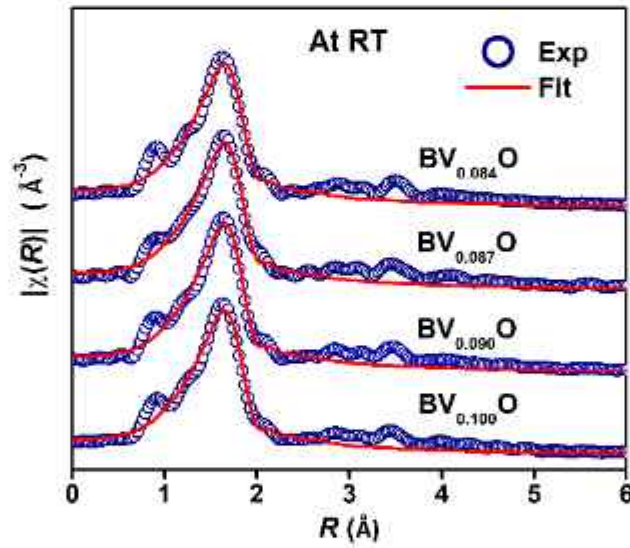


Figure 5.25: The best fit of $|\chi(R)|$ with a single three-oxygen-coordinated Bi-O shell is shown for BV_{0.084}O, BV_{0.087}O, BV_{0.090}O, and BV_{0.100}O samples

All the fits, irrespective of their composition or heat treatment, displayed good agreement between the experimental $|\chi(R)|$ and $k^2\chi(k)$ and the corresponding simulated lines using this model. However, minor discrepancies were noticed at higher k and R values, which were expected, since the fitting model only included the first coordination shell. The best-fit parameters obtained from the first shell fitting are listed in Table 5.15.

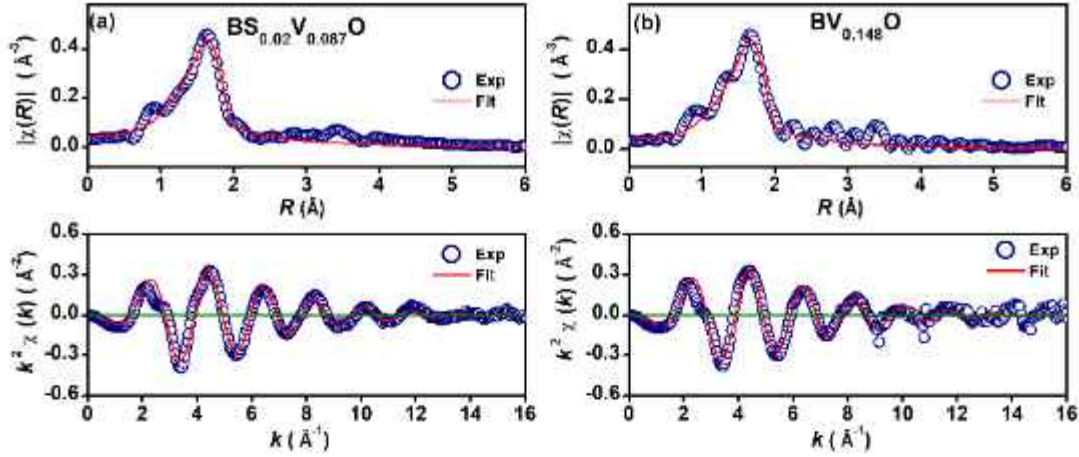


Figure 5.26: RT Bi L_3 -edge spectra (blue circle) of (a) $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and (b) $\text{BV}_{0.148}\text{O}$ compounds, fit (red line) with a single Bi-O shell.

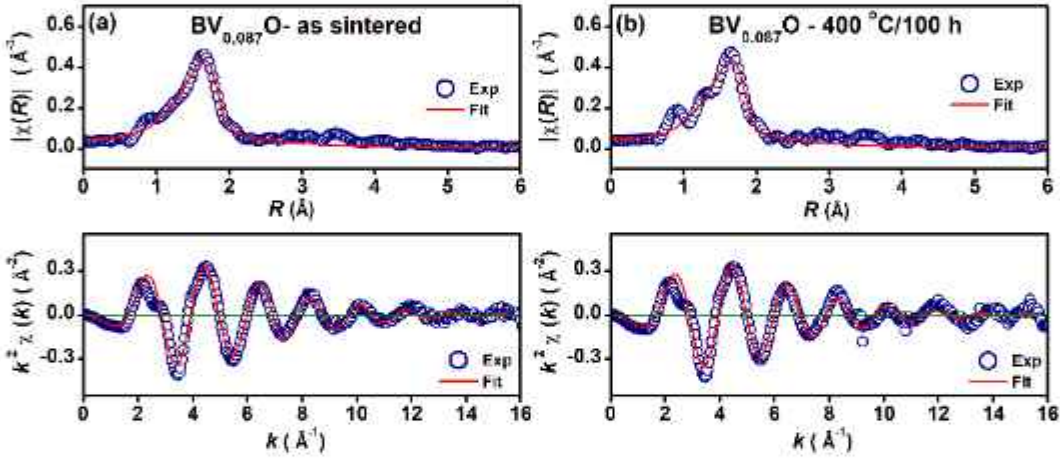


Figure 5.27: The fitting of $|\chi(R)|$ and $k^2\chi(k)$ for RT experimental Bi L_3 -edge EXAFS spectra (blue circles) with the best fit (red line) with a single three-oxygen-coordinated Bi-O shell corresponding to (a) $\text{BV}_{0.087}\text{O}$ as-sintered and (b) $\text{BV}_{0.087}\text{O}$ 400 °C/100 h annealed sample.

Although the first shell model aligned well with the experimental spectra, this model still did not account for the observed disorder or the influence of local structure on ionic conductivity of the synthesized materials. Therefore, to address this limitation, all the Bi-O and Bi-Bi correlations within the range of 1 Å to 4 Å for $R3m$ and the $I23$ phases were included in the fitting of the experimental data. Due to numerous correlations in this R range for both the phases, several constraints were required to successfully implement this model.

The bond distances were refined using a constraint represented by a constant (α) multiplied by the calculated bond distance (R_{eff}) from the lattice parameters, with

Table 5.15: Best-fit parameters obtained from single shell model

Best fit parameters of Bi L ₃ -edge EXAFS spectra at RT	Shell no.=1, $N_j = 3$, $R_j = 2.13 \text{ \AA}$, $\sigma^2 = 0.007 \text{ \AA}^2$
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independent constants used for the $R3m$ and $I23$ phases. Nearby scattering paths involving the same pair of atoms were assumed to have the same mean square disorder parameter, (σ^2). In total, eight different σ^2 were used in the fitting. The amplitude reduction factor (S_0^2) was kept fixed at a value obtained for Bi metal ($S_0^2 = 0.7$) and multiplied by an additional scaling constant, g to estimate the relative fractions of each phase. Overall, 13 independently varied parameters were used in fitting the experimental data. The resulting fittings achieved for as-sintered BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O, and BV_{0.148}O compositions in R -space and k -space are presented in Figure 5.28. The corresponding fit for 400 °C/ 100 h annealed BV_{0.087}O composition is also displayed in Figure 5.29 for comparison.

As observed from the figure and the corresponding refined parameters (Tables 5.16-5.18), the $R3m + I23$ phase correlations provided a reliable fit, with no noticeable discrepancies at higher k and R values. Thus, this analysis implied that the glass-like EXAFS signal was due to the local disorder caused by the biphasic nature of materials.

Fitting of Bi L₃ edge EXAFS signals of BV_{0.087}O, BS_{0.02}V_{0.087}O, BC_{0.02}V_{0.087}O and BV_{0.087}O-400 °C/100 h compositions provided similar parameters, with $R3m:I23$ phase fraction of 0.67:0.33. This relative phase ratio was in close agreement with that obtained from NPD analysis. In contrast, for BV_{0.148}O, the Bi-O1.4 and Bi-O1.5 scattering paths of the $I23$ phase were absent (Table 5.18). Furthermore, 4 Bi-Bi scattering paths in the $R3m$ phase exhibited large σ^2 (MSD), the refined $R3m:I23$ phase fraction for BV_{0.148}O was found to be 0.75:0.25.

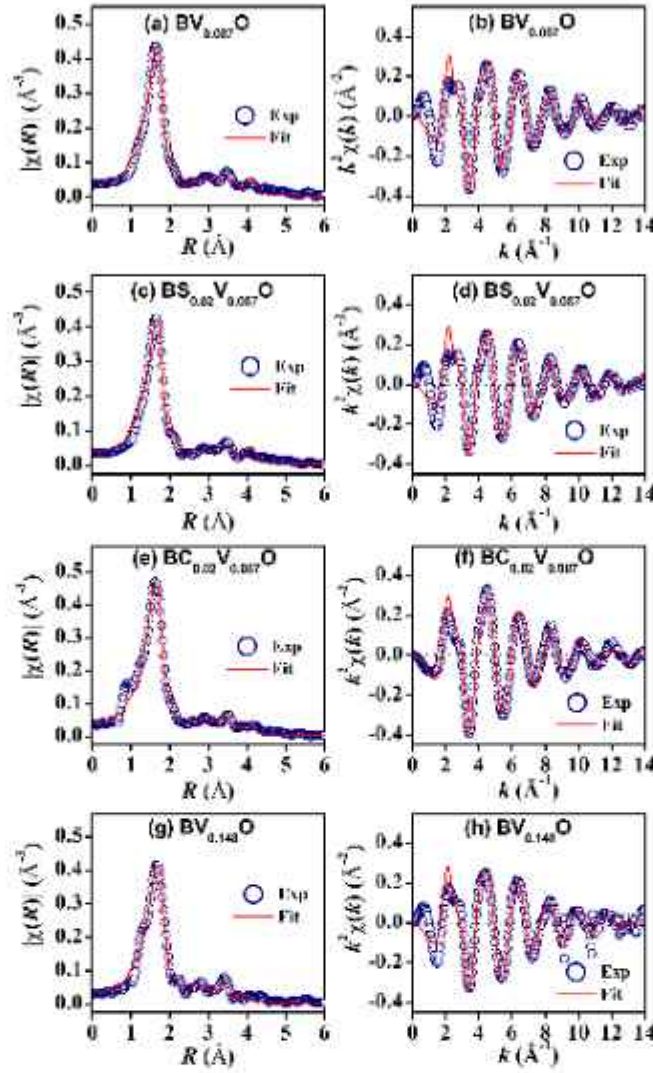


Figure 5.28: Results of the best fit with all possible Bi-O and Bi-Bi correlations in R range 1-4 Å as per $R3m$ and $I23$ models. The fit of $|\chi(R)|$ and $k^2\chi(k)$ are shown for (a, b) $BV_{0.087}O$, for (c, d) $BS_{0.02}V_{0.087}O$, for (e, f) $BC_{0.02}V_{0.087}O$, and for (g, h) $BV_{0.148}O$ respectively.

