Study on electrical conductivity and oxygen migration of the oxide-ion conductors $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$

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Abstract. Electrical performance and oxygen relaxation behaviour in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds were investigated. The oxide ion conductivity of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds increased first and then decreased with increasing Mg-doped content. The highest oxide ion conductivity of $4.7 \times 10^{-3} \text{ S cm}^{-1}$ at 773 K was observed for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ compound. A typical relaxation peak in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ samples was observed. The activation energy and pre-exponential factors were determined as (1.0 eV, $4.7 \times 10^{-16} \text{ s}$) and (0.94–1.0 eV, 6.8×10^{-14} – $3.1 \times 10^{-13} \text{ s}$) from internal friction and dielectric relaxation measurement, respectively. The lower oxide ion conductivity in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0.06, 0.08, 0.10$) compounds may arise from the lower vacancy mobility. Judging from the electrical performance and relaxation parameters, although lower-level Mg-doping can improve oxide ionic conductor, oxygen vacancy mobility in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds cannot be improved with increasing Mg-doping content. These results will be meaningful to ameliorate the electrical properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds and understand the relationship between the electrical properties and structure.

Keywords. Dielectric relaxation; internal friction; oxide ionic conductivity; enhanced factors; oxygen vacancy mobility.

1. Introduction

Oxide ionic conductor materials are widely applied in many important technological applications [1–6]. During the last few years, there has been much progress in the study of oxide ion conductors and several different structure oxide ion conductor materials have been investigated to seek better oxide ionic conductivity and electrochemistry stability in solid ionic conductor materials [5,7–11]. Sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, NBT) with a perovskite structure possesses a higher leakage conductivity [12], which originates from the oxide ionic conduction due to Bi-deficiency and oxygen vacancies induced during material processing.

In previously reported results, oxide ionic conductivity of NBT-based materials was improved by the monovalent Na^+ (Ca^{2+} or K^+)-doping on the trivalent Bi^{3+} -site to obtain a higher oxygen vacancy concentration in NBT materials [13–15]. The objective of the present study is to alter the tetravalent Ti^{4+} by divalent Mg^{2+} to determine the effect on the electrical properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds. The complex impedance spectroscopy technique is considered to be a promising non-destructive testing method to analyse the electrical performance and other characterization methods such as internal friction (IF) and dielectric relaxation were used to investigate the oxide ionic microscopic transport mechanism and the factors influencing oxide ion diffusion in oxide-ion conductors $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ were studied [13,16].

2. Experimental

Ceramic samples of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ with perovskite structure were synthesized through the conventional solid-state reaction method from stoichiometric quantities of Na_2CO_3 , MgO , Bi_2O_3 and TiO_2 with a purity of >99%. The detailed synthesis process can be found in ref. [17]: the raw material powders were ball-milled using agate balls for 8 h initially and heat-treated at 1073 K for 12 h. The powders were ball-milled, dried and then pressed into the bar (pellet) sample, which was annealed at 1323 K for 12 h to obtain the measuring samples [17]. The size of the pellet samples used for the electrical performance measurement has the diameter of about 11.4 mm and the thickness of about 2.1 mm. The size of the bar samples for IF measurement is about 45 mm $\times$ 4 mm $\times$ 1.1 mm.

The formation of the desired phase was checked by the powder X-ray diffraction (XRD) technique, recorded at room temperature on a θ/θ Bragg–Brentano X'Pert MPD PRO diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) over a wide range of Bragg angles ($10^\circ \leq 2\theta \leq 80^\circ$) with a step of 0.02° . The electrical measurements were performed using a Ag electrode (Ag paste was printed on the sample pellet and cured at 973 K for about 30 min) by AC impedance spectroscopy in the frequency range from 10 Hz to 1 MHz using an LCR meter (HIOKI IM3536 LCR, Japan). The IF measurements were carried out on a computer-controlled inverted torsion pendulum in the mode of forced vibration with a

Figure 1. The observed XRD patterns at room temperature for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$) compounds.

heating rate of 3 K min^{-1} and a shear strain amplitude of 3×10^{-5} .

3. Results and discussion

XRD patterns of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06, 0.08$ and 0.10) compounds are shown in figure 1. It can be seen that the samples with the MgO -doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds show pure perovskite structures, which indicates that the primary structure is not altered and Mg^{2+} is successfully doped on Ti^{4+} sites and formed $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ solid solutions.

