Influence of excess sodium addition on the structural characteristics and electrical conductivity of $Na_{0.5}Bi_{0.5}TiO_3$

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ABSTRACT

The current study investigates the influence of adding excess Na on the structure and conductivity of $Na_{0.5}Bi_{0.5}TiO_3$. Polycrystalline bulk samples were prepared via conventional solid-state reaction method. XRD confirmed the presence of rhombohedral perovskite as a primary phase in all the samples. SEM revealed the existence of secondary phases which were found to increase considerably with the higher addition of excess Na. Chemical analysis via EDXS indicates Na deficiency in the sintered sample of stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$, while the average Na/Bi molar ratio found to be more than unity in all the Na-excess compositions. Impedance spectroscopy studies showed at least 3 orders of magnitude conductivity difference between the Na-excess and pure $Na_{0.5}Bi_{0.5}TiO_3$ samples. The bulk conductivity was found to increase with the addition of excess Na, which was attributed to the increase in oxygen vacancy. Although partial substitution of Na for A-site Bi appears to be a promising strategy for the conductivity enhancement, these compositions show significant segregation of secondary phases on excess Na addition.

1. Introduction

Oxides with fast oxygen-ion conductivity are crucial for the development of various high-temperature energy technologies such as solid oxide fuel cells, oxygen separation membranes, oxygen sensors, oxygen pumps [1]. Apart from developing already known materials such as ZrO_2, CeO_2, etc. a vast amount of research in recent times aimed at discovering a new class of materials with superior oxygen-ion conductivity [1–4]. In a recent work, the high leakage conductivity observed in a few $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) based compositions was demonstrated to be caused by oxygen-ion conduction. NBT is a well-known relaxor ferroelectric with the potential to replace lead-based materials in a variety of applications such as electromechanical transducers, acoustic sensors, multilayer capacitors, etc. [5]. The discovery of oxygen-ion conductivity in these ferroelectric perovskite oxides opens up the possibilities of utilizing them for the electrolyte application in solid oxide fuel cells [6]. In the present work, the influence of partial substitution of Na for A-site Bi on the structure and conductivity of NBT has been explored.

Nominal NBT composition possesses a distorted perovskite structure with multiple phase transitions. The high-temperature cubic phase transforms to tetragonal phase at ~540 °C, whereas a complex low-temperature phase starts to appear around 300 °C on cooling. The tetragonal phase was found to co-exist with the low-temperature phase in

a broad temperature range (~250 °C). In earlier work, Jones et al. structurally refined the neutron powder diffraction data of the low-temperature phase in NBT to be rhombohedral with a space group of R3c [7]. However, in a more recent study, a monoclinic structure with a space group Cc was found to be a much better fit of the high-resolution synchrotron X-ray diffraction data of this phase [8]. Further, it was shown that the local atomic structure deviates from the average structure of NBT possibly because of a random distribution of Na and Bi and significant disorder occurring as a result of complex octahedral tilting and different cations displacements [8,9]. The presence of several lattice disorders in NBT was reported to facilitate the stabilization of high-temperature cubic phase and has a significant influence on the oxygen diffusional properties of NBT based compositions [6,10].

According to Li et al. [6], a dramatic enhancement in oxygen-ion conductivity can be achieved by introducing a low-level of A-site cation non-stoichiometry (< 1 at.%) in NBT. In particular, Bi-deficient or Na-excess NBT compositions show 3–4 orders of magnitude lower resistivity compared to Bi-excess or Na-deficient NBT compositions. The highly conductive Bi-deficient compositions were reported to exhibit activation energy of 0.8–0.9 eV and 0.4–0.5 eV at temperatures below and above 320 °C, respectively. The origin of oxygen-ion conductivity in these compositions was attributed to the high polarizability of Bi^{3+} cations (owing to the presence of $6s^2$ lone-pair electronic structure) which facilitates considerable lattice relaxation and displacement of

cations away from the mobile oxygen-ion. Further, a weak Bi-O covalent bond strength (~343 kJ/mol) enables the fast oxygen-ion migration through the opening of a critical triangle defined by two A-site cations and one B-site cation inside the perovskite lattice of NBT [11]. The high conductivity was also reported for nominal NBT composition and was associated with the generation of oxygen vacancies caused by the loss of a slight amount of Bi_2O_3 during the bulk sample preparation (as given in Eq. (1)).