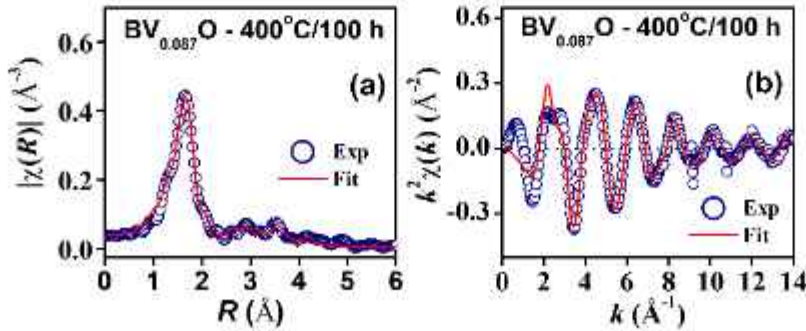


Figure 5.29: The fit of $|\chi(R)|$ and $k^2\chi(k)$ are shown for $BV_{0.087}O$ 400°C annealed sample with correlations from $R3m$ and $I23$ models

Table 5.16: Best fit parameters for as-sintered BV_{0.087}O

Path		Deg. (N)	Amp*0.7 (S ₀) ²	MSD σ^2	E ₀	delr	R _{eff}	R _{fitted}
[R3m]	O13.1	1	0.382	0.00042	0.76	-0.02967	2.1239	2.09423
[R3m]	O7.1	1	0.382	0.00356	0.76	-0.03089	2.2115	2.18061
[R3m]	O9.1	1	0.382	0.00356	0.76	-0.0314	2.2479	2.2165
[R3m]	O5.1	1	0.382	0.00327	0.76	-0.03431	2.4559	2.42159
[R3m]	O14.1	2	0.382	0.02294	0.76	-0.03788	2.7116	2.67372
[R3m]	Bi10.1	1	0.382	0.02831	0.76	-0.04993	3.5744	3.52447
[R3m]	Bi3.1	1	0.382	0.01991	0.76	-0.05296	3.7913	3.73834
[R3m]	Bi6.1	2	0.382	0.01991	0.76	-0.05389	3.8575	3.80361
[R3m]	Bi9.1	2	0.382	0.01991	0.76	-0.05465	3.9119	3.85725
[R3m]	Bi10.2	1	0.382	0.00457	0.76	-0.05539	3.9647	3.90931
[R3m]	Bi5.1	2	0.382	0.00457	0.76	-0.05685	4.0696	4.01275
[R3m]	Bi7.1	1	0.382	0.00457	0.76	-0.05801	4.1524	4.09439
[R3m]	Bi10.3	1	0.382	0.00457	0.76	-0.05856	4.1921	4.13354
[I23]	O1.1	1	0.318	0.00042	0.76	0.03305	2.0599	2.09295
[I23]	O1.2	2	0.318	0.00356	0.76	0.03546	2.2101	2.24556
[I23]	O1.3	1	0.318	0.02294	0.76	0.04184	2.6077	2.64954
[I23]	O3.1	1	0.318	0.02294	0.76	0.04279	2.6671	2.70989
[I23]	O1.4	1	0.318	0.01147	0.76	0.04841	3.017	3.06541
[I23]	O1.5	1	0.318	0.01147	0.76	0.05249	3.2713	3.32379
[I23]	Bi.1	3	0.318	0.02831	0.76	0.05856	3.6497	3.70826
[I23]	Bi.3	1	0.318	0.02831	0.76	0.05927	3.6943	3.75357
[I23]	Bi.4	3	0.318	0.01991	0.76	0.0605	3.7709	3.8314
[I23]	Bi.5	2	0.318	0.01991	0.76	0.06155	3.836	3.89755

Table 5.17: Best fit parameters for BV_{0.087}O 400 °C/100 h annealed sample

Path		Deg. (N)	Amp*0.7 (S ₀) ²	MSD σ^2	E ₀	delr	R _{eff}	R _{fitted}
[R3m]	O13.1	1	0.464	0.00031	0.403	-0.01324	2.1239	2.11066

<i>Table 5.17 continued</i>								
Path		Deg. (N)	Amp*0.7 (S ₀) ²	MSD σ^2	E ₀	delr	R _{eff}	R _{fitted}
[R3m]	O7.1	1	0.464	0.00573	0.403	-0.01378	2.2115	2.19772
[R3m]	O9.1	1	0.464	0.00573	0.403	-0.01401	2.2479	2.23389
[R3m]	O5.1	1	0.464	0.00861	0.403	-0.01531	2.4559	2.44059
[R3m]	O14.1	2	0.464	0.02144	0.403	-0.0169	2.7116	2.6947
[R3m]	Bi10.1	1	0.464	0.00623	0.403	-0.02228	3.5744	3.55212
[R3m]	Bi3.1	1	0.464	0.01392	0.403	-0.02363	3.7913	3.76767
[R3m]	Bi6.1	2	0.464	0.01392	0.403	-0.02404	3.8575	3.83346
[R3m]	Bi9.1	2	0.464	0.01392	0.403	-0.02438	3.9119	3.88752
[R3m]	Bi10.2	1	0.464	0.00806	0.403	-0.02471	3.9647	3.93999
[R3m]	Bi5.1	2	0.464	0.00806	0.403	-0.02536	4.0696	4.04424
[R3m]	Bi7.1	1	0.464	0.00806	0.403	-0.02588	4.1524	4.12652
[R3m]	Bi10.3	1	0.464	0.00806	0.403	-0.02613	4.1921	4.16597
[I23]	O1.1	1	0.236	0.00031	0.403	0.01579	2.0599	2.07569
[I23]	O1.2	2	0.236	0.00573	0.403	0.01694	2.2101	2.22704
[I23]	O1.3	1	0.236	0.02144	0.403	0.01998	2.6077	2.62768
[I23]	O3.1	1	0.236	0.02144	0.403	0.02044	2.6671	2.68754
[I23]	O1.4	1	0.236	0.01718	0.403	0.02312	3.017	3.04012
[I23]	O1.5	1	0.236	0.01718	0.403	0.02507	3.2713	3.29637
[I23]	Bi.1	3	0.236	0.00623	0.403	0.02797	3.6497	3.67767
[I23]	Bi.3	1	0.236	0.00623	0.403	0.02831	3.6943	3.72261
[I23]	Bi.4	3	0.236	0.01392	0.403	0.0289	3.7709	3.7998
[I23]	Bi.5	2	0.236	0.01392	0.403	0.0294	3.836	3.8654

Table 5.18: Best fit parameters for as-sintered BV_{0.148}O

Path		Deg. (N)	Amp*0.7 (S ₀) ²	MSD σ^2	E ₀	delr	R _{eff}	R _{fitted}
[I23]	O1.1	1	0.171	0.0009	-0.455	0.00518	2.0599	2.06508
[I23]	O1.2	2	0.171	0.00431	-0.455	0.00556	2.2101	2.21566
[I23]	O1.3	1	0.171	0.02419	-0.455	0.00656	2.6077	2.61426

<i>Table 5.18 continued</i>								
Path		Deg. (N)	Amp*0.7 (S ₀) ²	MSD σ^2	E ₀	delr	R _{eff}	R _{fitted}
[I23]	O3.1	1	0.171	0.02419	-0.455	0.00671	2.6671	2.67381
[I23]	Bi.1	3	0.171	0.0069	-0.455	0.00918	3.6497	3.65888
[I23]	Bi.3	1	0.171	0.0069	-0.455	0.00929	3.6943	3.70359
[I23]	Bi.4	3	0.171	0.01902	-0.455	0.00949	3.7709	3.78039
[I23]	Bi.5	2	0.171	0.01902	-0.455	0.00965	3.836	3.84565
[R3m]	O13.1	1	0.529	0.0009	-0.455	-0.00404	2.1239	2.11986
[R3m]	O7.1	1	0.529	0.00431	-0.455	-0.00421	2.2115	2.20729
[R3m]	O9.1	1	0.529	0.00431	-0.455	-0.00428	2.2479	2.24363
[R3m]	O5.1	1	0.529	0.00684	-0.455	-0.00467	2.4559	2.45123
[R3m]	O14.1	2	0.529	0.02419	-0.455	-0.00516	2.7116	2.70644
[R3m]	Bi10.1	1	0.529	0.0069	-0.455	-0.0068	3.5744	3.5676
[R3m]	Bi3.1	1	0.529	0.01902	-0.455	-0.00721	3.7913	3.78409
[R3m]	Bi6.1	2	0.529	0.01902	-0.455	-0.00734	3.8575	3.85016
[R3m]	Bi9.1	2	0.529	0.01902	-0.455	-0.00744	3.9119	3.90446
[R3m]	Bi10.2	1	0.529	0.04088	-0.455	-0.00754	3.9647	3.95716
[R3m]	Bi5.1	2	0.529	0.04088	-0.455	-0.00774	4.0696	4.06186
[R3m]	Bi7.1	1	0.529	0.04088	-0.455	-0.0079	4.1524	4.1445
[R3m]	Bi10.3	1	0.529	0.04088	-0.455	-0.00797	4.1921	4.18413

The variation of $|\chi(R)|$ at high temperatures for BV_{0.087}O (as-sintered and 400 °C/100 h annealed), BV_{0.148}O, and BS_{0.02}V_{0.087}O (as-sintered) compositions are displayed in Figure 5.30. It was noted that the amplitude of the main peak of $|\chi(R)|$ signal gradually decreased with increasing temperature. To understand this behavior, the EXAFS spectra were fitted with a room-temperature single Bi-O shell model, as shown in Figure 5.31. The best fit results revealed that with an increase in temperature, only the value of the MSD parameter (σ^2) gradually increased from 0.007 at RT to 0.011 at 500 °C. This variation of σ^2 with temperature for BS_{0.02}V_{0.087}O composition is also displayed in Figure 5.32.