For perovskite structure materials, tolerance factor is an important parameter in the performance and structure stability. The tolerance factor can be calculated from ionic radii as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (1)$$

where r_A and r_B are the mean ionic radii for A and B site cations respectively, and r_O is the radius of oxygen ion (0.140 nm). The radii of Ti^{4+} and Mg^{2+} at the B site (coordination number, $\text{CN}=6$) are 0.061 and 0.072 nm, respectively. The radius of Na^+ at the A site ($\text{CN}=12$) is 0.139 nm, while the Bi^{3+} size ($\text{CN}=12$) cannot be reported. In view of the facts that there are linear relationships between ionic radius and CN [19]. Figure 2 shows the curve of the Bi^{3+} radius with different CNs. In the curve, the Bi^{3+} radii at the CNs (5, 6 and 8) can be obtained from the Shannon's ionic radii table. Based on the linear relationship between the Bi^{3+} ionic radius and CNs [19], the radius of Bi^{3+} ionic radius ($\text{CN}=12$) can be calculated (about 0.144 nm). Furthermore, the tolerance factors of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds can be calculated by equation (1). The tolerance factors of the

Figure 2. The ionic radius against the CN of the Bi^{3+} ion.

Figure 3. The typical impedance spectrum of a $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) sample measured at 498 K.

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06, 0.08$ and 0.10) compounds are 0.990, 0.989, 0.988, 0.987, 0.986 and 0.985, respectively. There is very little change in the tolerance factors for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0, 0.02, 0.04, 0.06, 0.08$ and 0.10) compounds, indicating that there is negligible lattice distortion with the Mg^{2+} -doped on the Ti^{4+} site.

Figure 3 shows the typical impedance spectrum of a $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) sample measured at 498 K. In general, an impedance spectrum includes three different semicircles, considering that the representation of the impedance experimental data in the complex plane provides a semicircle, whose diameter is equal to the value of the electric resistance R . It is similar to that of the perovskite-type ion conductor (Li, La) TiO_3 , showing smaller bulk (grain interior) resistance at high-frequency side, a slightly larger grain-boundary contribution and a tail at the low-frequency side, suggesting blocking of the electrodes for

Figure 4. The AC impedance spectra and the fitting lines of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.98}\text{Mg}_{0.02}\text{O}_{2.98}$ samples at 498 and 548 K in air. An equivalent circuit consisting of the three R -CPE elements in series is shown.

Figure 5. The AC impedance spectra and the fitting lines of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ samples at 498 and 548 K in air. An equivalent circuit consisting of the three R -CPE elements in series is shown.

the mobile ions and that the investigated perovskite-type $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds are ionic in nature [20].

The impedance spectra of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) samples are given in figures 4 and 5, respectively. The impedance spectrum can be fit by an equivalent circuit consisting of three R -CPE elements in series as seen in the inset of figure 4. From the two figures, it can be found that the total fitting lines almost go through every experimental data point. All the fitting parameters are listed in table 1. The values of C_b (10^{-9} F) and C_{gb} (10^{-7} F) in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) samples are representative results for relaxation processes of bulk and grain boundary in ionic conductors [13]. Also, the conductivity can

be estimated from $\sigma = d/(SR)$, where d and S are the sample thickness and electrode area, respectively.

The Arrhenius plots of bulk conductivity σ_b for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0, 0.02, 0.04, 0.06, 0.08$ and 0.10) compounds are displayed in figure 6, while it is difficult to separate from the Arrhenius plots of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds. Thus figure 7 shows the curves of bulk conductivity of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds at 573 K vs. the Mg-doped content x . The bulk conductivity of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds increases with increasing dopant ($x < 0.04$) and then, the bulk conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ begins to decline with further increase in Mg-doping content ($0.04 < x < 0.10$). At $x = 0.10$, the bulk conductivity of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.90}\text{Mg}_{0.10}\text{O}_{2.90}$ sample is close to that of the NBT sample. For the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ ($x = 0.04$) sample, the bulk oxide ionic conductivity at 773 K is observed at $4.7 \times 10^{-3} \text{ S cm}^{-1}$, almost seven times higher than that of the NBT sample ($7 \times 10^{-4} \text{ S cm}^{-1}$) at the same measuring temperature (773 K) [12].

