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^{23}Na and ^{29}Si NMR Investigation of Na-SrSiO₃ Superior Ion Conductor

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Abstract. Present work reports the ^{23}Na , ^{29}Si NMR studies on the Sr_{0.55}Na_{0.45}SiO_{2.775} along with PXRD and ionic conductivity studies. NMR results indicate that Sr_{0.55}Na_{0.45}SiO_{2.775} consists of two phases, one being insulating crystalline α -SrSiO₃ and other being a Na⁺ conducting amorphous Na₂Si₂O₅. High temperature heat treatment of Sr_{0.55}Na_{0.45}SiO_{2.775} leads to the crystallization of amorphous phase into different polymorphs of Na₂Si₂O₅ phase.

Keywords: MAS NMR, solid electrolyte, ionic conductivity

PACS: 81.05.Je

INTRODUCTION

Recent report of a new family of layered monoclinic structured oxides bearing a generic formula of Sr_{1-x}Na_xSiO_{3-0.5x} has received intense attention due to their high ionic conductivity of 0.01 S cm⁻¹ only at 525 °C [1]. The nature of ionic conduction was proposed in terms of O²⁻ motion through oxygen vacancies created by A-site doping and located within the Si₃O₉ units between Sr and Na layers. Follow up studies showed that Na hardly substitute Sr sites rather the composition appears as a two-phase mixture, consisting of a crystalline SrSiO₃ phase and an amorphous Na₂Si₂O₅ phase (AM–Na₂Si₂O₅). The SrSiO₃ phase is an insulator while the AM–Na₂Si₂O₅ phase is a good Na⁺-ionic conductor. Therefore, high conductivity observed in Sr_{1-x}Na_xSiO_{3-0.5x} is essentially caused by the amorphous Na₂Si₂O₅ phase. AM–Na₂Si₂O₅ is known as an unstable phase at elevated temperatures shows amorphous to crystalline phase transformations resulting in reduction in Na⁺ motion, and thus conductivity degradation. Here we report ^{23}Na and ^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) results to identify the crystalline/amorphous phases in Sr_{0.55}Na_{0.45}SiO_{2.775} (SNS45) and in a devitrified SNS45 sample.

EXPERIMENTAL

Sample with nominal composition of Sr_{0.55}Na_{0.45}SiO_{2.775} was synthesized by a solid state reaction method from stoichiometric amounts of SrCO₃, Na₂CO₃ and SiO₂ powders which were thoroughly ground and heated to 1050 °C in air for 20 h [1]. A devitrified form of SNS45 was obtained after heating it to 580 °C further for 20 h. Pure amorphous Na₂Si₂O₅ was prepared by quenching the melt (at 900 °C) of stoichiometric amounts of starting materials. The phase composition of each of the samples was examined with powder X-ray diffraction with Cu-K_α radiation ($\lambda=1.5418$ Å) in the range of $2\theta=10^\circ-70^\circ$. The conductivity of the samples was determined by Impedance measurements at 500 °C using an Impedance analyzer. All solid state magic-angle spinning (MAS) NMR experiments were carried out at 11.7 T using Bruker Avance-III 500 MHz spectrometer loaded with 3.2 mm, and 7 mm Bruker probes and sample filled zirconia rotors were spun at 22 and 6 kHz MAS for ^{23}Na and ^{29}Si NMR respectively. The ^{23}Na spectra are calibrated with respect to 1M NaCl solution and ^{29}Si chemical shifts are quoted relative to neat tetramethylsilane (TMS) respectively.

RESULTS AND DISCUSSION

XRD and Ionic Conductivity

A stack plot of room temperature powder X-ray diffraction patterns (PXRD), recorded for the samples studied in this work, is shown in the Fig. 1. The PXRD pattern of the sample SNS45 was indexed in the monoclinic space group C12/c1 with lattice cell parameters matching with the previously reported values [1]. No spurious reflections can be identified in the sample. PXRD pattern of SNS45-580 °C/20 h and AM-Na₂Si₂O₅ 580 °C/20 h show additional reflections due to formation of recrystallized phases. PXRD pattern of the AM-Na₂Si₂O₅ exhibits pure amorphous signature.

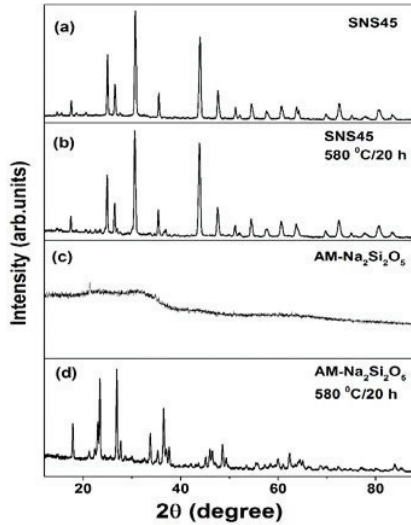


FIGURE 1. Powder XRD patterns of (a) SNS45, (b) SNS45-580 °C/20 h (c) AM-Na₂Si₂O₅ and (d) AM-Na₂Si₂O₅ 580 °C/20 h.