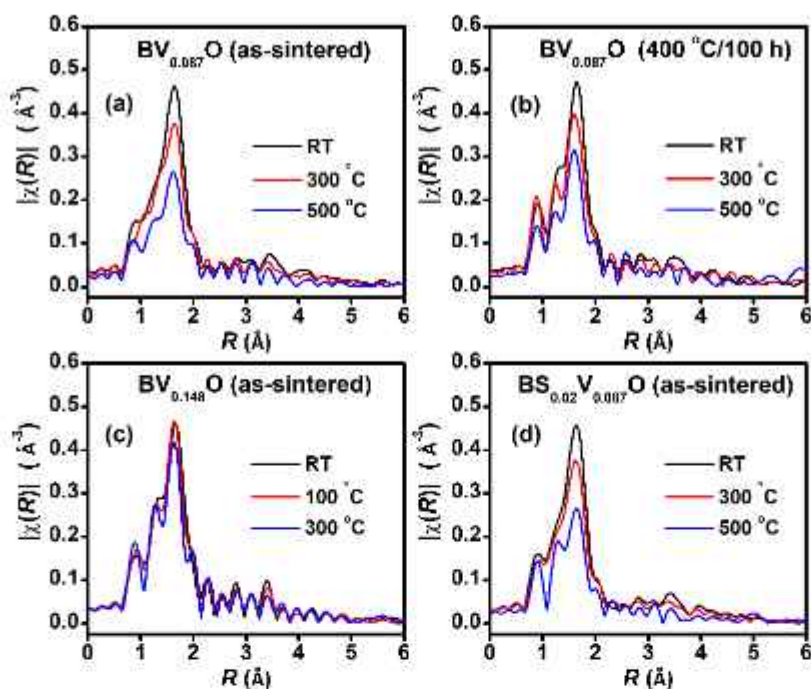


Figure 5.30: $|\chi(R)|$ of Bi L_{3} -edge EXAFS at high temperatures for (a) as-sintered $\text{BV}_{0.087}\text{O}$, (b) 400 °C/100 h annealed $\text{BV}_{0.087}\text{O}$, (c) as-sintered $\text{BV}_{0.148}\text{O}$, and (d) as-sintered $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$

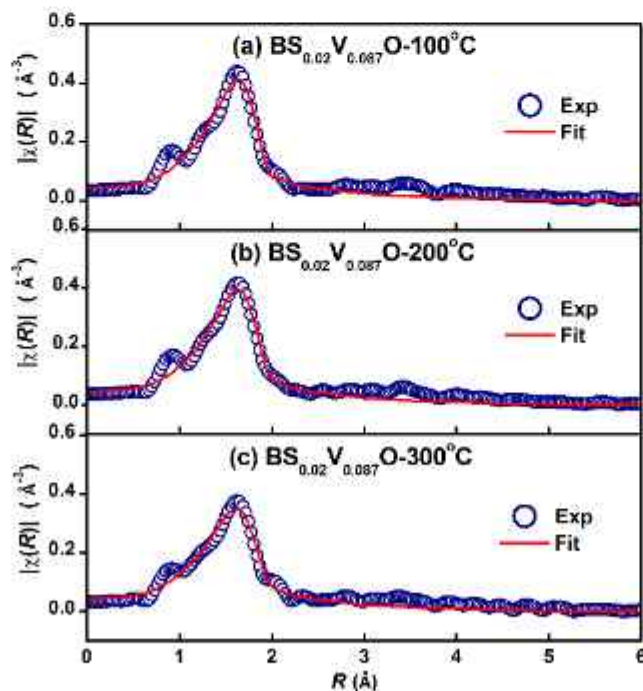


Figure 5.31: The best fit of $|\chi(R)|$ with a single three-oxygen-coordinated Bi-O shell are shown for $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ at different temperatures.

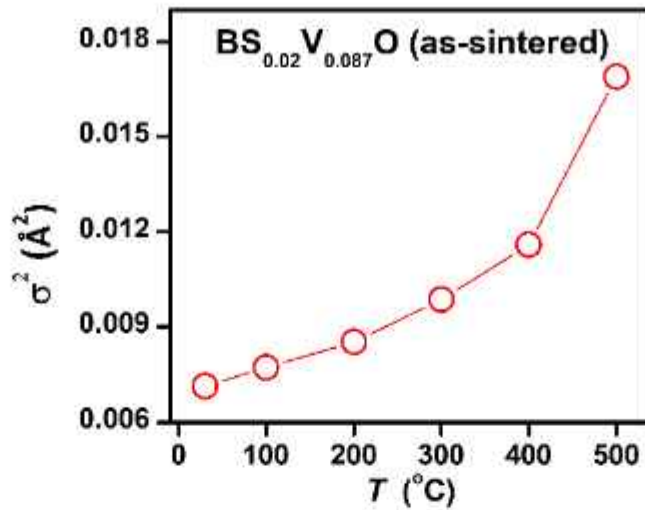


Figure 5.32: Temperature variation of mean square disorder parameter (σ^2), determined from first shell fitting of Bi L₃-edge EXAFS spectra recorded in BS_{0.02}V_{0.087}O.

This gradual increase of σ^2 was due to an increase in both static and thermal disorder at high temperature. With an increase in temperature, some oxygen ions in the first Bi-O shell may displace from normal sites to interstitial sites, leading to a decrease in the amplitude of the first correlation peak. In such a way, these ions may participate in the ion conduction mechanism. In BV_{0.148}O (Figure 5.30 c), negligible changes in $|\chi(R)|$ are observed, which may be partly attributed to the comparatively lower measuring temperature of 100 and 300 °C, unlike the 300 °C and 500 °C in other compositions, as well as reduced thermal disorder.

Earlier reports by Kuang *et al.*[27] (by ab-initio molecular dynamics) and Dunstan *et al.*[46] (by variable temperature ¹⁷O NMR) demonstrated that the conduction mechanism in V-substituted Bi₂O₃ involved the exchange of O²⁻ ion between the Bi-O and the V-O sublattices. This exchange was facilitated by the variability of the vanadium coordination environment. Therefore, in the present study, V coordination was examined through its oxidation state, which was probed using V K-edge XANES.

The vanadium K-edge XANES spectra of BV_{0.087}O, BS_{0.02}V_{0.087}O, and BV_{0.148}O are shown in Figure 5.33, along with those of the reference compounds of V₂O₅

and vanadium oxyacetylacetonate ($\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$).

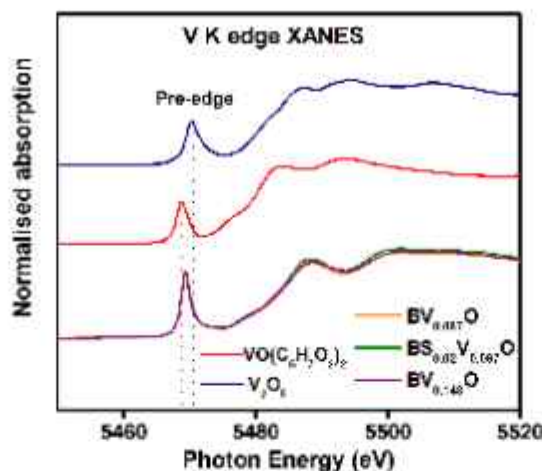


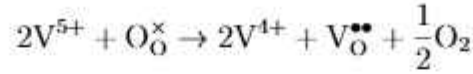
Figure 5.33: V K-edge XANES spectra for $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, V_2O_5 , $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BV}_{0.148}\text{O}$ samples at RT

In the V K-edge XANES spectra, a distinct pre-edge peak was observed in the energy range of (5467-5472 eV). The presence of such a pre-edge peak in V-containing systems has been attributed to the symmetry-forbidden $1s \rightarrow 3d$ electronic transition. The intensity of this pre-edge feature is enhanced by p and d orbital mixing, due to a change in coordination geometry from octahedral to five-coordinate or tetrahedral, and/or metal-ligand π bonding.[59] In the present case, the pre-edge peaks of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BV}_{0.148}\text{O}$ compositions in the superimposed XANES spectra were found to almost overlap, indicating similar local coordination environments around vanadium atoms in these samples. For comparison, two reference compounds of vanadium (V) oxide (V_2O_5) and vanadium (IV) oxyacetylacetonate ($\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$) representing the oxidation states of +5 and +4, respectively, were also analyzed.

Relative to these references, the positions of the pre-edge peaks in the studied compositions were located between those corresponding to V^{4+} and V^{5+} . This implied that the average cationic charge of V is +4.5 in the samples.

An average cationic charge between the +4 and +5, suggests the coexistence of mixed valence V^{4+} and V^{5+} states. It is well established that the reduction of $\text{V}^{5+} \rightarrow \text{V}^{4+}$ is accompanied by the formation of oxygen vacancies ($\text{O}_\square$), as

described by the defect equation[60],



Therefore, the average cationic charge of +4.5 implies the presence of additional oxygen vacancies ($O_{\square}$) or smaller oxygen coordination around vanadium ions in current systems. The strong interaction between vanadium ions and the associated oxygen vacancy can act as trapping centers and affect the ionic transport. Therefore, at higher V-doping decrease in bulk conductivity is expected. This interpretation is consistent with comparatively lower bulk conductivity observed for the high V-doped BV_{0.148}O composition. Furthermore, similar behavior has also been reported in Sr/V co-doped system, where a MD simulation study on Scheelite material system of Bi_{1-x}Sr_xVO_{4-0.5x}, demonstrated strong dopant-vacancy interactions and corresponding reduction in conductivity.[43]

5.3.4 Investigating the effect of Sr concentration in as-sintered and annealed compositions

Among the prepared compositions, Sr/V co-doped BS_{0.02}V_{0.087}O composition demonstrated better stability of high conducting *R3m* phase even after the long-term temperature exposure, which usually leads to the aging effects in other doped Bi₂O₃ systems. Therefore, to examine whether the Sr/V co-doped system can maintain its structural stability and conductivity, with further increase in Sr content, higher Sr-doped compositions of Bi_{0.873}Sr_{0.04}V_{0.087}O_{1.567} and Bi_{0.853}Sr_{0.06}V_{0.087}O_{1.557} were synthesized. Additionally, these compositions were also subjected to similar annealing treatments of 400 °C/100 h and 600 °C/100 h to study the effects of aging. Figures 5.34(a) compares the XRD patterns of as-sintered BS_{0.02}V_{0.087}O, BS_{0.04}V_{0.087}O, and BS_{0.06}V_{0.087}O compositions, whereas 5.34(b-c) displays the comparison of XRD patterns of BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions with BS_{0.02}V_{0.087}O after annealing.

