Effects of A-site nonstoichiometry on oxide ion conduction in $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 ceramics

Sasiporn Prasertpalichat*, Whitney Schmidt and David P. Cann
*Materials Science, School of Mechanical Industrial and Manufacturing Engineering
Oregon State University, Corvallis, OR 97331, USA*
*sprasertpalichat@gmail.com

Received 17 December 2015; Revised 10 April 2016; Accepted 11 April 2016; Published 2 June 2016

Lead free $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – 0.06BaTiO_3 ceramics were prepared by conventional solid-state mixed oxide route with the A-site stoichiometry modified to incorporate donor-doping (through Bi-excess) and acceptor-doping (through Na-excess). Both stoichiometric and nonstoichiometric ceramics exhibited a single perovskite phase with pseudo-cubic symmetry. A significant improvement in the dielectric properties was observed in Bi-excess compositions and a deterioration in the dielectric properties was observed in Na-excess compositions. Impedance spectroscopy was utilized to analyze the effects of A-site nonstoichiometry on conduction mechanisms. Compositions with Bi-excess resulted in an electrically homogeneous microstructure with an increase in resistivity by ~ 3 – 4 orders of magnitude and an associated activation energy of 1.57 eV which was close to half of the optical bandgap. In contrast, an electrically heterogeneous microstructure was observed in both the stoichiometric and Na-excess compositions. In addition, the Na-excess compositions exhibited low resistivities ($\rho \sim 10^3 \Omega\text{-cm}$) with characteristic peaks in the impedance data comparable to the recent observations of oxide ion conduction in $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$. Long term annealing studies were also conducted at 800°C to identify changes in crystal structure and electrical properties. The results of this study demonstrates that the dielectric and electrical properties of $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – 0.06BaTiO_3 ceramics are very sensitive to Bi/Na stoichiometry.

Keywords: A-site nonstoichiometry; oxide ion conduction; lead free BNT–BT; ceramics; impedance spectroscopy; ceramics.

1. Introduction

The $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) devices have been dominating the piezoelectric material market for more than half a century due to the excellent piezoelectric properties at the morphotropic phase boundary (MPB).¹ Not only has it been used in both thin film and ceramic embodiments, but nanoscale structured PZT has also been investigated for use in ferroelectric memory applications.² However, environmental and health concerns regarding the toxicity of lead (Pb^{2+}) has led to a restriction on its use in many electronic and electrical devices as seen in legislation in the European union³ and other countries.^{4–6} Therefore, a search for lead-free piezoelectric materials with comparable properties to that of PZT is a topic of significant current interest.⁷

The perovskite compound $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is one of the most promising candidates due to high remanent polarization (P_r of $38 \mu\text{C}/\text{cm}^2$) and high maximum temperature (T_m of 320°C).⁸ However, high leakage currents⁹ and a high coercive field ($E_c = 73 \text{ kV}/\text{cm}$) make the poling process very difficult, thus preventing high piezoelectric properties from being achieved. To overcome these issues, a number of BNT-based solid solutions were explored e.g., BNT– BaTiO_3 (BNT–BT),^{10–12} BNT– $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BNT–BKT),¹³ BNT–BT– $\text{K}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT–BT–KNN)¹⁴ and BNT– NaNbO_3 (BNT–NN).¹⁵ Among BNT-based materials, BNT–BT-based

solid solutions have attracted a great deal of attention due to the existence of the MPB at a composition 0.94BNT – 0.06BT that is characterized by ferroelectric rhombohedral and tetragonal phases. Similar to PZT, compositions near this MPB are accompanied by an enhancement in dielectric permittivity and piezoelectric coefficients.¹² Later studies further refined the location of the MPB of $x\text{BT}$ – $(1-x)\text{BNT}$ to the compositional range $x = 0.06$ – 0.08 .^{11,12,16,17}

Reports about the crystal structure at the MPB reveal that it is quite complex. There exists a discrepancy between the local structure and the average long-range structure. In addition, upon application of an electric field there is a shift in the MPB position as well as a change in the structure of the MPB.¹⁸ For $x = 0.06$, within the resolution limits of laboratory-scale XRD instrumentation, independent studies from Refs. 19 and 20 reported the room temperature structure to be pseudocubic. Later studies from high resolution neutron diffraction²¹ confirmed the structure to be pseudocubic with slight tetragonal and rhombohedral distortions. However, the local structure as determined by using TEM^{22,23} appeared to be a mixture of complex domain ($R3c$) and nanodomain ($P4bm$) structures. Similarly, the average structure of the $x = 0.07$ composition obtained from high resolution synchrotron XRD showed pseudocubic symmetry²⁴ whereas a TEM study revealed only nanodomain features corresponding to $P4bm$ symmetry. In addition, recent *in situ* TEM results showed that

the MPB (i.e., $x = 5.5$, 6 and 7%) was not stable under an applied electric field and the constituent ($R3c$) and ($P4bm$) phases can be created or destroyed. For example, for compositions at $x = 5.5$ and 6% BT, an initial MPB with coexisting $R3c$ and $P4bm$ phases completely transformed to pure $R3c$ (i.e., the MPB was destroyed) through the phase sequence $P4bm > P4mm > R3c$.