Ionic conductivity values of the samples SNS45 and AM-Na₂Si₂O₅ at 500 °C obtained from impedance measurements are 7.1×10^{-4} and 1.2×10^{-3} S cm⁻¹ respectively. The absolute value of conductivity of the pure AM-Na₂Si₂O₅ is higher than the conductivity of the sample SNS45. The conductivity value of SNS45 is in agreement with the data reported for the same nominal composition prepared by Tealdi et. al [2].

²⁹Si NMR

²⁹Si (nuclear spin $I=1/2$) MAS NMR spectra of SNS45, SNS45-580 °C/20 h, AM-Na₂Si₂O₅ and AM-Na₂Si₂O₅ 580 °C/20 h are plotted together in the Fig. 2(a, b, c and d). ²⁹Si spectrum of SNS45 contains a broad peak centered at -88.0 ppm and another sharp resonance at -85.0 ppm. Fig. 2(c) shows the ²⁹Si spectrum of AM-Na₂Si₂O₅ containing one broad peak at -88.0 ppm confirming that same AM-Na₂Si₂O₅ phase is present in SNS45 and other sharp peak is due

to crystalline SrSiO₃. ²⁹Si MAS NMR spectra of devitrified SNS45-580 °C/20 h and AM-Na₂Si₂O₅ 580 °C/20 h samples clearly show the appearance of several crystalline phases along with broad background due to amorphous phase [Fig. 4(b, d)]. Based on the previously reported chemical shift positions [3], we assign resonances at -94.5 ppm as crystalline α-Na₂Si₂O₅ phase, -88.5 ppm as one Si environment of crystalline β-Na₂Si₂O₅ phase, line at -90.5 ppm as one Si environment of crystalline δ-Na₂Si₂O₅ and line at -86.5 ppm as another Si environment of β-Na₂Si₂O₅ respectively. The relative amounts of α-, β-, δ-Na₂Si₂O₅ phases are significantly different in SNS45-580 °C/20 h compare to AM-Na₂Si₂O₅-580 °C/20 h sample.

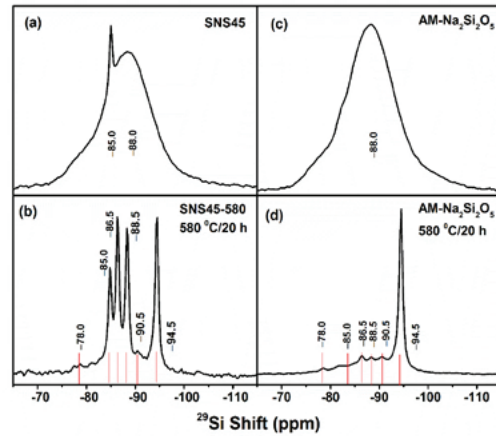


FIGURE 2. ²⁹Si NMR spectra of (a) SNS45, (b) SNS45-580 °C/20 h, (c) AM-Na₂Si₂O₅ and (d) AM-Na₂Si₂O₅ 580 °C/20 h.

²³Na NMR

The ²³Na (nuclear spin $I=3/2$) MAS NMR spectra of the samples studied in this work are plotted in Fig. 3(a, b, c and d). The ²³Na spectrum of SNS45 displays a broad line shape with a long tail at low frequency side similar to AM-Na₂Si₂O₅ in Fig. 3(c). The long tail at the low frequency end results from a distribution of quadrupolar couplings and indicates the presence of significant structural disorder and a range of Na sites. ²³Na spectra of SNS45 and AM-Na₂Si₂O₅ look almost similar indicating that the ²³Na signal in SNS45 is solely due to AM-Na₂Si₂O₅ phase. This observation discards the possibility of Na doping at Sr-sites.