$$2Bi_{Bi}^{\times} + 3O_O^{\times} \rightarrow Bi_2O_3 + 2V_{Bi}^{///} + 3V_O^{\bullet\bullet} \tag{1}$$
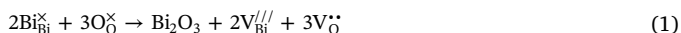
To further enhance the oxygen-ion conductivity, Mg^{2+} was utilized as acceptor dopant on the B-site of NBT. Li et al. [6] tested $Na_{0.5}Bi_{0.49}Ti_{0.98}Mg_{0.02}O_{2.965}$ composition and reported two orders of magnitude improvement in diffusion coefficient compared to nominal NBT at 632 °C. Further, the addition of Mg^{2+} was reported to be beneficial from three perspectives - 1) lowering of grain boundary resistivity, 2) ionic conduction remains dominant to much lower partial pressures of oxygen, and 3) reduction of sintering temperature from 1100 °C to 950 °C. The bulk conductivity in $Na_{0.5}Bi_{0.49}Ti_{0.98}Mg_{0.02}O_{2.965}$ was found to be at least an order of magnitude higher than that of conventional 8 mol.% Y_2O_3-ZrO_2. The above results provide the scope for further conductivity enhancement in NBT by optimizing the chemical composition using an appropriate doping strategy.

Recent density function theory work by He et al. [10] has shown that the entropy effect because of a random distribution of Na and Bi cations at A-site is critical for the stabilization of cubic phase in NBT at high temperature (> 1500 K); however, the A-site cation sublattice ordering may also lead to higher oxygen-ion diffusion. By calculating and correlating the decomposition energies of NBT with various dopants, it was predicted that adding excess Na for A-site Bi (i.e., $Na_{0.54}Bi_{0.46}TiO_{3-\delta}$) can render better phase stability in comparison to compositions having B-site doping. Further, A-site doping of NBT has been computationally shown to lower the large migration barrier which exists because of high binding energy between oxygen-ion and the B-site dopant such as Mg^{2+} and improves the oxygen-ion conduction through a triangle formed by the B-site Ti and A-site Na/Bi. Using ab initio molecular dynamics, the conductivity of $Na_{0.54}Bi_{0.46}TiO_{3-\delta}$ was found to be 30 mS·cm^{-1} at 900 K, which is almost three times higher than that of $Na_{0.5}Bi_{0.49}Ti_{0.96}Mg_{0.04}O_{2.965}$. Moreover, the activation energy for oxygen diffusion was determined to be 0.38 eV which is nearly half of the value found in $Na_{0.5}Bi_{0.49}Ti_{0.96}Mg_{0.04}O_{2.965}$ (0.66 eV). Thus, it was concluded that the excess Na in the A-site of NBT could provide a significant enhancement in ionic conductivity [10]. Following He et al.'s [10] computational work, Wang et al. [12] measured the bulk oxygen-ion conductivity of $Na_{0.54}Bi_{0.46}TiO_3$ using impedance spectroscopy and reported it to be 1.6×10^{-3} S·cm^{-1} at 400 °C. The obtained value was nearly five times higher than that of nominal NBT composition.

As previous studies on NBT primarily looked at diffusion mechanism in Na-excess or Bi-deficient compositions, the effect of the addition of high levels of excess Na (> 1 atm.%) on the phase stability and conductivity of NBT remains unexplored. The present work aims to systematically investigate the influence of adding excess Na in place of Bi on the oxygen-ion conductivity of NBT bulk samples with the stoichiometry of $Na_{0.5+x}Bi_{0.5-x}TiO_{3-\delta}$ (where $x = 0$, 0.02, and 0.06).