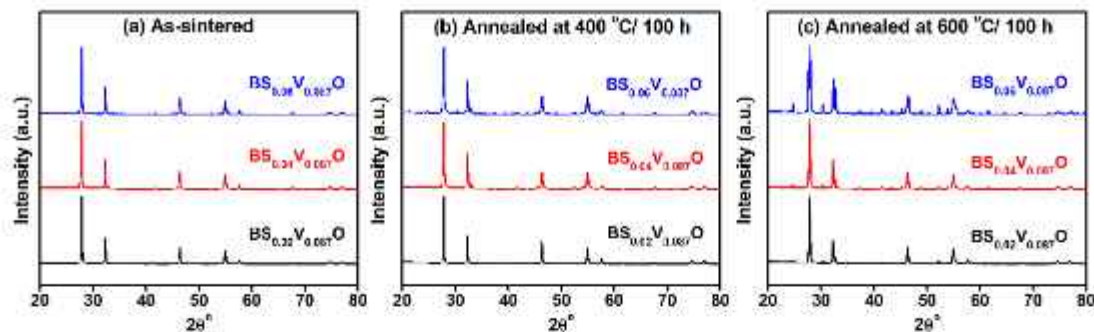


Figure 5.34: XRD stack plot of as-sintered and annealed BS_xV_{0.087}O for $x=0.02$, 0.04, and 0.06 samples

In the as-sintered compositions (Figure 5.34 a), the XRD patterns remained mostly similar with higher Sr substitution. However, upon annealing at 400 °C/100 h, BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions showed the presence of additional Bragg peaks, unlike the BS_{0.02}V_{0.087}O compositions. These Bragg peaks became more pronounced when the annealing temperature was increased to 600 °C/100 h. Consistent with the $R3m + I23$ structural model employed for BS_{0.02}V_{0.087}O composition, the two higher Sr compositions were also refined using the same model through Rietveld refinement. The refinement results of as-sintered and annealed BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O samples are presented in Figures 5.35 and 5.36, respectively. The corresponding refined lattice parameters and phase ratios are also listed in Table 5.19 for reference. It was noted that the conversion rates of the stabilized $R3m$ to $I23$ phase in BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions were faster compared to the BS_{0.02}V_{0.087}O sample.

The as-sintered compositions with 4 and 6 mole% of Sr concentrations displayed ~ 8 -9% of $I23$ phase. For the samples annealed at 400 °C/100 h, the extent of phase conversion showed only a marginal difference between the two higher Sr-substituted compositions, with an increase of 12.6% and 14 % for BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O, respectively. In contrast, annealing at 600 °C/100 h led to pronounced phase conversion of 14.6% in BS_{0.04}V_{0.087}O to 28.3% in BS_{0.06}V_{0.087}O. The consistently higher fraction of $I23$ phase in higher Sr-substituted compositions indicated that BS_{0.02}V_{0.087}O compositions offered optimal phase stability.

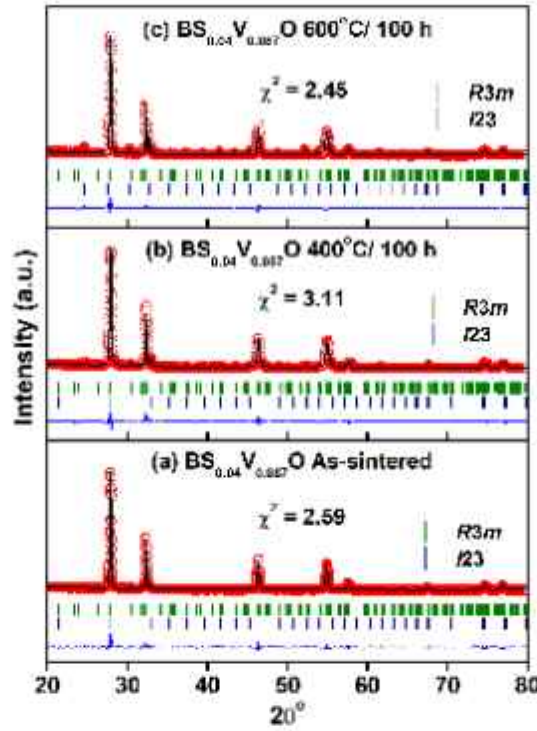


Figure 5.35: (a-c) Room-temperature XRD patterns of $\text{BS}_{0.04}\text{V}_{0.087}\text{O}$ with Rietveld refinement fit for as-sintered and annealed samples

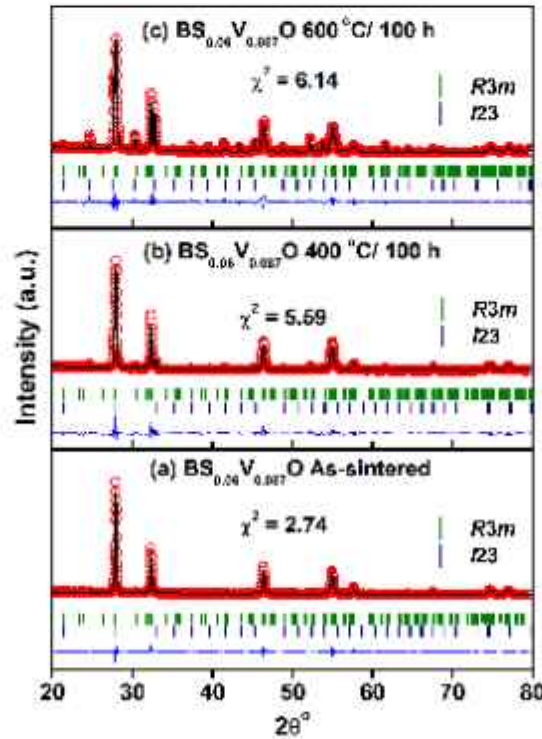


Figure 5.36: (a-c) Room-temperature XRD patterns of $\text{BS}_{0.06}\text{V}_{0.087}\text{O}$ with Rietveld refinement fit for as-sintered and annealed samples

Table 5.19: Rietveld refined lattice parameters and phase percentages of BS_xV_{0.087}O ($x = 0.04, 0.06$) for as-sintered and annealed (aged) compositions.

Samples	Lattice parameters		<i>R3m:I23</i> (%)
	<i>R3m</i>	<i>I23</i>	
BS _{0.04} V _{0.087} O as-sintered	$a = b = 11.739(2) \text{ \AA}$ $c = 28.874(8) \text{ \AA}$	$a = b = c$ $= 10.189(2) \text{ \AA}$	91.8:8.1
BS _{0.04} V _{0.087} O 400 °C/100 h	$a = b = 11.728 \text{ \AA}$ $c = 28.870(6) \text{ \AA}$	$a = b = c$ $= 10.190(3) \text{ \AA}$	87.4:12.6
BS _{0.04} V _{0.087} O 600 °C/100 h	$a = b = 11.739(9) \text{ \AA}$ $c = 28.880(5) \text{ \AA}$	$a = b = c$ $= 10.216(1) \text{ \AA}$	85.4:14.6
BS _{0.06} V _{0.087} O as-sintered	$a = b = 11.732(2) \text{ \AA}$ $c = 28.848(6) \text{ \AA}$	$a = b = c$ $= 10.189(2) \text{ \AA}$	91.3:8.7
BS _{0.06} V _{0.087} O 400 °C/100 h	$a = b = 11.729(5) \text{ \AA}$ $c = 28.887(4) \text{ \AA}$	$a = b = c$ $= 10.187(1) \text{ \AA}$	85.9:14.1
BS _{0.06} V _{0.087} O 600 °C/100 h	$a = b = 11.717(5) \text{ \AA}$ $c = 28.881(9) \text{ \AA}$	$a = b = c$ $= 10.208(7) \text{ \AA}$	71.7:28.3

Furthermore, to investigate the effect of higher Sr doping on ionic conductivity, EIS was carried out in the as-sintered and annealed BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions. The value of total conductivity at 400 and 500 °C are listed in Table 5.20.

Table 5.20: Conductivity values of BS_xV_{0.087}O compositions at 400 and 500 °C

Samples	$\sigma_{400 \text{ } ^\circ\text{C}}$ (S/cm)	$\sigma_{500 \text{ } ^\circ\text{C}}$ (S/cm)
BS _{0.02} V _{0.087} O as-sintered	3.31×10^{-2}	1.06×10^{-1}
BS _{0.02} V _{0.087} O 400 °C/100 h	2.50×10^{-2}	1.09×10^{-1}
BS _{0.02} V _{0.087} O 600 °C/100 h	9.98×10^{-3}	5.60×10^{-2}
BS _{0.04} V _{0.087} O as-sintered	2.44×10^{-2}	8.77×10^{-2}
BS _{0.04} V _{0.087} O 400 °C/100 h	1.23×10^{-2}	5.55×10^{-2}
BS _{0.04} V _{0.087} O 600 °C/100 h	1.41×10^{-2}	6.07×10^{-2}
BS _{0.06} V _{0.087} O as-sintered	1.90×10^{-2}	4.10×10^{-2}
BS _{0.06} V _{0.087} O 400 °C/100 h	1.09×10^{-2}	5.21×10^{-2}
BS _{0.06} V _{0.087} O 600 °C/100 h	4.17×10^{-3}	1.73×10^{-2}

The total conductivity measured at 400 °C and 500 °C in as-sintered samples decreased with an increase in the Sr content for BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions. On annealing at 400 °C/100 h, the BS_{0.02}V_{0.087}O composition retained a stable conductivity of $\sim 10^{-1}$ S/cm, which is comparable to its as-sintered value, whereas the BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O compositions exhibited a marginal

reduction in conductivity. In contrast, annealing at 600 °C/100 h resulted in noticeable conductivity drop in BS_{0.02}V_{0.087}O and BS_{0.04}V_{0.087}O, while BS_{0.06}V_{0.087}O compositions. Arrhenius plots for the as-sintered and annealed compositions of BS_{0.02}V_{0.087}O, BS_{0.04}V_{0.087}O, and BS_{0.06}V_{0.087}O are depicted in Figure 5.37(a-c). Additionally, the total conductivity at 500 °C as a function of synthesis condition is plotted in Figure 5.37(d) for comparison.