The depolarization temperature (T_d) and the temperature at which the dielectric constant is maximum (T_m) for MPB compositions were reported to be in a range of ~ 90 – 105°C and ~ 255 – 288°C ,²⁵ respectively. Recent studies proposed that the T_d at the MPB ($x = 0.06$) does not involve any phase change from a ferroelectric to antiferroelectric state but is instead the result of an evolution of the coexistence of $R3c$ and $P4bm$ polar nanoregions at increasing temperatures.²⁶

For the BNT end member compound, a small change in the stoichiometry of the A-site cation, which is most likely due to the volatility of Na and Bi cations during sintering, was found to significantly affect the conductivity, the dielectric properties and the piezoelectric properties. For example, Hiruma *et al.*²⁷ observed an improvement in dielectric properties with an enhancement in resistivity by one order of magnitude in BNT samples which have a Bi/Na ratio greater than 1 (e.g., Bi-excess or Na-deficient samples). Also, Sung *et al.*²⁸ showed an improvement in resistivity and d_{33} but a decrease in T_d in samples prepared with excess bismuth (e.g., $\text{Bi}_{0.5+x}\text{Na}_{0.5}\text{TiO}_3$, $x = 0.01$, 0.02). Although these previous studies attempted to control the Bi/Na ratio, some reports fail to address the hygroscopic nature of the NaCO_3 starting reagent. A recent study by Li *et al.* focused on the effect of drying the NaCO_3 starting reagent and found that the transport properties are sensitive to the control of stoichiometry.²⁹ In addition, a recent study by Li *et al.*³⁰ explicitly showed that oxygen vacancies were responsible for the high leakage current in Bi-deficient BNT, and consequently revealed that BNT has great potential for oxide ion conductor applications.

In BNT, the effects of A-site nonstoichiometry on the electrical properties has been extensively investigated and the results were very helpful in explaining the resultant changes in dielectric, ferroelectric and piezoelectric properties in BNT. However, no study regarding the effect of A-site nonstoichiometry in $(1-x)\text{BNT}-x\text{BT}$ compositions near the MPB have been reported in the literature. Therefore, in this study, the effects of A-site acceptor-doped (through Na excess) and A-site donor-doped (through Bi excess) modifications on the composition $94\text{BNT}-6\text{BT}$ (i.e., near the MPB) on electrical properties will be investigated by using impedance spectroscopy (IS). The annealing effects on each composition were also studied. In addition, our previous study³¹ demonstrated hardening similar to the hardening characteristics that are typically observed in hardened PZT in acceptor-doped (Na excess) $\text{BNT}-x\text{BT}$ in the compositions $x = 0.055$, 0.06 and 0.07 (i.e., MPB compositions). Therefore, this study will help clarify the effects of A-site nonstoichiometry on the

electrical properties as well as giving more insight into the observed hardening in our previous study.

2. Experimental Procedure

Ceramics of the composition $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3$ (denoted as 6BT (s) hereafter) were prepared by a conventional solid-state mixed oxide route. A-site donor- and acceptor-doping compositions were synthesized according to the chemical formula $0.94(\text{Bi}_{0.51}\text{Na}_{0.50})\text{TiO}_3-0.06\text{BaTiO}_3$ (denoted as 6BT (Bi)) and $0.94(\text{Bi}_{0.50}\text{Na}_{0.505})\text{TiO}_3-0.06\text{BaTiO}_3$ (denoted as 6BT (Na)), respectively. Prior to batching, Na_2CO_3 powders were dried at 150°C for 10 h due to concerns regarding its hygroscopic nature. The reagent grade powders of Bi_2O_3 (99.9%, Alfa Aesar), Na_2CO_3 (99.5%, Alfa Aesar), TiO_2 (99.9%, Sigma Aldrich) and BaCO_3 (99.9%, Alfa Aesar) were weighed according to the batch formula and then vibratory-milled in ethanol using yttria-stabilized zirconia media for 6 h. Powders were calcined at 800°C for 2 h before re-milling and drying again in order to achieve sub-micron sized powder. Calcined powders were mixed with 3 wt.% polyvinyl butyral (PVB) before uniaxially cold-pressing at 150 MPa to form a 12.7 mm diameter disc. A covered crucible with a sacrificial powder of the same composition was used in order to minimize the loss of volatile Bi and Na components during sintering. The sintering temperatures for donor-, stoichiometric- and acceptor-doped 94BNT-6BT were 1170°C , 1160°C and 1150°C , respectively. For the annealing study, sintered pellets were buried in the powders of the same compositions in covered crucibles and annealed at 800°C in air for seven days.

