Temperature dependent conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics induced by Sr dopants

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Abstract: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an important lead-free ferroelectric material. Doping modification of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has attracted great attention to improving its performances. In this work, the effect of Sr dopants on the microstructure, dielectric, and conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic was investigated by XRD, SEM, and AC impedance spectroscopy. Substitution of 1 at% Sr for Bi decreased the grain size, suppressed the dielectric dispersion of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic at room temperature, and resulted in different effects on the conductivity of grains and grain boundaries. The conductivity of grains in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic was increased by the small amount of Sr dopants in the whole experimental temperature range. While the grain boundaries of 1 at% Sr-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ exhibited lower conductivity than pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ below $\sim 380^\circ\text{C}$ and higher conductivity above $\sim 380^\circ\text{C}$. The experimental phenomena were interpreted in term of compensating defects for Sr dopants.

Keywords: dielectric; impedance analysis; electrical properties; defects; Aurivillius compound

1 Introduction

Bismuth-based layer-structured ferroelectrics (BLSF) known as Aurivillius compounds are generally represented by a formula $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}(\text{Bi}_2\text{O}_2)^{2+}$, where A denotes mono-, di-, or trivalent cations or a mixture of those at the 12-coordinated site, B stands for tri-, tetra-, or pentavalent cations at the 6-coordinated site, and n indicates the number of perovskite units [1,2]. Its crystal structure is built up by perovskite blocks $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ and fluorite structure layers $(\text{Bi}_2\text{O}_2)^{2+}$ alternatively stacking up along the pseudo-tetragonal c -axis. Aurivillius compounds have

attracted great attention in high-temperature piezoelectric devices [3,4], transducers [5,6], and memory devices [7,8] which are beneficial from their high ferroelectric transition temperature (T_c) and fatigue-free characteristics [9,10]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a typical 3-layered Aurivillius compound with $T_c = 675^\circ\text{C}$ [11]. However, high electric leakage limits its extensive application. The substitution of alkali metal, alkaline-earth metal, and rare earth metal ions for Bi is a desirable method to suppress the leakage and tune the physical properties [12]. Several applicable $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based compounds have been developed, such as $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ [13], $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ [14], $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ [15], and $\text{La}_{0.75}\text{Bi}_{3.25}\text{Ti}_3\text{O}_{12}$ [16]. Although two Sr-containing BIT compounds were prepared, the effect of small amount of Sr substituting for Bi on the phase stability and properties of the

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Aurivillius compounds have not been systematically investigated.

The leakage of BIT is believed to be closely related to the oxygen vacancies induced by the evaporation of Bi at the sintering temperature. The Sr–O bond has the higher bond energy (454 kJ/mol) than the Bi–O bond (343 kJ/mol) [17], so it is expectable that the Sr doping maybe suppress the evaporation of Bi to decrease the leakage. Meanwhile, the aliovalent Sr^{2+} substitution for Bi^{3+} can work as acceptors to compensate for the electrons from the ionization of oxygen vacancies, which would further inhibit the leakage of BIT. Therefore, it is necessary to experimentally investigate the effect of Sr dopants on the conduction of BIT.

In this work, Sr-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (SBIT) samples were prepared by conventional solid-state reaction. The effect of small amount of Sr dopants on dielectric properties and electrical conduction of BIT was studied by AC impedance spectroscopy because the impedance analysis is a powerful technique to distinguish the different contributions of microstructural components (i.e., grains, grain boundaries, and electrode interfaces) to the conduction of materials. The experiments provided some referential results for modification of BIT related materials.

2 Experiment

Sr-doped BIT ceramics with nominal compositions of $(\text{Bi}_{1-x}\text{Sr}_x)_4\text{Ti}_3\text{O}_{12-2x}$ (SBIT, $x = 0, 0.01, 0.02, 0.05$) were synthesized by conventional solid-state reaction method, which are denoted as BIT, 1%Sr, 2%Sr, and 5%Sr, respectively. For comparison, a $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ sample was also prepared. Stoichiometric amounts of Bi_2O_3 , TiO_2 , and SrCO_3 with purity > 99.9% were thoroughly mixed in ethanol medium in an agate mortar. The mixed raw material was initially pre-calcined at 780 °C for 3 h in air and calcined at 850 °C for 3 h in air. The obtained powders were ground and uniaxially pressed into pellets with thickness of 1 mm and diameter of 12 mm. The pressed pellets were sintered at 1100 °C for 2 h in air. X-ray powder diffraction (XRD, Cu K α , X'pert Pro, PANalytical B.V., Almelo, Netherlands) technique was used to identify the phase constituent of the sintered samples. The microstructure of the sintered pellets was observed by using a scanning electron microscope (SEM, HITACHI S-4800, Hitachi Ltd., Tokyo, Japan). For dielectric measurement, both sides of the pellets