2. Experimental

Polycrystalline bulk samples of Na-excess NBT i.e., $Na_{0.5+x}Bi_{0.5-x}TiO_{3-\delta}$ (where $x = 0.02$ and 0.06) were prepared by conventional solid-state reaction method. For comparison, samples for stoichiometric NBT were also synthesized under similar experimental conditions. The stoichiometry of synthesized compositions and their corresponding nomenclature are given in Table 1. The raw materials

Na_2CO_3 (99.50% purity, Alfa Aesar), Bi_2O_3 (99.975% purity, Alfa Aesar) and TiO_2 (99.90% purity, Alfa Aesar) were initially heat treated for 8 h at 300 °C, 180 °C and 800 °C, respectively, to eliminate any adsorbed moisture and/or CO_2, and to ensure correct starting stoichiometry [11]. The stoichiometric amounts of raw materials were weighed and ball-milled using zirconia ball media for 24 h in ethanol with 2 wt% ammonium polyacrylate as a dispersant. The ball-milled slurries were dried overnight at 100 °C, and the dried powders were ground using agate mortar and pestle, and subsequently sieved with a 90 μm mesh. Powders were calcined at 900 °C for 4 h in air followed by ball milling for 24 h and overnight drying at 100 °C.

The calcined powders were initially uniaxially pressed into disk-shaped pellets (8 mm diameter and thickness ~2–3 mm) using approximately 2 wt% polyvinyl alcohol as a binder and then cold-isostatically pressed at 300 MPa for 5 min. All the samples were sintered at 1100 °C for 4 h using dense alumina setters. To avoid Bi vaporization during sintering, pressed pellets were placed on a powder bed and completely covered with the powder of the same composition. Densities calculated using the Archimedes principle were found to be 95% of theoretical density or above for all the samples.

The crystalline phases present in sintered samples were detected by analyzing X-ray diffraction (XRD) pattern collected using a laboratory X-ray diffractometer (Panalytical XPert with line detector) with CuKα incident radiation (λ = 1.54056 Å) in the 2θ range from 10 to 70° using a scan rate of 0.3 s/step and a step size of 0.01°. For the measurement, sintered samples were crushed to fine-sized powder followed by annealing at 400 °C for 3 h to remove residual strain. Refinement of structural parameters was carried out using Rietveld analysis of powder XRD data in the FullProf Program.

The microstructure of both polished and thermally etched pellets was studied using a scanning electron microscope (SEM, CARL ZEISS EVO 50) at an accelerating voltage of 20 kV. The samples were thermally etched at 1000 °C for 1 h. SEM was equipped with an Oxford Link ISIS (Oxford Instruments Ltd., Oxfordshire, UK) Energy Dispersive X-ray Spectroscopy (EDXS) detector.

Impedance spectroscopy technique was used to evaluate the bulk conductivity in polycrystalline ceramic samples as a function of temperature in air. For the impedance measurement, sintered pellets were first polished by silicon carbide papers (up to grit size #1500). Au paste (Siltech Corporation, Bangalore, India) was brushed onto both polished surfaces of the disk-shaped pellet to serve as the electrode. The impedance data acquisition was performed using impedance analyzer (Solartron 1260A, UK) between 500 °C to 700 °C across a frequency range of 1 Hz–32 MHz with an applied voltage of 50 mV. A typical impedance spectrum of an electroded pellet consisted of a high-frequency grain arc, an intermediate-frequency grain boundary depressed semicircle, and a low-frequency electrode arc. The bulk resistance was calculated by fitting the observed impedance spectrum with an analog electric equivalent circuit having three parallel pairs of resistor-constant phase element connected in series. An inductor, L, was used in the electric circuit to account for the inductance from experimental set-up, which was apparent only at high frequencies and at high temperatures.

3. Results and discussion

3.1. Phase analysis by XRD

Fig. 1 shows the XRD profiles collected at room temperature for all the compositions of $Na_{0.5+x}Bi_{0.5-x}TiO_{3-\delta}$ (where $x = 0$, 0.02, and 0.06). XRD pattern revealed the formation of ABO_3 perovskite phase with the rhombohedral symmetry in all the compositions. A weak superlattice reflection at 38°, which is a characteristic of anti-phase rotation of TiO_6 octahedra about $[111]_p$ pseudocubic axis, was also observed in all the XRD profiles [13]. Rietveld method was utilized to refine the lattice parameters of rhombohedral phase using the space group $R3c$. The refined goodness of fit (GOF) parameters, lattice