The experimental curves of dielectric loss ($\tan \delta$) changing with measuring temperature in the range from 350 to about 625 K for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06$) samples are given in figures 8, 9 and 10, respectively. An apparent loss peak is observed at around 500 K at the measuring frequency of 0.2 kHz. By increasing the measuring frequency, the peak apparently moves to a higher temperature with decrease in the peak height, indicating that the dielectric loss peaks in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06$) samples originate from the thermally activated process [21]. The dielectric loss peak can be well-fit by the non-linear fitting method [22] as seen in figures 8–10. According to the Arrhenius law $\tau = \tau_0 \exp(E/K_B T)$ and the formula $2\pi f\tau = 1$ (f : measuring frequency) at the dielectric loss peak position, the relaxation parameters (relaxation activation energy E and relaxation time τ_0) can be obtained by changing the frequency measurement. The Arrhenius plots for the dielectric loss peak of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06$) samples are given in the inset of figures 8, 9 and 10, respectively. From the insets, the relaxation parameters of the dielectric relaxation peaks are $E = 0.94 \text{ eV}$, $\tau_0 = 3.1 \times 10^{-13} \text{ s}$ for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.98}\text{Mg}_{0.02}\text{O}_{2.98}$ sample, $E = 0.98 \text{ eV}$, $\tau_0 = 6.8 \times 10^{-14} \text{ s}$ for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample and $E = 1.0 \text{ eV}$, $\tau_0 = 1.14 \times 10^{-13} \text{ s}$ for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.06}\text{O}_{2.94}$ sample, respectively. It can be found that the relaxation time is about $10^{-14} - 10^{-13} \text{ s}$, indicating that the relaxation peaks in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds originate from the point defects diffusion in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds [23].

As we all know that Na_2O and Bi_2O_3 are very volatile under higher temperature condition (1323 K for 12 h) in the sample preparation process it is possible that there are sodium ion vacancies and oxygen vacancies. To explore the mechanism of the relaxation peaks in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds, the IF method was employed as a probe to investigate the relaxation mechanism in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds.

Table 1. Fitting parameters of the impedance data for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0.02, 0.04$) samples at 498 and 548 K.

x	Temperature (K)	R_b (K Ω)	C_b (F)	R_{gb} (K Ω)	C_{gb} (F)	R_{el} (K Ω)	C_{el} (F)
0.02	498	57.3	1.5×10^{-9}	147.6	2.4×10^{-7}	941	1.8×10^{-6}
	548	7.15	1.6×10^{-9}	23.3	4.8×10^{-7}	391	3.4×10^{-6}
0.04	498	32	1.5×10^{-9}	122.8	1.7×10^{-7}	458	3.1×10^{-6}
	548	5.1	1.47×10^{-9}	19.6	2.2×10^{-7}	440	7.6×10^{-6}

Figure 6. The Arrhenius plots of bulk conductivity for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$) compounds. **Figure 7.** The bulk conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$) compounds at 573 K.

The temperature dependence of IF (Q^{-1}) and relative modulus (M) of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ (1 and 4 Hz) samples is presented in figure 11. Three different IF peaks

Figure 8. Temperature variation of dielectric loss ($\tan \delta$) measured at different frequencies and non-linear fitting lines for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.98}\text{Mg}_{0.02}\text{O}_{2.98}$ sample. The Arrhenius plot can be seen in the inset. **Figure 9.** Temperature variation of dielectric loss ($\tan \delta$) measured at different frequencies and non-linear fitting lines for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample. The Arrhenius plot can be seen in the inset.

(designed P_1 , P_2 and P_3 from low temperature to high temperature) were observed. For P_1 peak, the IF peak moves towards a higher temperature region with increasing measurement

Figure 10. Temperature variation of dielectric loss ($\tan \delta$) measured at different frequencies and non-linear fitting lines for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.94}\text{Mg}_{0.06}\text{O}_{2.94}$ sample. The Arrhenius plot can be seen in the inset.

Figure 11. IF Q^{-1} and modulus M vs. temperature for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample measured at different frequencies (1 and 4 Hz) in the temperature range from 300 to 650 K.

frequency and apparent relative soft modulus was found at the peak positions, which indicates that the P_1 peak may correspond to a thermal-activated relaxation process. By changing frequency measurement, the P_1 peak relaxation parameters can be obtained. IF curves and non-linear fitting results of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ compound are shown in figure 12. The Arrhenius plots for the P_1 peak is shown in figure 13. The relaxation parameters $E = 1.0$ eV, $\tau_0 = 4.7 \times 10^{-16}$ s for the P_1 peak are obtained by the linear-fitting method.