Phase purity and crystal structure determination was carried out on crushed sintered pellets using X-ray diffraction (XRD, Bruker AXS D8) with $\text{CuK}\alpha$ radiation in a standard Bragg-Brentano geometry. Prior to electrical measurements, samples were ground and polished to ~ 0.7 mm thick and then silver electrodes (Heraeus C1000) were applied to both sides and fired at 700°C for 0.5 h. Dielectric measurements were conducted over a wide temperature range (25 – 600°C) using a high temperature measurement cell (NorECS ProboStat) equipped with an LCR meter (Agilent 4284A). IS measurements were conducted at different temperatures over the frequency range of 0.1 Hz to 1 MHz by using an impedance gain/phase analyzer (Solatron 1260A), which was equipped with Solatron 1296A dielectric interface in order to improve data accuracy at low frequencies. Before impedance measurements were carried out at each temperature step, the sample was held at temperature for 1 h to ensure temperature homogeneity.

3. Results and Discussions

Bulk densities of the 6BT (Bi), 6BT (s) and 6BT (Na) ceramics determined using Archimedes method were found to be 95%, 93% and 90% of the theoretical density, respectively, suggesting that relatively high density samples were

obtained. Within the resolution of laboratory XRD, all compositions showed a single-phase perovskite with no trace of secondary phases. The stoichiometric compositions did not show any splitting of the characteristic rhombohedral (111) peaks or the characteristic (200) tetragonal peaks, indicating a pseudocubic structure. This result is in agreement with recent studies from both laboratory and synchrotron XRD data in which the crystal structure of the MPB was reported to be nearly cubic¹⁹ or pseudocubic.^{21,24} In the doped compositions, donor doping did not show any change in the crystal structure, while a slight rhombohedral distortion was observed in acceptor-doped samples.

Figure 1 shows temperature dependence of the dielectric constant and dielectric loss ($\tan \delta$) of donor-, stoichiometric and acceptor-doped 6BT compositions. While room temperature relative permittivity values for the stoichiometric composition are comparable to published values,¹² at temperatures above 200°C, an anomalously high dielectric constant was measured at relatively low frequencies (e.g., 100 Hz and 1 kHz) and high dielectric losses were observed. This could be attributed to the presence of Bi and Na vacancy defects ($V_{\text{Bi}}^{\bullet\bullet}$, $V_{\text{Na}}^{\bullet}$) which were generated during the high temperature sintering process along with their compensating positively charged defects ($V_{\text{O}}^{\bullet}$, $h^{\bullet}$) as shown in Eq. (1):

$$e' + 3[V_{\text{Bi}}^{\bullet\bullet}] + [V_{\text{Na}}^{\bullet}] = 2[V_{\text{O}}^{\bullet}] + h^{\bullet}. \quad (1)$$

A further deterioration in the dielectric properties was observed in acceptor-doped (1% Na excess) compositions as seen in Fig. 1(c). Due to the similar ionic radii between Bi ($r_{\text{Bi}^{3+}} = 1.34 \text{ \AA}$)³² and Na ($r_{\text{Na}^{+}} = 1.39 \text{ \AA}$),³³ some excess Na could replace Bi and result in a negatively charged defect $\text{Na}_{\text{Bi}}^{\bullet\bullet}$, thus leading to a further increase in compensating oxygen vacancies and/or holes as shown in Eq. (2). This would explain the degradation of the dielectric properties as seen in Fig. 1(c).

$$e' + 3[V_{\text{Bi}}^{\bullet\bullet}] + [V_{\text{Na}}^{\bullet}] + 2(\text{Na}_{\text{Bi}}^{\bullet\bullet}) = 2[V_{\text{O}}^{\bullet}] + h^{\bullet}. \quad (2)$$