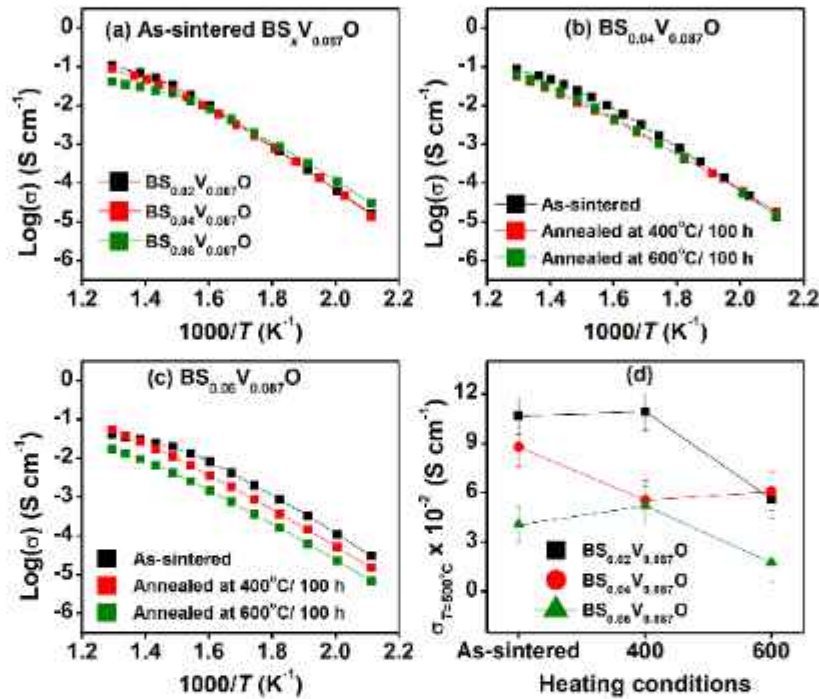


Figure 5.37: (a-c) Arrhenius plot of total conductivity (σ) of BS_xV_{0.087}O ($x=0.02, 0.04$, and 0.06) for as-sintered and annealed samples.

As shown in Figure 5.37(a), the conductivity of as-sintered BS_{0.04}V_{0.087}O composition was slightly lower than that of BS_{0.02}V_{0.087}O over the entire temperature range up to 500 °C. In contrast, as-sintered BS_{0.06}V_{0.087}O showed slightly higher conductivity at ~ 200 °C, followed by noticeable reduction above ~ 350 °C. For BS_{0.04}V_{0.087}O, the annealed compositions displayed comparable conductivity values across the measured temperature range; however, these values remained lower than those of the corresponding as-sintered composition. In the BS_{0.06}V_{0.087}O composition, a systematic decrease in conductivity was observed from the as-sintered state to samples annealed at 400 and 600 °C.

Unlike the 400 °C/100 h annealed BS_{0.02}V_{0.087}O composition, the XRD pattern of the BS_{0.04}V_{0.087}O and BS_{0.06}V_{0.087}O revealed prominent phase conversion with increasing Sr content, accompanied by a decrease in conductivity. This implied that in the present case, the reduction in measured conductivity cannot be attributed solely to the aging effect, but was more likely associated with the coexistence of two conducting phases, which may have impeded effective ion transport.

5.4 Understanding the Composition-Property relationship in V- and Sr/Ca co-doped Bi₂O₃ system

The phase and structural stability of doped Bi₂O₃ materials are dependent on the dopant cation radius and its concentration. In Ln³⁺ doped Bi₂O₃ materials, it was noted that for a fixed dopant concentration, the stability of the ionic conducting *fcc* phase decreases with an increase in the dopant cation radii.[10] Conversely, an increase in dopant cation radii enhances the stability of the disordered structure.[3], [10], [20], [50] Consequently, the stability of the disordered structure and *fcc* phase exhibited opposing trends with respect to Ln³⁺ radii, thereby limiting the design of simultaneously stable and highly conductive oxide ion conductors through Ln³⁺ doping.

In the present study, this limitation of attaining phase and disordered structure stability was mitigated by V and Sr/Ca co-doping of 8.7 and 2 mole%, respectively. X-ray and neutron diffraction studies revealed that the V and Sr/Ca co-doped compositions (BS_{0.02}V_{0.087}O and BC_{0.02}V_{0.087}O) crystallized into a mixture of *R3m* and *I23* phases. Notably, high-temperature NPD measurement conducted over the duration of 4 days also did not reveal any change in structural/phase with temperature, thereby confirming structural stability in these compositions.

Furthermore, NPD analysis revealed that the *R3m* crystal structure of these compositions adopted a 3×3×3 fluorite-type superstructure, with a layer sequence

closely similar to that of *fcc* δ -Bi₂O₃. This analysis also indicated that V and Sr/Ca dopants occupy every third cationic layer (L3), which disrupts the ionic conduction pathways and subsequently leads to a reduction in ionic conduction. EXAFS study was used to characterize the local environment of Bi in as-sintered as well as annealed (aged) samples. The EXAFS results indicated that the Bi-O correlations above $\sim 2.13 \text{ \AA}$ were highly disordered, primarily due to the partial oxygen occupancy around Bi and V ions. This disordered environment remained unchanged even after annealing at 400 °C/100 h and 600 °C/100 h. Therefore, in the present EXAFS study, we were unable to resolve the difference between the local disordered structure of the as-sintered BV_{0.087}O sample and the ordered structure of annealed BV_{0.087}O samples. Nevertheless, it was evident that the oxygen ion conductivity in Bi₂O₃-based materials is maximized in structures exhibiting a high degree of oxygen site disorder.

The oxide-ion conduction mechanism was investigated using soft BVS analysis for the V/Sr co-doped composition. In these materials, ionic transport is governed by the number of movable vacancies. The soft BVS study demonstrated that the majority of the ionic conductivities occurred through L1 and L2 layers, rather than L3 layers that are preferentially occupied by Sr/Ca and V-ions. As a result, the pure δ -Bi₂O₃ phase, characterized by a higher number of conduction channels and a continuous 3D network of oxygen conduction pathways, remained a superior oxide ion conductor for HT-SOFC application, compared to both BS_{0.02}V_{0.087}O and BC_{0.02}V_{0.087}O materials. However, for the LT-SOFC application, the BS_{0.02}V_{0.087}O composition can serve as a potential candidate.

Finally, the stability of BV_{0.087}O, BS_{0.02}V_{0.087}O, and BC_{0.02}V_{0.087}O compositions was evaluated under reducing conditions. Figure 5.38 compares the XRD patterns of these samples before and after annealing at 400 °C for 5 h in reducing conditions (mixture of 25% H₂-75% N₂ gas).

From the figure, it was observed that, even after the compositions were subjected to reducing conditions, there was no emergence of new diffraction peaks associated

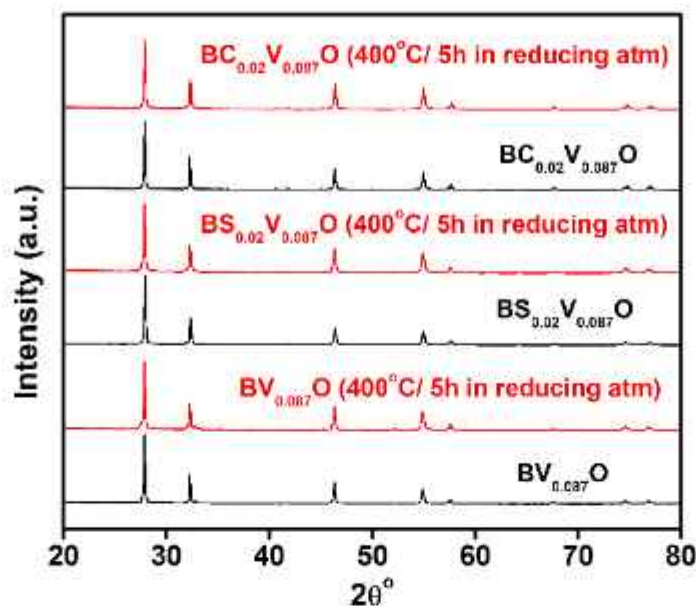


Figure 5.38: XRD plots of $\text{BV}_{0.087}\text{O}$, $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$, and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ specimens annealed at $400^\circ\text{C}/5\text{ h}$ in reducing atmosphere (25% H_2 -75% N_2)

with the reduction of Bi or V ions. This indicated that the compositions remained stable under reducing conditions, which thereby supports their suitability for operation in the SOFC environment.

5.5 Conclusion

In the present work, we have systematically investigated the effect of V and Sr/Ca as co-doping on phase stabilization and conduction behavior of Bi_2O_3 . A stable high oxide ion conducting phase was obtained in $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ compositions. Both these materials exhibited conductivity $\sim 3 \times 10^{-2}\text{ S/cm}$ at 400°C and $\sim 1.0 \times 10^{-1}\text{ S/cm}$ at 500°C , where they showed no phase transformation or aging effect. For the design of LT-SOFC and oxygen separation membranes, electrolyte materials with an ionic conductivity of $\sim 10^{-2}\text{ S/cm}$ are generally required. Accordingly, both $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ materials satisfied the primary requirements for LT-SOFC electrolyte device and offered excellent potential to replace known conductors such as stabilized $\delta\text{-Bi}_2\text{O}_3$, BIMEVOX, YSZ, apatite silicate/germinate/niobate systems, etc.[6]

In contrast, the purely V-doped Bi_2O_3 samples (BV_xO) showed inferior electrochemical performance compared to $\text{BS}_{0.02}\text{V}_{0.087}\text{O}$ and $\text{BC}_{0.02}\text{V}_{0.087}\text{O}$ samples, due to their tendency to form ordered structures. Furthermore, we have also shown that the degree of the oxygen (dis)ordering around cations was strongly dependent on the sample synthesis history. Collectively, these findings provide valuable insights into the structure-property relationship governing the oxide ion transport and can be utilized to design new oxide ion conductors for renewable energy devices.