To further analyse the formation mechanism of the relaxation P_1 peak in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds, the IF experiments of the different Mg-doping content in the NBT compounds were carried out. Figure 14 shows IF (Q^{-1}) vs. measuring temperature T for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$

Figure 12. IF Q^{-1} vs. temperature for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample at different measuring frequencies in the temperature range from 280 to 480 K. The results of the single peak fitting at 1 Hz are given for demonstration.

Figure 13. The Arrhenius plot for the IF subpeaks (P_1 peak) for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample.

($x = 0, 0.02, 0.04, 0.06$) compounds at 1 Hz. The peak height increases with the increment of Mg-doped content in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x = 0, 0.02, 0.04, 0.06$) compound. Compared with NBT compound, the IF peak height can reach around 0.019 at 1 Hz when the Mg-doped content reaches 4 mol% to form the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.96}\text{Mg}_{0.04}\text{O}_{2.96}$ compound. In addition, it is worth to note that there is a higher peak temperature and height of the P_1 peak in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1.94}\text{Mg}_{0.06}\text{O}_{2.94}$ compound.

According to the electroneutrality principle, when the 0.01 mol Ti^{4+} is substituted by the equivalent Mg^{2+} in the NBT compound, 0.01 mol oxygen vacancies will be introduced into the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds, which indicates that oxygen vacancy concentrations increase with the rise of Mg-doped content in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$

Figure 14. IF (Q^{-1}) vs. temperature in the temperature range from room temperature to about 440 K for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0, 0.02, 0.04, 0.06$) compounds at 1 Hz.

compounds. Based on the point defect theory [24], the IF peak height is proportional to the relaxation units. Thus, the IF P_1 peaks can be employed to reflect oxygen vacancy mobility in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06$) compounds. Considering the relaxation parameters and the dielectric measuring results, the relaxation peaks may be derived from oxygen ions via vacancies short-distance diffusion in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds.

Based on the above results, oxide ion conductivities of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x < 0.04$) samples increase with increasing Mg-doped content. According to the study by Hayashi *et al* [18], the electrical properties of perovskite-type oxide ion conductors mainly depend on the tolerance factor, specific free volume, oxygen deficiency concentration and oxygen vacancy mobility. The tolerance factors of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds are from 0.985 to 0.990 when the value of the Mg-doped content changes from 0.10 to 0, respectively. The tolerance factors of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds are very close to that of the ideal perovskite structure, which indicates that there is very little lattice distortion resulting from Mg^{2+} doped on the Ti^{4+} site. Combined with the tolerance factors and the specific free volume define formula [18], the specific free volume parameters of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0, 0.02, 0.04, 0.06, 0.08, 0.10$) compounds can be calculated as 0.270, 0.272, 0.274, 0.275, 0.277 and 0.278, respectively. When the Mg-doped content raises from 0 to 0.1, the specific free volume increases from 0.270 to 0.278, with a changing rate of 2.9%, indicating that it is helpful for increasing the specific free volume to partially substitute Ti^{4+} ions by Mg^{2+} ions.

In addition to the above factors, oxygen vacancies play an important role in the electrical performance of oxide ion conductors. The bulk conductivity performance of the different structure oxide ion conductors mainly depends on two decisive factors: oxide ion vacancy concentration and oxide ion mobility. Compared with the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ compound, the bulk conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$

(NBT-Mg4) sample is about $8.3 \times 10^{-4} \text{ S cm}^{-1}$ at 673 K, which is lower than that of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample at the same measuring temperature ($1.6 \times 10^{-3} \text{ S cm}^{-1}$ at around 673 K). Compared with the IF curves of NBT-Mg4 and $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample [13], the height of the oxygen relaxation IF peak P_1 in $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample is 0.016 at 1 Hz, which is lower than that of the oxygen relaxation IF peak P_1 in NBT-Mg4 sample at 1 Hz. The lower peak height in the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample reflects the less mobile oxygen vacancy concentration. Thus, the reason for the bulk conductivity of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample is higher than that of NBT-Mg4 sample may be from the better oxygen vacancy mobility in the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ sample, which can be reflected by the higher oxygen migration activation energy in the NBT-Mg4 compound.