In contrast, a significant improvement in dielectric properties was observed in donor-doped 6BT (2% Bi excess) as seen

from a persistence of low dielectric loss (<3% at 1 kHz) up to high temperature (450°C) and the disappearance of the anomalous high dielectric constant at low frequencies. There are two likely reasons for this result. First, excess Bi compensates for Bi loss during sintering, leading to a decrease in both $V_{\text{Bi}}^{\bullet\bullet}$ defects and the corresponding positively charged defects ($V_{\text{O}}^{\bullet}$ and $h^{\bullet}$).³⁴ Second, it is most likely that some excess Bi substitutes for Na which results in the formation of positively charged $\text{Bi}_{\text{Na}}^{\bullet}$ defects which then need to be compensated either by an increase in negatively charged defects (e.g., $V_{\text{Bi}}^{\bullet\bullet}$, $V_{\text{Na}}^{\bullet}$, e') or by a decrease in positively charged defects (i.e., $V_{\text{O}}^{\bullet}$, $h^{\bullet}$). However, due to the observation of improved dielectric properties, it is most likely that the latter is a dominant mechanism.

$$e' + 3[V_{\text{Bi}}^{\bullet\bullet}] + [V_{\text{Na}}^{\bullet}] + 2(\text{Na}_{\text{Bi}}^{\bullet\bullet}) = 2[V_{\text{O}}^{\bullet}] + h^{\bullet} + 2\text{Bi}_{\text{Na}}^{\bullet}. \quad (3)$$

To gain a better understanding about the influence of A-site acceptor and donor doping on the conductivity and electrical structure, IS measurements were conducted at different frequencies and temperatures. Impedance complex plane plots (Z^* plot) for 6BT (Bi), 6BT (s) and 6BT (Na) are shown in Fig. 2.

For the stoichiometric composition (6BT (s), Fig. 2(b)), the Z^* plots at all temperatures feature a slightly distorted semicircle at low frequency corresponding to the grain-boundary response and a much smaller second semicircle at higher frequency corresponding to the bulk response which can be seen more clearly in an enlarged scale in the inset of Fig. 2(b). The corresponding spectroscopic plots of the imaginary component of the impedance (Z'') and electric modulus (M'') are shown in Fig. 2(e). Since the Debye-like peak magnitude is weighted according to the R value in the Z'' spectra and the C^{-1} value in the M'' spectra, a region with relatively higher resistance and capacitance (i.e., grain boundary) will appear as a dominant peak in the Z'' spectra and a minor peak in the M'' spectra,^{30,35} which agrees well with Z'' and M'' peak characteristics shown in the low frequency data of Fig. 2(e). Accordingly, a region with lower resistance and capacitance (i.e., bulk) will display the

Fig. 1. Temperature dependence of the dielectric constant and dielectric loss ($\tan \delta$) of as-sintered (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (1Na).

Fig. 2. Complex plane plots of (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (Na) compositions with the inset in (b) and (c) showing the high frequency data on an enlarged scale to highlight the bulk response. Corresponding normalized Z'' and M'' spectroscopic plots at $\sim 500^\circ\text{C}$ are shown for (d) 6BT (Bi), (e) 6BT (s) and (f) 6BT (Na).

opposite characteristics (i.e., a dominant peak in the M'' spectra and a minor peak in the Z'' spectra), which can be seen in high frequency data in Fig. 2(e). In addition, at 500°C , the dielectric constant extracted from capacitance associated with high frequency semicircle is ~ 1970 , which is in a good agreement with high frequency bulk dielectric constant obtained from direct dielectric measurement shown in Fig. 1(b). These two observations confirm the assignment of the peaks to the bulk and grain boundary components.

Similar to the 6BT (s) composition, acceptor-doped compositions (6BT (Na), Fig. 2(c)) showed two semicircles corresponding to bulk and grain boundary components,

indicating that an electrically inhomogeneous microstructure was present. However, compared to 6BT(s), both the bulk and grain boundary resistivity significantly decreased in magnitude as seen in Table 1. In addition, it could also be seen from Table 1 that acceptor doping resulted in a modest decrease in grain boundary resistivity but a considerable decrease ($\sim$ one order of magnitude lower) in bulk resistivity. This could suggest that the effect of acceptor doping is not limited to the grain boundary but the bulk was also affected. On the other hand, one can infer from this result that the observed changes in dielectric properties might be related more to the properties of the bulk than that of the grain boundary. This finding is

Table 1. A comparison of bulk and grain boundary resistivity (ρ) among 6BT (Bi), 6BT (s) and 6BT (Na) at selected temperatures. Due to the electrical homogeneity of 6BT (Bi), only the bulk component resistivity is shown.

