Important influence of Bi deficiency on the conducting property of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ perovskite oxide

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Important Influence of Bi Deficiency on the Conducting Property of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ Perovskite Oxide

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Abstract. Recently it has been reported that low levels of Bi nonstoichiometry (only ±1 atomic %) in the nominal starting composition of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) ceramics can lead to dramatic changes in the conduction property. Present article present the results of powder XRD, $^{23}$Na MAS NMR and impedance spectroscopy in nominal starting compositions, Na$_{0.5}$Bi$_{0.5+x}$TiO$_{3+3x/2}$ with $x = 0.0$ and $-0.02$. Room temperature XRD data analysis indicates both NBTs have a rhombohedral (space group $R3c$) structure. While, $^{23}$Na MAS NMR results demonstrate a complex local structure and significant disordering of Na coordination environment. Impedance spectroscopy reveals high levels of oxide-ion conduction in NBT. 2 at-% Bi-deficient NBT (Na$_{0.5}$Bi$_{0.48}$TiO$_{2.97}$) exhibits higher conductivity of $\sigma \sim 1.3 \times 10^{-4}$ S/cm at 500 °C and activation energy, $E_a = 0.85$ eV. Present results therefore substantiate the A-site nonstoichiometry sensitive electrical property of NBT.

1. INTRODUCTION

The perovskite oxide Na$_{0.5}$Bi$_{0.5}$TiO$_3$ based solid solution material is one of the extensively studied piezoelectric material. It replaces well-known lead zirconate titanate [Pb(Zr$_{1-x}$Ti$_x$)O$_3$, PZT] for applications in actuators, sensors, and transducers [1]. There is a considerable amount of controversy on the room temperature crystal structure of NBT. A rhombohedral structure ($R3c$) was confirmed by neutron diffraction studies [2]. Later high resolution synchrotron powder X-ray diffraction data proposed a monoclinic structure with space group $Cc$ [3]. In addition to that it is observed that the average structure determined by neutron and x-ray diffraction is different from the complex local structure studied by extended x-ray absorption fine structure (EXAFS) analysis [4]. The complex nature of the local structure has profound impact on the perceived global structure and ferroelectric properties. Results of transmission electron microscopy (TEM), pair distribution function (PDF) analysis are also recently reported by different groups. But true structure is not understood yet.

Interest in NBT has expanded recently soon after the discovery of dramatic influence of A-site nonstoichiometry on the conduction property by Li et al. [5]. The reported NBT with general formula Na$_{0.5}$Bi$_{0.5+x}$TiO$_{3+3x/2}$ is an oxygen-ion conductor for $x = 0.0$ (NBT). Significantly higher oxygen-ion conductivity $\sim 10^{-3}$ S cm$^{-1}$ at 500 °C is measured for $x = -0.01$ (NB$_{0.49}$T) composition. Bi excess composition with $x = 0.01$ (NB$_{0.51}$T) whereas is an insulator [5]. High oxygen ion conductivity in NBT and NB$_{0.49}$T is attributed to the high oxide-ion mobility associated weak Bi-O bonds. This report has opened a new application possibility of NBTs as electrolyte material for intermediate temperature solid oxide fuel cells (ITSOFC) because total conductivity of NB$_{0.49}$T is higher than the well-known SOFC electrolyte, yttria-stabilized zirconia (YSZ) [6]. Therefore, it is also important to understand how such a small compositional change in the A-site stoichiometry of the undoped perovskite can induce high levels of oxygen-ion conductivity. In this article, we present the results of powder XRD, $^{23}$Na MAS NMR and impedance spectroscopy.
in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ with $x = 0.0$ and $-0.02$. Local structural disorder in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples is observed and high conductivity is measured.

2. EXPERIMENTAL

Polycrystalline samples of nominal compositions of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ with $x = 0.0$ and $-0.02$ were prepared by solid state reaction methods. Highly pure preheated reagents of Na$_2$CO$_3$, Bi$_2$O$_3$ and TiO$_2$ were used as raw materials. Stoichiometric amounts were first mixed in isopropanol, dried, and then calcined at 800 °C for 2 h in air. The calcined powders were then ground properly and then calcined for second time at 850 °C for another 2 h. Finally calcined powders were pressed in a die and pellets were sintered at 1150 °C for 2 h. While sintering all pellets were covered with calcined powder of the same composition.

Powder x-ray diffraction method (Rigaku) was applied to identify the room temperature phase structure and phase purity of the samples using Cu K$_\alpha$ radiation. The lattice parameters were refined using FullProf software. The total electrical conductivity ($\sigma$) of NBT samples at different temperatures were determined by analyzing the electrochemical impedance spectroscopy (PSM1735–NumetriQ, make: Newtons4th Ltd, UK) data. An ac amplitude of 0.5V and the frequency range of 10 Hz-1 MHz were used to record impedance data. The samples were coated with commercial Ag paste on the parallel surfaces and fired at 500 °C for 2 h before impedance measurements. $^{23}$Na magic angle spinning (MAS) NMR experiments were done using Bruker Avance III 500 MHz spectrometer. $^{23}$Na spectra were recorded using a short single radio frequency (r.f.) pulse (0.45 $\mu$s with r. f. amplitude of 92 kHz) and a relaxation delay of 1 s. 1M NaCl solution was used to calibrate $^{23}$Na spectra.