References

- [1] T. Takahashi, H. Iwahara, and Y. Nagai, *Journal of Applied Electrochemistry*, vol. 2, no. 2, pp. 97–104, May 1972.
- [2] T. Takahashi and H. Iwahara, *Journal of Applied Electrochemistry*, vol. 3, no. 1, pp. 65–72, Feb. 1973.
- [3] P. Shuk, H. Wiemhöfer, U. Guth, W. Göpel, and M. Greenblatt, *Solid State Ionics*, vol. 89, no. 3, pp. 179–196, 1996, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/0167-2738\(96\)00348-7](https://doi.org/10.1016/0167-2738(96)00348-7).
- [4] H. Harwig and A. Gerards, *Journal of Solid State Chemistry*, vol. 26, no. 3, pp. 265–274, 1978, ISSN: 0022-4596. DOI: [https://doi.org/10.1016/0022-4596\(78\)90161-5](https://doi.org/10.1016/0022-4596(78)90161-5).
- [5] E. Wachsman and K. Lee, *Science (New York, N.Y.)*, vol. 334, pp. 935–939, Nov. 2011. DOI: 10.1126/science.1204090.
- [6] L. Malavasi, C. A. J. Fisher, and M. S. Islam, *Chem. Soc. Rev.*, vol. 39, pp. 4370–4387, 11 2010. DOI: 10.1039/B915141A.
- [7] T. Takahashi and H. Iwahara, *Materials Research Bulletin*, vol. 13, no. 12, pp. 1447–1453, 1978, ISSN: 0025-5408. DOI: [https://doi.org/10.1016/0025-5408\(78\)90138-1](https://doi.org/10.1016/0025-5408(78)90138-1).
- [8] T. Takahashi, T. Esaka, and H. Iwahara, *Journal of Applied Electrochemistry*, vol. 5, no. 3, pp. 197–202, Aug. 1975.
- [9] T. Takahashi, H. Iwahara, and T. Esaka, *Journal of The Electrochemical Society*, vol. 124, no. 10, p. 1563, Oct. 1977. DOI: 10.1149/1.2133111.
- [10] N. Jiang and E. D. Wachsman, *Journal of the American Ceramic Society*, vol. 82, no. 11, pp. 3057–3064, 1999. DOI: <https://doi.org/10.1111/j.1151-2916.1999.tb02202.x>.
- [11] M. J. Verkerk and A. J. Burggraaf, *Journal of The Electrochemical Society*, vol. 128, no. 1, p. 75, Jan. 1981. DOI: 10.1149/1.2127391.

- [12] X. Wang, W. Zhou, J. B. DeLisio, G. C. Egan, and M. R. Zachariah, *Phys. Chem. Chem. Phys.*, vol. 19, pp. 12 749–12 758, 20 2017. DOI: 10.1039/C6CP08532F.
- [13] A. A. Yaremchenko, V. V. Kharton, E. N. Naumovich, and A. A. Vecher, *Journal of Solid State Electrochemistry*, vol. 2, no. 3, pp. 146–149, Apr. 1998.
- [14] D. S. Khacrudini, G. Guan, P. Zhang, and A. Abudula, *Ionics*, vol. 22, no. 1, pp. 93–97, Jan. 2016.
- [15] C. D. Ling et al., *Journal of the American Chemical Society*, vol. 135, no. 17, pp. 6477–6484, 2013. DOI: 10.1021/ja3109328.
- [16] S. Lin and W. Wei, *Journal of the European Ceramic Society*, vol. 31, no. 16, pp. 3081–3086, 2011, ISSN: 0955-2219. DOI: <https://doi.org/10.1016/j.jeurceramsoc.2011.04.015>.
- [17] T. Saito and R. Miida, *Japanese Journal of Applied Physics*, vol. 38, no. 8R, p. 4838, Aug. 1999. DOI: 10.1143/JJAP.38.4838.
- [18] J. Darriet, J. Launay, and F. Zúñiga, *Journal of Solid State Chemistry*, vol. 178, no. 6, pp. 1753–1764, 2005, ISSN: 0022-4596. DOI: <https://doi.org/10.1016/j.jssc.2005.03.013>.
- [19] H. Iwahara, T. Esaka, T. Sato, and T. Takahashi, *Journal of Solid State Chemistry*, vol. 39, no. 2, pp. 173–180, 1981, ISSN: 0022-4596. DOI: [https://doi.org/10.1016/0022-4596\(81\)90328-5](https://doi.org/10.1016/0022-4596(81)90328-5).
- [20] M. Drache, P. Roussel, and J.-P. Wignacourt, *Chemical Reviews*, vol. 107, no. 1, pp. 80–96, 2007. DOI: 10.1021/cr050977s.
- [21] G. Meng, C. Chen, X. Han, P. Yang, and D. Peng, *Solid State Ionics*, vol. 28–30, pp. 533–538, 1988, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/S0167-2738\(88\)80097-3](https://doi.org/10.1016/S0167-2738(88)80097-3).

- [22] K. Huang, M. Feng, and J. B. Goodenough, *Solid State Ionics*, vol. 89, no. 1, pp. 17–24, 1996, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/0167-2738\(96\)00260-3](https://doi.org/10.1016/0167-2738(96)00260-3).
- [23] S. Arasteh, A. Maghsoudipour, M. Alizadeh, and A. Nemat, *Ceramics International*, vol. 37, no. 8, pp. 3451–3455, 2011, ISSN: 0272-8842. DOI: <https://doi.org/10.1016/j.ceramint.2011.04.136>.
- [24] S.-F. Wang, Y.-F. Hsu, W.-C. Tsai, and H.-C. Lu, *Journal of Power Sources*, vol. 218, pp. 106–112, 2012, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2012.06.056>.
- [25] D. Mercurio, M. El Farissi, B. Frit, J. Reau, and J. Sencgas, *Solid State Ionics*, vol. 39, no. 3, pp. 297–304, 1990, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/0167-2738\(90\)90410-S](https://doi.org/10.1016/0167-2738(90)90410-S).
- [26] R. Pun, A. M. Feteira, D. C. Sinclair, and C. Greaves, *Journal of the American Chemical Society*, vol. 128, no. 48, pp. 15386–15387, 2006. DOI: [10.1021/ja065961d](https://doi.org/10.1021/ja065961d).
- [27] X. Kuang, J. L. Payne, J. D. Farrell, M. R. Johnson, and I. R. Evans, *Chemistry of Materials*, vol. 24, no. 11, pp. 2162–2167, 2012. DOI: [10.1021/cm3008107](https://doi.org/10.1021/cm3008107).
- [28] R. D. Shannon, *Acta Crystallographica Section A*, vol. 32, no. 5, pp. 751–767, 1976. DOI: <https://doi.org/10.1107/S0567739476001551>.
- [29] X. Kuang, J. L. Payne, M. R. Johnson, and I. Radosavljevic Evans, *Angewandte Chemie International Edition*, vol. 51, no. 3, pp. 690–694, 2012. DOI: <https://doi.org/10.1002/anie.201106111>.
- [30] J. Rodríguez-Carvajal, *Physica B: Condensed Matter*, vol. 192, no. 1, pp. 55–69, 1993, ISSN: 0921-4526. DOI: [https://doi.org/10.1016/0921-4526\(93\)90108-I](https://doi.org/10.1016/0921-4526(93)90108-I).
- [31] H. Chen, L. L. Wong, and S. Adams, *Acta Crystallographica Section B*, vol. 75, no. 1, pp. 18–33, Feb. 2019. DOI: [10.1107/S2052520618015718](https://doi.org/10.1107/S2052520618015718).

- [32] K. Momma and F. Izumi, *Journal of Applied Crystallography*, vol. 41, no. 3, pp. 653–658, Jun. 2008. DOI: 10.1107/S0021889808012016.
- [33] A. Cicco et al., *Journal of Physics: Conference Series*, vol. 190, Nov. 2009. DOI: 10.1088/1742-6596/190/1/012043.
- [34] B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, vol. 12, no. 4, pp. 537–541, Jul. 2005. DOI: 10.1107/S0909049505012719.
- [35] M. L. Tate, Ph.D. dissertation, Durham University, 2017.
- [36] S. Kashida, T. Hori, and K. Nakamura, *Journal of the Physical Society of Japan*, vol. 63, no. 12, pp. 4422–4426, 1994. DOI: 10.1143/JPSJ.63.4422.
- [37] S. F. Radaev, V. I. Simonov, and Y. F. Kargin, *Acta Crystallographica Section B*, vol. 48, no. 5, pp. 604–609, 1992. DOI: <https://doi.org/10.1107/S0108768192003847>.
- [38] X. Kuang, J. L. Payne, J. D. Farrell, M. R. Johnson, and I. R. Evans, *Chemistry of Materials*, vol. 24, no. 11, pp. 2162–2167, 2012. DOI: 10.1021/cm3008107.
- [39] W. Zhou, *Journal of Solid State Chemistry*, vol. 76, no. 2, pp. 290–300, 1988, ISSN: 0022-4596. DOI: [https://doi.org/10.1016/0022-4596\(88\)90222-8](https://doi.org/10.1016/0022-4596(88)90222-8).
- [40] D. W. STRICKLER and W. G. CARLSON, *Journal of the American Ceramic Society*, vol. 47, no. 3, pp. 122–127, 1964. DOI: <https://doi.org/10.1111/j.1151-2916.1964.tb14368.x>.
- [41] M. Malys, J. Dygas, M. Holdynski, A. Borowska-Centkowska, W. Wrobel, and M. Marzantowicz, *Solid State Ionics*, vol. 225, pp. 493–497, 2012, Solid State Ionics 18 Proceedings of the 18th International Conference on Solid State Ionics Warsaw, Poland, July 3 -8, 2011, ISSN: 0167-2738. DOI: <https://doi.org/10.1016/j.ssi.2012.03.025>.
- [42] O. Turkoglu and I. Belenli, *Journal of Thermal Analysis and Calorimetry*, vol. 73, no. 3, pp. 1001–1012, Sep. 2003.