Compositions	Resistivity (ρ , $\Omega\cdot\text{cm}$)					
	$\sim 440^\circ\text{C}$		$\sim 470^\circ\text{C}$		$\sim 500^\circ\text{C}$	
	bulk	gb	bulk	gb	bulk	gb
6BT (Bi)	1.4×10^8	—	5.0×10^7	—	1.8×10^7	—
6BT (s)	3.4×10^4	1.3×10^5	2.2×10^4	7.4×10^4	1.5×10^4	4.6×10^4
6BT (Na)	3.0×10^3	8.6×10^4	2.2×10^3	6.9×10^4	1.5×10^3	4.4×10^4

consistent with the study of Yoon *et al.* on Mg-doped BaTiO₃ which observed a substantial change in bulk resistivity along with a small change in grain boundary resistivity.³⁶ The corresponding Z'' and M'' spectroscopic plots of 6BT (Na) are shown in Fig. 2(f). In the Z'' spectroscopic plot, due to a considerable decrease in bulk resistivity, a previously observed shoulder at high frequency corresponding to the bulk response in 6BT (s) was nearly absent in 6BT (Na). In addition, it should be noted that a shoulder appeared at a very low frequencies (~ 10 Hz) which might suggest an ionic conduction mechanism which was not noticeable in the data of 6BT (s).³⁰

In contrast, within the measured frequency range used, the Z^* plot of donor doping (6BT (Bi)) exhibited a single semicircle as seen in Fig. 2(a) indicating that sample was electrically homogeneous. At 500°C, the dielectric constant extracted from capacitance values associated with this semicircle was ~ 2300 which agrees well with the high frequency dielectric constant obtained from direct dielectric measurement at the same temperature shown in Fig. 1(a), thus confirming that it originates from the bulk. Compared to 6BT (s), it can be seen from Table 1 that donor doping resulted in an

increase in bulk resistivity by 3 to 4 orders of magnitude. This is fully consistent with recent studies on Bi-excess compositions in Bi_{0.5}Na_{0.5}TiO₃ (BNT) by Li *et al.*³⁰ The corresponding Z'' and M'' spectroscopic plots are shown in Fig. 2(d) where the Z'' and M'' peaks were coincident at the same frequency, confirming that the sample is electrically homogeneous.

Arrhenius-type plots for all the three compositions are shown in Fig. 3. The activation energy for the bulk and grain boundary responses for each sample has been determined from analysis of the temperature dependence. For the electrically homogeneous 6BT (Bi) composition, an activation energy of 1.57 eV was observed, which is approximately half of the bandgap ($E_g/2$), suggesting that the conduction mechanism in this sample is primarily dominated by an intrinsic electronic conduction mechanism.^{30,37} In contrast, for 6BT (s) and 6BT (Na) the activation energies for the bulk and grain boundary component ranged between 0.5 and 0.7 eV, which is consistent with conduction mechanisms dominated by extrinsic defects.^{30,35}

The observed increase in the resistivity of donor-doped compositions (6BT (Bi)) seen in the impedance data agrees

Fig. 3. Arrhenius-type plots of the bulk and grain boundary conductivity for (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (Na). Only the bulk component is shown in the 6BT (Bi) sample due to the electrically homogeneous structure.

Fig. 4. Temperature dependence of dielectric constant and dielectric loss ($\tan \delta$) for (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (Na) samples, which was annealed in air at 800°C for seven days.

Fig. 5. Complex plane plots for annealed samples of (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (Na) compositions with an inset in (b) and (c) to include high frequency data on an enlarged scale to highlight the bulk response. Corresponding normalized Z'' , M'' spectroscopic plots at $\sim 500^\circ\text{C}$ are shown for (d) 6BT (Bi), (e) 6BT (s) and (f) 6BT (Na).

well with the observed low $\tan \delta$ values seen in the dielectric measurements. Similarly, a decrease in resistivity seen in acceptor-doped (6BT (Na)) compositions was also consistent with the observation of high dielectric loss values. The trend in the change in resistivity with doping suggests that p-type charge carriers (e.g., $[V_{\text{O}}], h^+$) are dominant in the stoichiometric 6BT (s) composition. Furthermore, Li *et al.*³⁰ reported that the oxygen ionic transport number (t_i) in stoichiometric and Mg acceptor-doped BNT was greater than 0.9, suggesting that the conduction mechanism in the 6BT (s) specimen in this study may be dominated by oxygen vacancies (V_{O}) as well.

3.1. Annealing effects

Samples subjected to annealing in air at 800°C for seven days showed no noticeable change in crystal structure. The XRD data of all samples showed a single perovskite phase with no trace of any secondary phase. A pseudocubic structure similar to as-sintered sample was still observed, indicating that there is no change in long-range order after annealing.