Based on the above results, oxygen migration activation energy in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ samples increases with increasing Mg-doping content. Hence, the increasing Mg-doping content does not lead to improved oxygen vacancies diffusion in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$, which is consistent with the results by first-principle calculation. The higher oxide ion diffusion barriers were caused by the Mg^{2+} ions at the B sites in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds, suggesting that there is stronger binding between the oxygen vacancies and Mg^{2+} ions at the B sites. As opposed to the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ compound [13], there is a larger oxide ion relaxation energy in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06$) compound, indicating that the method of the Mg-doped on the Ti-site in the NBT compound makes no contribution to the oxygen vacancy mobility. The prior oxide ion conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) compounds is more inclined to the increase in oxygen vacancy concentration.

However, oxide ion conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compound begins to decline when Mg-doped content exceeds 4 mol%. Although more oxygen vacancies were included in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compound with the increase in Mg-doped content, the IF peak moves to higher temperature when the value of Mg-doped content reaches 0.06 mol%, which indicates that the oxygen vacancy mobility in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.94}\text{Mg}_{0.06}\text{O}_{2.94}$ (NBT-Mg6) compound is inferior to that in the NBT-Mg4 compound. In addition, figure 15 shows the curves of the dielectric loss ($\tan \delta$) vs. frequency for the NBT-Mg4 and NBT-Mg6 samples at 573 K, respectively. By the non-linear fitting, the relaxation time can be obtained by the condition ($\tau = 1/(2\pi f)$) at the peak position and can be seen in the inset. From the inset, the relaxation time of oxygen ion migration in NBT-Mg4 sample is shorter than that of the NBT-Mg6 sample, indicating that there is better oxygen vacancy mobility in the NBT-Mg4 sample [25]. Therefore, the lower oxygen vacancy mobility is the possible reason that the bulk conductivity of NBT-Mg6 compound with more oxygen vacancy content is lower than that of the NBT-Mg4 compound.

According to the reported results [26], there are three different phase structures of the NBT compound in the

Figure 15. The curves of the dielectric loss ($\tan \delta$) vs. frequency for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.04, 0.06$) samples at the measuring temperature of 573 K, respectively. The curves of the relaxation time vs. temperature (T) are given in the inset.

temperature range from room temperature to around 600 K: rhombohedral, orthorhombic and tetragonal phases. From figure 11, the P_2 and P_3 peaks hardly move with changing measuring frequency and there is apparent transform at the peak position in the modulus curve, which indicates that the P_2 and P_3 are the typical phase transition peaks. Therefore, P_2 and P_3 peaks may correspond to the phase transition process of the rhombohedral phase to orthorhombic phase and the orthorhombic phase to tetragonal phase, respectively.

4. Conclusions

1. The $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04, 0.06, 0.08, 0.1$) samples were prepared. The conductivities of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) compounds increase with the increment of Mg-doped content and the conductivity begins to decline when Mg-doped content exceeds 4 mol%. The bulk conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.96}\text{Mg}_{0.04}\text{O}_{2.96}$ sample at 773 K is around $4.7 \times 10^{-3} \text{ S cm}^{-1}$. The relaxation parameters measured by the dielectric relaxation method are $E=0.94\text{--}1.0 \text{ eV}$, $\tau_0 = 6.8 \times 10^{-14}\text{--}3.1 \times 10^{-13} \text{ s}$. The relaxation parameters measured by the IF method are $E=1.0 \text{ eV}$, $\tau_0 = 4.7 \times 10^{-16} \text{ s}$. The relaxation peak results from the oxide ion diffusion by oxygen vacancies in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds.
2. The electrical conductivities of perovskite-type oxide ion conductors $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1$) compounds were analysed. For the lower doping level, the influence of the tolerance factor and specific free volume on the enhanced oxide ion conductivity is very limited. Judging from the larger relaxation activation energies, the method

of Mg-doped on the Ti-site in the NBT compounds is not beneficial to improve the oxide ion mobility in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ compounds. The conductivity improvement of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3-x}$ ($x=0.02, 0.04$) compounds is more inclined to the increment of oxygen vacancy concentration while the lower oxygen vacancy mobility results in the decline of oxide ion conductivity at higher Mg-doped content ($x > 0.04$). These results will be meaningful to ameliorate electrical properties of the NBT-based oxide ion conductors.

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