- [43] X. Yang et al., *Nature Communications*, vol. 9, no. 1, p. 4484, Oct. 2018.
- [44] S. Beg, S. Hancsf, and N. A. Al-Arcqi, *Phase Transitions*, vol. 83, no. 12, pp. 1114–1125, 2010. DOI: 10.1080/01411594.2010.509642.
- [45] S. Beg, S. Hafecz, and N. A. Al-Arcqi, *Phase Transitions*, vol. 83, no. 3, pp. 169–181, 2010. DOI: 10.1080/01411591003607263.
- [46] M. T. Dunstan, D. M. Halat, M. L. Tate, I. R. Evans, and C. P. Grey, *Chemistry of Materials*, vol. 31, no. 5, pp. 1704–1714, 2019. DOI: 10.1021/acs.chemmater.8b05143.
- [47] J. R. Peet et al., *Journal of the American Chemical Society*, vol. 141, no. 25, pp. 9989–9997, 2019. DOI: 10.1021/jacs.9b03743.
- [48] B. Schwaighofer, M. A. Gonzalcz, M. Appel, M. M. Koza, and I. R. Evans, *Chemistry of Materials*, vol. 35, no. 3, pp. 1125–1133, 2023. DOI: 10.1021/acs.chemmater.2c03103.
- [49] R. A. Huggins, *Ionics*, vol. 8, no. 3, pp. 300–313, May 2002.
- [50] K. Z. Fung, J. Chen, and A. V. Virkar, *Journal of the American Ceramic Society*, vol. 76, no. 10, pp. 2403–2418, 1993. DOI: <https://doi.org/10.1111/j.1151-2916.1993.tb03961.x>.
- [51] N. Jiang, R. Buchanan, D. Stevenson, W. Nix, J. Li, and J. Yang, *Materials Letters*, vol. 22, no. 5, pp. 215–219, 1995, ISSN: 0167-577X. DOI: [https://doi.org/10.1016/0167-577X\(95\)00271-5](https://doi.org/10.1016/0167-577X(95)00271-5).
- [52] N. Jiang, R. Buchanan, F. Henn, A. Marshall, D. Stevenson, and E. Wachsmann, *Materials Research Bulletin*, vol. 29, no. 3, pp. 247–254, 1994, ISSN: 0025-5408. DOI: [https://doi.org/10.1016/0025-5408\(94\)90020-5](https://doi.org/10.1016/0025-5408(94)90020-5).
- [53] S. Adams, *Solid State Ionics*, vol. 136–137, pp. 1351–1361, 2000, ISSN: 0167-2738. DOI: [https://doi.org/10.1016/S0167-2738\(00\)00576-2](https://doi.org/10.1016/S0167-2738(00)00576-2).

- [54] S. Adams, *Journal of Power Sources*, vol. 159, no. 1, pp. 200–204, 2006, ISSN: 0378-7753. DOI: <https://doi.org/10.1016/j.jpowsour.2006.04.085>.
- [55] A. K. Bera and S. M. Yusuf, *The Journal of Physical Chemistry C*, vol. 124, no. 8, pp. 4421–4429, 2020. DOI: 10.1021/acs.jpcc.9b11191.
- [56] K. S. Chikara, A. K. Bera, A. Kumar, and S. M. Yusuf, *ACS Applied Electronic Materials*, vol. 5, no. 5, pp. 2704–2717, 2023. DOI: 10.1021/acsaelm.3c00176.
- [57] T. Saito et al., *J. Mater. Chem. C*, vol. 10, pp. 17 925–17 935, 47 2022. DOI: 10.1039/D2TC03718A.
- [58] N. Kamijo et al., *Journal of the Physical Society of Japan*, vol. 55, no. 7, pp. 2217–2231, 1986. DOI: 10.1143/JPSJ.55.2217.
- [59] A. Levina, A. I. McLeod, and P. A. Lay, *Chemistry – A European Journal*, vol. 20, no. 38, pp. 12 056–12 060, 2014. DOI: <https://doi.org/10.1002/chem.201403993>.
- [60] D. O. Scanlon, A. Walsh, B. J. Morgan, and G. W. Watson, *The Journal of Physical Chemistry C*, vol. 112, no. 26, pp. 9903–9911, 2008. DOI: 10.1021/jp711334f.

CHAPTER 6

Summary

In all-solid-state battery (ASSBs) and solid oxide fuel cell (SOFC) systems, the solid electrolyte plays a key role, enabling ion transport between the electrode components. For this, a solid electrolyte is required to exhibit a high ionic conductivity and good interfacial contact with the electrodes, in addition to other stability attributes. In this thesis work, the NASICON-based ceramic system is designed to achieve a high ionic conductivity. Whereas, the polymer-ceramic composite with $(\text{PEO})_{15}\text{-NaNO}_3\text{-}x$ wt% NASICON has been developed to balance conductivity and mechanical compliance.

In the ceramic NASICON system, the prototype composition, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, was tuned by adjusting the Si/P ratio (2.0/1.0, 2.4/0.6, and 2.2/0.8) and scandium substitution at the Zr site. Accordingly, the three compositions of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$, and $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ were formulated to understand the effect of compositional and structural parameters on the bulk conductivity of these samples. The influence of synthesis routes was also examined by employing two preparation methods for sample synthesis, i.e., the solid state reaction method (SSR) and the hydrothermal-based solid state reaction method (HT-SSR). The objective of using two different routes was to improve the grain boundary conductivity by optimizing sintering conditions in the SSR method and by lowering calcined particle powder size in the HT-SSR method. Among all compositions, HT-SSR-prepared $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ showed the highest room temperature conductivity of 3.2 mS/cm. It has been understood that this conductivity improvement

is due to an overall increment in both its bulk and grain-boundary conductivities. Figure 6.1 compares the Arrhenius plot of the present $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ HT-SSR with other reported well-known Na^+ -ion conductors.

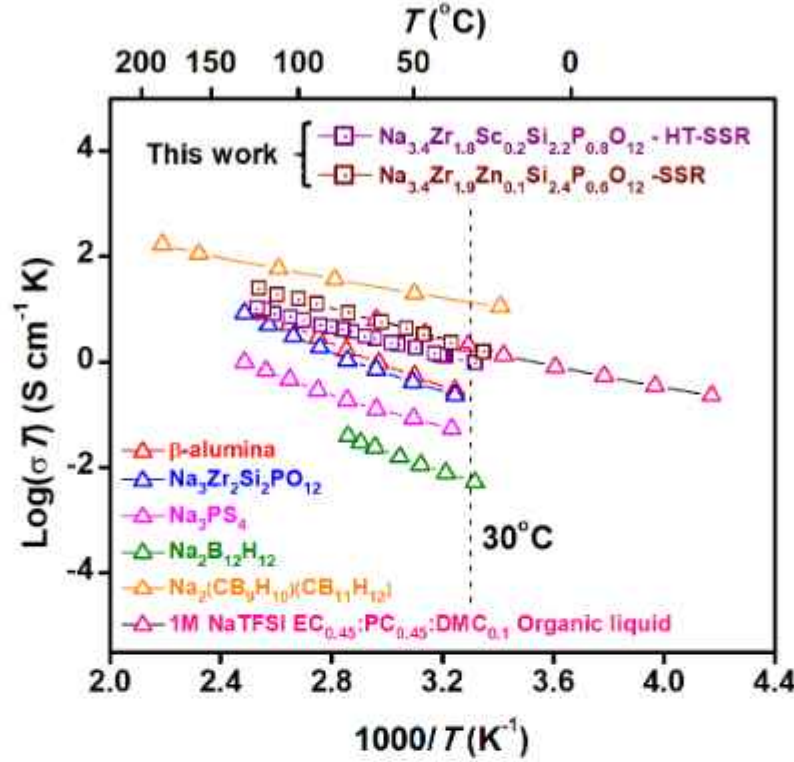


Figure 6.1: Comparison of Arrhenius plot of well-known Na^+ -ion type conductors with NASICON compositions prepared in this work. [1], [2], [3]

The electrochemical performance of the $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ composition was also tested to check the feasibility of its application. It has been observed that the said material displays a good electrochemical stability with Na metal and consistent cycling performance in a solid $\text{Na}|\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}|\text{Na}$ symmetrical cell.

For the composite polymer electrolyte preparation, three optimized NASICON compositions were chosen as fillers: $\text{Na}_{3.4}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$, $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Nb}_{0.1}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ and $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$, each prepared by distinct synthesis route. Among all three compositions, the $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ exhibited the highest RT conductivity of 5.27 mS/cm, while the Nb- and Sc- doped samples displayed a value of ~ 3.42 and 3.19 mS/cm, respectively. The temperature-dependent conductivity of

$\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ composition is also displayed in Figure 6.1. The comparison of the ceramic compositions prepared in this work with $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and other Na^+ -ion conductors like β -alumina and Na_3PS_4 shows that Sc- and Zn-doped NASICON exhibits superior ionic conductivity.

By using 60 wt% of $\text{Na}_{3.4}\text{Zr}_{1.9}\text{Zn}_{0.1}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ (NZZSP) filler, optimum room temperature conductivity $\sim 10^{-4}$ S/cm was achieved in the composite polymer films. In contrast, at 60 wt% of Nb- and Sc- doped fillers, composites exhibited a conductivity value $\sim 10^{-5}$ S/cm. It was revealed that NASICON, as an active filler, can enhance conductivity by increasing the amorphous phase fraction of the PEO matrix and introducing additional ion-conducting pathways at polymer-ceramic interfaces. However, its effectiveness in facilitating these conduction pathways is strongly governed by filler characteristics such as particle size and bulk conductivity. Furthermore, the electrochemical performance of the optimal $(\text{PEO})_{15}\text{-NaNO}_3\text{-60 wt\% NZZSP}$ composite was evaluated, demonstrating stable behavior, which makes the composite a promising electrolyte candidate for sodium-ion batteries.

The RT conductivities of Zn-, Nb- and Sc- doped NASICON (NZZSP, NZNSP and NZSSP) composites of CE60Zn, CE60Nb and CE60Sc are presented in Table 6.1 alongside other reported composites. The comparison indicates that the CE60Zn composite exhibits higher conductivity at ambient temperature, while the CE60Nb and CE60Sc shows comparable values.