Figure 4 shows temperature dependence of dielectric constant and dielectric loss of all annealed samples. For donor doping (6BT (Bi), Fig. 4(a)) and acceptor doping (6BT (Na), Fig. 4(c)), the dielectric properties remained almost the

same as compared to the as-sintered samples. For 6BT (Bi), while no change in dielectric constant was observed, it should be noted that a high dielectric loss values shifted to slightly lower temperatures. For 6BT (Na), both the dielectric constant and dielectric loss values remained nearly the same.

In contrast, a significant improvement in dielectric properties was clearly observed in the stoichiometric composition, 6BT (s), where a considerable decrease in the dielectric loss and a decrease in the anomalously high dielectric constant at 100 Hz at temperatures above 300°C was clearly evident. This suggests that the concentration of electrically active defects in this composition substantially decreased after annealing.

Table 2. A comparison of bulk and grain boundary resistivity (ρ) for each composition before and after annealing at 800°C for seven days. Only the bulk component was shown for 6BT (Bi) and 6BT (s) sample due to homogeneity.

Compositions	Resistivity at $\sim 500^\circ\text{C}$ (ρ , $\Omega\cdot\text{cm}$)			
	As-sintered		Annealed 800°C , 7 days	
	bulk	gb	bulk	gb
6BT (Bi)	1.8×10^7	—	1.0×10^7	—
6BT (s)	1.5×10^4	4.6×10^4	3.9×10^5	—
6BT (Na)	1.5×10^3	4.4×10^4	5.8×10^2	2.4×10^3

Fig. 6. Arrhenius-type plot of bulk and grain boundary conductivity for annealed (a) 6BT (Bi), (b) 6BT (s) and (c) 6BT (Na). Only bulk component is shown in 6BT (Bi) and 6BT (s) samples due to electrical homogeneity.

IS was performed on these annealed specimens to analyze the defect mechanisms in this series of compositions. The complex plane plots and corresponding Z'' , M'' spectroscopic plots of each compositions are shown in Figs. 5(a)–5(f).

For the donor-doped composition (6BT (Bi)), a single semicircle (Fig. 5(a)) as well as coincident Z'' and M'' peaks (Fig. 5(d)) were observed indicating that the 6BT (Bi) sample remained electrically homogeneous as it was for the as-sintered sample. A small decrease in the resistivity was observed after annealing as seen in Table 2, which supports the finding of the increase in dielectric loss shown in Fig. 4(a). For the annealed acceptor-doped sample (6BT (Na) sample (Fig. 5(c))), two semicircles are clearly observed corresponding to bulk and grain boundary components similar to that of the as-sintered sample, suggesting that the sample is still electrically heterogeneous. Similar to 6BT (Bi), annealing also resulted in a small decrease of resistivity as seen in Table 2.

As opposed to the doped annealed samples 6BT (Bi) and 6BT (Na), a significant change in the impedance response was observed in annealed 6BT (s) sample as seen from a single semicircle in Fig. 5(b) and the corresponding coincident Z'' and M'' peaks in Fig. 5(e). In addition, an increase in the resistivity by one order of magnitude was observed as seen in Table 2, which is consistent with the overall improvement in dielectric properties.

Arrhenius plots of the bulk and grain boundary conductivity of all annealed samples are shown in Figs. 6(a)–6(c). For the 6BT (Bi) sample, annealing resulted in a minor decrease in the activation energy from 1.57 eV to 1.23 eV whereas for the stoichiometric 6BT (s) sample E_a increased significantly from 0.56 to 1.00 eV. For annealed acceptor-doped sample 6BT (Na), the bulk activation energy remained unchanged, whereas the grain boundary activation energy increased from 0.56 to 0.70 eV upon annealing.

The significant improvement in electrical homogeneity and resistivity in the annealed stoichiometric sample 6BT (s) along with the absence of any significant change in the doped 6BT (Bi) and 6BT (Na) samples can be explained with two

competing mechanisms: (1) the loss of volatile cations Bi and Na, which can lead to additional oxygen loss and (2) a re-oxidation process, which can reduce the oxygen vacancy concentration. Considering the overall change in properties with annealing of the stoichiometric composition, the concentration of oxygen vacancies established from the initial as-sintered sample must have decreased during annealing due to the re-oxidation process, thus resulting in an electrically homogeneous structure and an increase in overall resistivity. The lack of any significant change in the electrical properties with the doped 6BT (Bi) and 6BT (Na) samples suggests that there is no significant loss of Bi or Na during the annealing process.