²³Na spectra of SNS45-580 °C/20 h and AM-Na₂Si₂O₅-580 °C/20 h show overlap of more than one phase. To know about the phases that are present in ²³Na spectrum of SNS45-580 °C/20 h, we have performed the deconvolution using DM-fit [4] and the deconvoluted phases are shown in the Fig. 4. To model

the glass/amorphous phase a Czjzek and Gaussian distributions were assumed, the average isotropic ^{23}Na

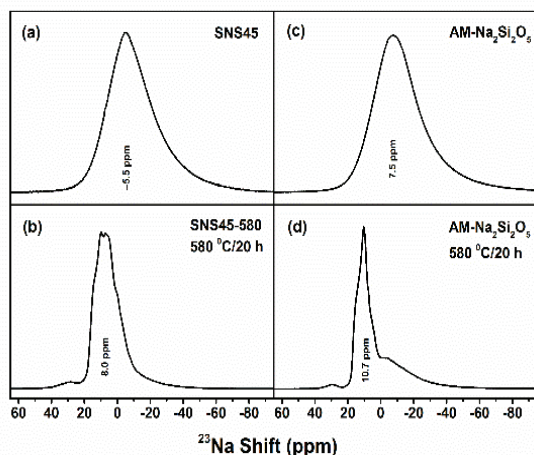


FIGURE 3. ^{23}Na NMR spectra of (a) SNS45, (b) SNS45-580 °C/20 h, (c) AM- $\text{Na}_2\text{Si}_2\text{O}_5$ and (d) AM- $\text{Na}_0\text{Si}_2\text{O}_5$ 580 °C/20 h.

chemical shift (δ_{iso}), and root-mean-square (rms) quadrupolar product $C_{Q\eta} = C_Q(1 + \eta^2/3)^{1/2}$ are estimated. Here C_Q and η denote quadrupolar coupling constant and asymmetry parameter of the electric field gradient respectively. All other crystalline phases are modeled with second order quadrupolar line shape to obtain isotropic position (δ_{iso}) and quadrupolar coupling constant C_Q and η . For AM- $\text{Na}_2\text{Si}_2\text{O}_5$ phase, quadrupolar product is estimated as 2.9 MHz. For remaining phases, the best fitted data are listed in TABLE 1. All polymorphs of $\text{Na}_2\text{Si}_2\text{O}_5$ are clearly detected in SNS45-580 °C/20 h sample and this observation is consistent with ^{29}Si NMR results.

TABLE 1. Best fit parameters of ^{23}Na MAS NMR for the sample SNS45-580 °C/20 h

Phases	δ_{iso} (± 0.5 ppm)	C_Q (MHz)	η_Q
α - $\text{Na}_2\text{Si}_2\text{O}_5$	17.0	1.89	0.83
β - $\text{Na}_2\text{Si}_2\text{O}_5$ (1)	9.3	2.19	0.56
β - $\text{Na}_2\text{Si}_2\text{O}_5$ (2)	16.3	2.37	0.75
δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (1)	16.3	1.16	0.45
δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (2)	7.6	2.54	1.0

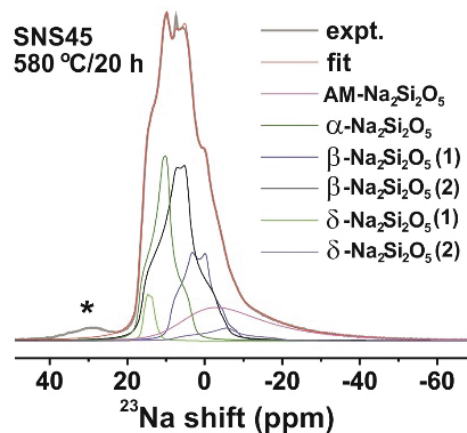


FIGURE 4. ^{23}Na NMR spectrum of SNS45-580 °C/20 h along with deconvoluted phases shown in color lines. * sign indicate the outer satellite transition.

CONCLUSIONS

The ^{23}Na , ^{29}Si MAS NMR results presented here clearly demonstrate that the solid-state NMR is a uniquely useful tool for identifying the phases in Na-Sr SiO_3 system. The NMR results showed that the $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ consists of a crystalline SrSiO_3 phase with zero Na-doping and a glass/amorphous $\text{Na}_2\text{Si}_2\text{O}_5$ phase. Hence high ionic conductivity of $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ is basically originated from the glass/amorphous $\text{Na}_2\text{Si}_2\text{O}_5$ phase. High temperature heat treatment of $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ and AM- $\text{Na}_2\text{Si}_2\text{O}_5$ resulted into amorphous-to-crystalline phase transformation but in slightly different ways. The conducting amorphous phase of $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ transforms into different polymorphs of $\text{Na}_2\text{Si}_2\text{O}_5$, namely α -, β -, δ - $\text{Na}_2\text{Si}_2\text{O}_5$. Whereas, pure amorphous $\text{Na}_2\text{Si}_2\text{O}_5$ preferably recrystallized into α - $\text{Na}_2\text{Si}_2\text{O}_5$.

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