3. RESULTS AND DISCUSSIONS

3.1 XRD analysis

XRD patterns of as-prepared Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples with $x = 0.0$ and $-0.02$ are plotted in the left panel of the figure 1 which exhibits identical Braggs peaks. Regardless of the considerable amount of debates on the actual room temperature crystal structure of NBT, the rhombohedral structure with space group $R3c$ is still widely considered model to fit polycrystalline phase.

**FIGURE 1.** Left panel: Stack plot of powder XRD patterns of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples ($x = 0.0, -0.02$). Right panel: Le Bail profile fit of Na$_{0.5}$Bi$_{0.5}$TiO$_3$. 

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We have carried out Le Bail profile fitting of XRD patterns of Na$_{0.5}$Bi$_{0.5+x}$TiO$_{3+3x/2}$ samples using rhombohedral unit cell. One representative fit is displayed in the right panel of the figure for Na$_{0.5}$Bi$_{0.5}$TiO$_3$ sample. Refined lattice parameters values are $a = 5.4930$ Å, $c = 13.5026$ Å. They are in close agreement with the previous reports [2].

### 3.2 $^{23}$Na MAS NMR

Figure 2 shows the centre band (CB) region of the $^{23}$Na MAS NMR spectrum recorded in the two NBT compounds. Both the spectrum has similar line shape, peak position (-4.0 ppm) and full width at half maximum height (4.0 ppm). This implies that the local coordination environment of Na did not change significantly in the Bi-deficient compound. $^{23}$Na is a quadrupolar nucleus with spin $I=3/2$ and is thus subject to quadrupole interactions with electric field gradients (EFG) which is a structural parameter determined by the local symmetry. Nuclear quadrupolar interaction causes broadening and distortion of the spectral peaks and displacement from their isotropic chemical shift position. MAS can narrow the resonances but the second-order quadrupolar broadening cannot be completely removed. Hence MAS CB will be a second order quadrupole perturbed powder pattern. Both $^{23}$Na MAS NMR spectrum do not display characteristic second order quadrupolar line shapes. Rather they display a broad line shape with a long tail at the low frequency side. The long tail at the low frequency-end results from a distribution of chemical shifts and/or quadrupolar couplings, as would be expected from disordered phase. Thus present $^{23}$Na MAS NMR results directly displays the local structural disorder in NBT compounds.

![FIGURE 2. $^{23}$Na MAS NMR spectrum in Na$_{0.5}$Bi$_{0.48}$TiO$_{2.97}$ and Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples recorded with MAS frequency of 30 kHz](image)

### 3.3 Conductivity

The total conductivity of the Na$_{0.5}$Bi$_{0.5+x}$TiO$_{3+3x/2}$ samples was determined from the AC impedance data recorded in the temperature range of 50-500 °C. All the data were corrected for sample geometry (thickness/area of pellet) and analyzed with EIS spectrum analyzer software. Typical Nyquist plots (complex impedance plane, $Z^*$ plots) prepared from 400 °C impedance data are shown in the figures 3(a) and 3(d) for Na$_{0.5}$Bi$_{0.48}$TiO$_{2.97}$ and Na$_{0.5}$Bi$_{0.5}$TiO$_3$, respectively. Both $Z^*$ plots show a large arc in the measured frequency range of 1 Hz-1 MHz. The large arc was modelled to a single parallel resistor-constant phase element (R-CPE) in the first attempt. But fittings were not satisfactory. Acceptable fittings of experimental $Z^*$ throughout the temperature range were obtained using an equivalent circuit which is shown in the figure 3(g). Figures 3(b, c, e, f) shows the variations of impedance and phase angle with frequency along with the fits. Values of conductivities for both the sample were calculated by $\sigma = 1/R_3$. The Arrhenius plot of the temperature dependence of the conductivity [figure 3(h)] shows both the compound are conducting with activation energy, $E_a = 0.85$ eV. The maximum conductivity of $\sigma \sim 1.3 \times 10^{-4}$ S/cm and $8.8 \times 10^{-5}$ S/cm are determined at 500 °C in the compound Na$_{0.5}$Bi$_{0.48}$TiO$_{2.97}$ and Na$_{0.5}$Bi$_{0.5}$TiO$_3$, respectively. Present conductivity values are slightly smaller compared to the earlier report [5].
4. SUMMARY

Sodium bismuth titanates, Na$_{0.5}$Bi$_{0.5-x}$TiO$_{3-\delta/2}$ with $x = 0.0, -0.02$ have been synthesized. Bulk and local structure are analyzed by powder XRD and $^{23}$Na MAS NMR. Finally conductivity in the temperature range 50-500 °C has been measured by impedance spectroscopy. Le Bail analysis of XRD patterns indicates a rhombohedral structure. $^{23}$Na MAS NMR results reveals disordered local coordination environment of Na. Both NBTs are found conducting as confirmed by electrochemical impedance spectroscopy results. Higher conductivity is measured in the Bi deficient compound of Na$_{0.5}$Bi$_{0.5}$TiO$_{3-\delta}$. Further information about the composition and temperature dependent local structure of the Na$_{0.5}$Bi$_{0.5+x}$TiO$_{3-\delta/2}$ can be extracted from $^{23}$Na MAS NMR and Bi-edge EXAFS studies. We anticipate that these results will help to clarify the local structural role on the conduction property.

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