4. Conclusion

Single-phase perovskite ceramics of the composition $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3$ were prepared with stoichiometric variations incorporating A-site donors (through Bi excess) and A-site acceptor doping (through Na excess). All of the sintered ceramics exhibited pseudo-cubic symmetry using laboratory scale XRD. Significant improvements in dielectric properties were observed including low dielectric loss in donor-doped compositions. In contrast, a degradation in the dielectric properties was observed with acceptor doping including an increase in dielectric loss. IS analysis revealed that stoichiometric and acceptor-doped compositions had an electrically heterogeneous microstructure. In addition, it was observed that acceptor doping resulted in a decrease in the resistivity by one order of magnitude with respect to stoichiometric 6BT. In contrast, donor doping resulted in an electrically homogeneous microstructure with an increase in resistivity by over three orders of magnitudes and the associated activation energy was 1.57 eV ($E_a \sim \frac{1}{2}E_g$), suggesting intrinsic electronic conduction as the primary conduction mechanism. Annealing studies revealed that the electrical homogeneity and resistivity of compositions with moderate

oxygen vacancy concentrations (i.e., 6BT (s)) could be improved. This study confirms that small changes in the A-site stoichiometry in $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – 0.06BaTiO_3 can result in a large change in electrical properties, from highly insulating behavior in donor-doped compositions to highly conductive behavior in acceptor-doped compositions.

Acknowledgment

This work was supported by scholarship from the Higher Education Commission of Thailand.

References

- G. H. Haertling, Ferroelectric ceramics: History and technology, *J. Am. Ceram. Soc.* **82**(4), 797 (1999).
- J. Varghese, T. Ghoshal, N. Deepak, C. O'Regan, R. W. Whatmore, M. A. Morris and J. D. Holmes, Fabrication of arrays of lead zirconate titanate (PZT) nanodots via block copolymer self-assembly, *Chem. Mater.* **25**(8), 1458 (2013).
- Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS), EU-Directive 2002/95/EC, ed. O. J. E. Union (2003).
- Law for promotion of effective utilization of resources: Minister of Economy, Trade and Industry, Japan (2001).
- Solid waste: Hazardous electronic waste, U.S. California Senate Bill No. 50 (2004).
- Measures for the Administration on Pollution Control of Electronic Information Products, Ministry of Information Industry China Order No. 39 (2006).
- Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Lead-free piezoceramics, *Nature* **432**(7013), 84 (2004).
- G. Smolenskii, V. Isupov, A. Agranovskaya and N. Krainik, New ferroelectrics of complex composition, *Sov. Phys. Solid State* **2**(11), 2651 (1961).
- H. Nagata, T. Shinya, Y. Hiruma, T. Takenaka, I. Sakaguchi and H. Haneda, Piezoelectric properties of bismuth sodium titanate ceramics, in *Developments in Dielectric Materials and Electronic Devices* (Wiley, 2012), pp. 213–221.
- M. Chen, Q. Xu, B. H. Kim, B. K. Ahn, J. H. Ko, W. J. Kang and O. J. Nam, Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics, *J. Eur. Ceram. Soc.* **28**(4), 843 (2008).
- C. Xu, D. Lin and K. Kwok, Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – BaTiO_3 lead-free piezoelectric ceramics, *Solid State Sci.* **10**(7), 934 (2008).
- T. Takenaka, K.-I. Maruyama and K. Sakata, $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 system for lead-free piezoelectric ceramics, *Jpn. J. Appl. Phys.* **30**(9B), 2236 (1991).
- K. Yoshii, Y. Hiruma, H. Nagata and T. Takenaka, Electrical properties and depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ lead-free piezoelectric ceramics, *Jpn. J. Appl. Phys.* **45**, 4493 (2006).
- S.-T. Zhang, A. B. Kounga, E. Aulbach, T. Granzow, W. Jo, H.-J. Kleebe and J. Rödel, Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – BaTiO_3 – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. I. Structure and room temperature properties, *J. Appl. Phys.* **103**(3), 034107 (2008).
- T. Takenaka, T. Okuda and K. Takegahara, Lead-free piezoelectric ceramics based on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – NaNbO_3 , *Ferroelectrics* **196**(1), 175 (1997).
- Q. Xu, X.-L. Chen, W. Chen, B.-H. Kim, S.-L. Xu and M. Chen, Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ ceramics made by a citrate method, *J. Electroceram.* **21**(1–4), 617 (2008).
- B.-J. Chu, D.-R. Chen, G.-R. Li and Q.-R. Yin, Electrical properties of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ – BaTiO_3 ceramics, *J. Eur. Ceram. Soc.* **22**(13), 2115 (2002).
- W. Jo, J. E. Daniels, J. L. Jones, X. Tan, P. A. Thomas, D. Damjanovic and J. Rödel, Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 piezoceramics, *J. Appl. Phys.* **109**(1), 014110 (2011).
- R. Ranjan and A. Dwiwedi, Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$, *Solid State Commun.* **135**(6), 394 (2005).
- S.-T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg and J. Rödel, Giant strain in lead-free piezoceramics $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – BaTiO_3 – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ system, *Appl. Phys. Lett.* **91**(11), 112906-06-3 (2007).
- H. Simons, J. Daniels, W. Jo, R. Dittmer, A. Studer, M. Avdeev, J. Rödel and M. Hoffman, Electric-field-induced strain mechanisms in lead-free 94% $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ –6% BaTiO_3 , *Appl. Phys. Lett.* **98**(8), 082901 (2011).
- C. Ma and X. Tan, Phase diagram of unpoled lead-free–ceramics, *Solid State Commun.* **150**(33), 1497 (2010).
- C. Ma and X. Tan, *In situ* transmission electron microscopy study on the phase transitions in lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ ceramics, *J. Am. Ceram. Soc.* **94**(11), 4040 (2011).
- J. E. Daniels, W. Jo, J. Rödel and J. L. Jones, Electric-field-induced phase transformation at a lead-free morphotropic phase boundary: Case study in a 93% $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ –7% BaTiO_3 piezoelectric ceramic, *Appl. Phys. Lett.* **95**(3), 032904-04-3 (2009).
- J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow and D. Damjanovic, Perspective on the development of lead-free piezoceramics, *J. Am. Ceram. Soc.* **92**(6), 1153 (2009).
- W. Jo, S. Schaab, E. Sapper, L. A. Schmitt, H.-J. Kleebe, A. J. Bell and J. Rödel, On the phase identity and its thermal evolution of lead free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ –6 mol% BaTiO_3 , *J. Appl. Phys.* **110**(7), 074106 (2011).
- Y. Hiruma, H. Nagata and T. Takenaka, Thermal depoling process and piezoelectric properties of bismuth sodium titanate ceramics, *J. Appl. Phys.* **105**(8), 084112-12-8 (2009).
- Y. Sung, J. Kim, J. Cho, T. Song, M. Kim and T. Park, Effects of Bi nonstoichiometry in $(\text{Bi}_{0.5+x}\text{Na})\text{TiO}_3$ ceramics, *Appl. Phys. Lett.* **98**(1), 012902 (2011).
- M. Li, H. Zhang, S. N. Cook, L. Li, J. A. Kilner, I. M. Reaney and D. C. Sinclair, The dramatic influence of A-site non-stoichiometry on the electrical conductivity and conduction mechanisms in the perovskite oxide $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, *Chem. Mater.* **27**, 629 (2015).
- M. Li, M. J. Pietrowski, R. A. De Souza, H. Zhang, I. M. Reaney, S. N. Cook, J. A. Kilner and D. C. Sinclair, A family of oxide ion conductors based on the ferroelectric perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, *Nat. Mater.* **13**(1), 31 (2014).
- S. Prasertpalichat and D. P. Cann, Hardening in non-stoichiometric $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $x\text{BaTiO}_3$ lead-free piezoelectric ceramics, *J. Mater. Sci.* **51**(1), 476 (2016).