A part of present work also focused on stabilizing the high conducting $\delta\text{-Bi}_2\text{O}_3$ phase for intermediate-temperature SOFC (IT-SOFC) applications. The study identified optimum V concentration for achieving high O^{2-} -ion conductivity, revealing values of $\sim 10^{-1}$ S/cm at 500 °C, within the V range of $x=0.084\text{-}0.090$. We observed that instead of the cubic $\delta\text{-Bi}_2\text{O}_3$ phase, V substitution leads to a rhombohedral phase. Further increase in x range resulted in lower conducting monoclinic phase, with a conductivity value an order of magnitude lower. In the optimized composition, effect of Sr/Ca as co-dopants was also investigated, and it

Table 6.1: Conductivities of Na⁺-ion based polymer electrolytes with composite film synthesized in this work

Compositions	RT conductivity(S/cm)
(PEO) ₁₀ :NaClO ₄ -25 wt% Na ₃ Zr ₂ Si ₂ PO ₁₂	1.7×10^{-5} [4]
10NaCF ₃ SO ₃ -90(0.40PEO- 0.60Na ₃ Zr ₂ Si ₂ PO ₁₂)	5×10^{-4} at 50 °C [5]
10NaI -90(PEO _{0.3} (NaTi ₂ (PO ₄) ₃) _{0.7})	4×10^{-5} at 40 °C [6]
40% Na _{3.4} Zr _{1.8} Mg _{0.2} Si ₂ PO ₁₂ - PEO ₁₂ -NaFSI	4.4×10^{-5} [7]
NaTFSI-PEO ₁₄ +50wt% Na _{3.4} Zr _{1.8} Mg _{0.2} Si ₂ PO ₁₂	6×10^{-5} [8]
(PEO) ₁₅ -NaNO ₃ -60 wt% NZZSP (CE60Zn)	2.20×10^{-4} (this work)
(PEO) ₁₅ -NaNO ₃ -60 wt% NZNSP (CE60Nb)	3.22×10^{-5} (this work)
(PEO) ₁₅ -NaNO ₃ -60 wt% NZSSP (CE60Sc)	2.64×10^{-5} (this work)

was revealed to have conductivity comparable to the optimum V composition. The effect of annealing at 400 and 600 °C /100 h (simulating operation conditions) was also investigated in the synthesized compositions. The single V-doped composition of Bi_{0.913}V_{0.087}O_{1.587} suffered conductivity degradation on annealing, attributed to aging phenomenon. In contrast, the Sr/Ca co-doped Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} and Bi_{0.893}Ca_{0.02}V_{0.087}O_{1.577} compositions showed stabilized conductivity, indicating increased resistance to aging. Additionally, the Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} composition also demonstrated stability under reducing conditions. A comparison of the as-prepared and aged Bi_{0.893}Sr_{0.02}V_{0.087}O_{1.577} composition with other oxide ion conductors is presented in Figure 6.2, indicating that the Sr- doped composition exhibits higher conductivity in the intermediate-temperature range (marked by yellow region).

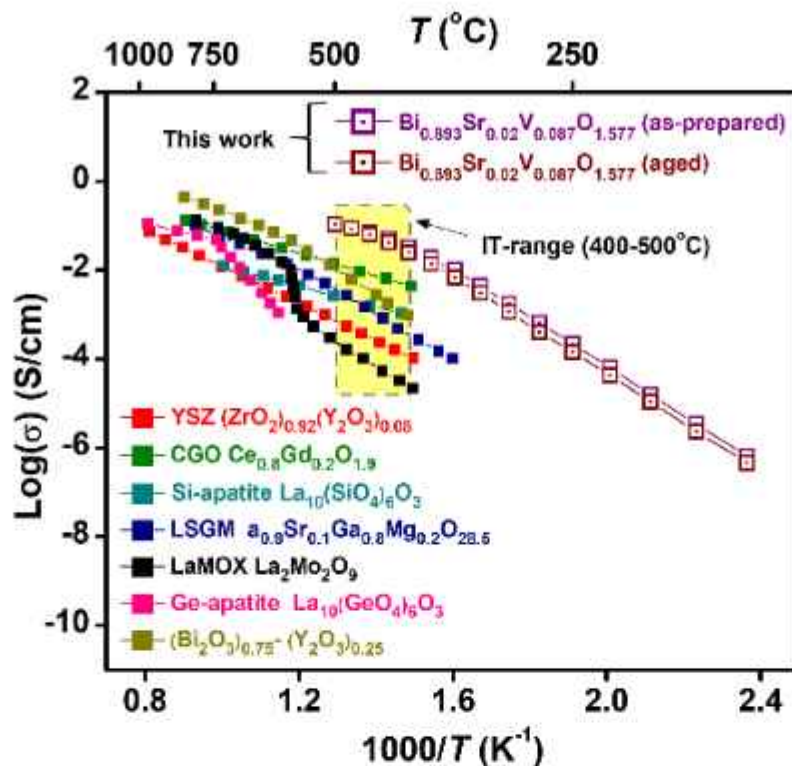


Figure 6.2: Comparison of Arrhenius plot of well-known oxide-ion conductors with Sr/V co-doped compositions synthesized (as-prepared and aged) in this work.[9], [10]

References

- [1] S. Song, H. M. Duong, A. M. Korsunsky, N. Hu, and L. Lu, *Scientific Reports*, vol. 6, no. 1, p. 32 330, Aug. 2016.
- [2] Q. Ma and F. Tietz, *ChemElectroChem*, vol. 7, no. 13, pp. 2693–2713, 2020. DOI: <https://doi.org/10.1002/celec.202000164>.
- [3] Y. He, X. Zhang, C. Liu, Y. Yang, and X. Rui, *Metals Advances*, 2026, ISSN: 3117–7220. DOI: <https://doi.org/10.1016/j.metadv.2026.02.033>.
- [4] A. A. Shindrov, K. V. Mishchenko, O. A. Podgornova, A. A. Shapovalova, and N. V. Kosova, *Solid State Ionics*, vol. 406, p. 116 485, 2024, ISSN: 0167–2738. DOI: <https://doi.org/10.1016/j.ssi.2024.116485>.
- [5] Ncha and A. Dalvi, *Materials Science and Engineering: B*, vol. 289, p. 116 252, 2023, ISSN: 0921–5107. DOI: <https://doi.org/10.1016/j.mseb.2022.116252>.
- [6] M. Dinachandra Singh, A. Dalvi, and D. Phase, *Materials Research Bulletin*, vol. 118, p. 110 485, 2019, ISSN: 0025–5408. DOI: <https://doi.org/10.1016/j.materresbull.2019.05.010>.
- [7] Z. Zhang et al., *J. Mater. Chem. A*, vol. 4, pp. 15 823–15 828, 41 2016. DOI: [10.1039/C6TA07590H](https://doi.org/10.1039/C6TA07590H).
- [8] Z. Zhang et al., *Journal of Power Sources*, vol. 372, pp. 270–275, 2017, ISSN: 0378–7753. DOI: <https://doi.org/10.1016/j.jpowsour.2017.10.083>.
- [9] L. Malavasi, C. A. J. Fisher, and M. S. Islam, *Chem. Soc. Rev.*, vol. 39, pp. 4370–4387, 11 2010. DOI: [10.1039/B915141A](https://doi.org/10.1039/B915141A).
- [10] T. Takahashi, H. Iwahara, and T. Arao, *Journal of Applied Electrochemistry*, vol. 5, no. 3, pp. 187–195, Aug. 1975.

CHAPTER 7

Future Scopes

In NASICON ceramic compositions, future work may be focused on synthesis of Zn-doped and Nb-doped compositions using the SA/HT-SSR method. In addition, a more detailed investigation of the electrochemical performance, including the rate capability, specific capacitance and specific energy density, can be undertaken for the studied NASICON systems. Furthermore, the feasibility and electrochemical performance of full cells, pairing NASICON based cathode materials with studied NASICON electrolytes can also be tested.

In polymer-ceramic composites system, a series with variation of Nb- and Sc-filler % can be explored to understand the optimum filler concentration and corresponding effect on conductivity. Additionally, composites can also be prepared with alternative salts like NaTFSI combined with Zn- and Nb- doped NASICON fillers. Moreover, the mechanical strength can also be characterized to better understand the effect of filler concentration in composites. In addition, a detailed investigation of the electrochemical performance, including the rate capability, specific capacitance, and specific energy density, can be undertaken.

In V-Bi₂O₃-based system, different dopants can be explored to enhance conductivity of high V-concentration composition, which intrinsically shows better aging resistance. The conductivity and transference number can be measured in fuel cell setup to understand the practical working. Furthermore, the feasibility of pairing of these optimized compositions with doped cerium oxide to develop bilayer type electrolytes can also be attempted.

Publications and Conferences

List of Publications

- Karmalkar, D. N.; Dutta, D.; Bera, A. K.; Yusuf, S. M.; Pahari, B. Synthesis of High Na⁺ Ion-Conducting NASICON-Based Electrolytes and Insights from Diffraction and Positron Annihilation Lifetime Spectroscopy Studies. *J. Phys. Chem. C* 128 (2): 768-777, 2024.
- Karmalkar, D. N.; Priolkar, K. R.; Chikara, K. S.; Bera, A. K.; Yusuf, S. M.; Pahari, B. Enhanced Phase Stability and Oxide-Ion Conductivity in V- and Sr/Ca-Codoped Bi₂O₃ Ceramics. *J. Phys. Chem. C* 129 (1): 107-120, 2025.
- Karmalkar, D. N.; Dutta, D.; Kumar, A.; Dey, K. K.; Pahari, B. Electrochemical Performance of PEO–NaNO₃–NASICON Polymer–Ceramic Composite Electrolytes: The Roles of Composition and Particle Size of Ceramic Filler. *J. Phys. Chem. C*, 129 (46): 20495-20505, 2025.

List of Conferences attended

- Presented a poster titled ‘Optimizing the Sodium-ion Conductivity of NASICON based electrolytes’ and an oral presentation at 66th DAE conference held at BITS, Mesra, December 18-22, 2022.
- Presented a poster titled ‘Vanadium doped bismuth oxides as fast oxide-ion conducting solid electrolytes at ICAM-2023 conference, February 20-24, 2023.
- Presented a poster titled ‘Exploring high Na⁺ ion conducting NASICON-based electrolytes: An investigation using Diffraction and Positron Annihilation spectroscopy’ at DAE-BRNS theme meeting on Nuclear probes for

material, medicine and industry (NPMMI) at BARC, Mumbai, June 7-8, 2024.