- ³²R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Rehrig, W. Hackenberger and S.-E. Park, New high temperature morphotropic phase boundary piezoelectrics based on Bi(Me)O₃–PbTiO₃ ceramics, *Jpn. J. Appl. Phys.* **40**(10R), 5999 (2001).
- ³³R. t. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr., Sect. A* **32**(5), 751 (1976).
- ³⁴R.-A. Eichel, Structural and dynamic properties of oxygen vacancies in perovskite oxides — analysis of defect chemistry by modern multi-frequency and pulsed EPR techniques, *Phys. Chem. Chem. Phys.* **13**(2), 368 (2011).
- ³⁵F. D. Morrison, D. C. Sinclair and A. R. West, Characterization of lanthanum-doped barium titanate ceramics using impedance spectroscopy, *J. Am. Ceram. Soc.* **84**(3), 531 (2001).
- ³⁶S. H. Yoon, C. A. Randall and K. H. Hur, Effect of acceptor (Mg) concentration on the resistance degradation behavior in acceptor (Mg)-doped BaTiO₃ bulk ceramics: I. impedance analysis, *J. Am. Ceram. Soc.* **92**(8), 1758 (2009).
- ³⁷M. Bousquet, J.-R. Duclère, E. Orhan, A. Boule, C. Bachelet and C. Champeaux, Optical properties of an epitaxial Na_{0.5}Bi_{0.5}TiO₃ thin film grown by laser ablation: Experimental approach and density functional theory calculations, *J. Appl. Phys.* **107**(10), 104107 (2010).