were polished smooth and parallel, and coated by silver paint. The pasted pellets were heated at 620 °C for 15 min. The dielectric and impedance responses were measured using impedance analyzer (impedance analyzer, WK6510B, Wayne Kerr, UK) in the frequency range from 50 Hz to 10 MHz from room temperature to 720 °C. The polarization–electric field (P – E) loop measurement was performed using an aixACT TF 2000 analyzer. The measurement was performed by applying to the samples single sinusoidal waveforms of 100 Hz. During the measurements, the samples were immersed in silicone oil.

3 Results

3.1 Phase identification and microstructure

Phase identification of prepared SBIT samples was performed by XRD as shown in Fig. 1(a). The XRD patterns of the samples with $x = 0$ and 0.01 well match with that of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (JCPDS No. 35-0795); however, the sample of $x = 0.05$ fits with two phases of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ (JCPDS No. 31-1342). The enlarged parts of XRD patterns clearly show that the single peaks at $\sim 16.2^\circ$ and $\sim 30^\circ$ in the samples of $x = 0$ and 0.01 become two peaks in the sample of $x = 0.05$, evidencing the existence of two Aurivillius phases. For the sample of $x = 0.02$, the peak at $\sim 16.2^\circ$ has a tail on the high angle side, suggesting the possible existence of a minor phase. In addition, a small amount of Bi-rich oxide ($\text{Bi}_{20}\text{TiO}_{32}$) is observed in the samples of $x = 0.05$ and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$, which is evidenced by the weak peak at $\sim 28^\circ$. The XRD patterns of $x = 0, 0.01$, and 0.02 are well indexed with the monoclinic structure $B2cb$. The lattice parameters are obtained by fitting the XRD patterns with the Fullprof software [18] and plotted in Figs. 1(b) and 1(c). It is found that the unit cell volume expands with increasing the Sr content. The volume expansion of Sr-doped BIT may be caused by the substitution of Sr^{2+} ions which has larger size ($r = 1.26 \text{ \AA}$, coordination number CN = 8) than Bi^{3+} ions ($r = 1.17 \text{ \AA}$, CN = 8) [19]. The results demonstrate that the Sr^{2+} cations are incorporated into the lattice structure of BIT. The lattice parameters of the 2%Sr sample do not follow the linear expansion relation of the BIT and 1%Sr samples, in consistent with the observation of minor second phase in the 2%Sr sample. The solubility of Sr in $(\text{Bi}_{1-x}\text{Sr}_x)_4\text{Ti}_3\text{O}_{12}$ is less than 0.02 according to the experimental results.

Fig. 1 (a) XRD patterns of SBIT ceramics with different compositions and enlarged parts around 16.2° and 30°; (b) lattice constants of different Sr contents; (c) cell volumes of different Sr contents.

Figure 2 shows the SEM images of the samples. All the ceramics are composed of plate-like grains, which is a typical characteristic of layer-structured compounds. It is found that the undoped BIT ceramic has the largest grain size with the length from 5 to 10 μm and the thickness about 2 μm on average, and the Sr doping significantly decreases the grain size. The 1%Sr sample has the smallest grain size with the length of 1–2.5 μm and the thickness of ~0.7 μm. With increasing the Sr content, the grain size of doped samples becomes larger.

3.2 Dielectric and impedance analysis

Frequency dependence of real part (ϵ'_r) and imaginary part (ϵ''_r) of complex relative permittivity at various temperatures is displayed in Fig. 3. At room temperature (RT), the BIT sample shows more intensive dielectric dispersion than the Sr-containing samples at low

Fig. 2 SEM micrographs of SBIT ceramics with different compositions: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$.

frequency, and much larger ϵ''_r value than the 1%Sr and 2%Sr samples. The small amount of Sr dopants ($x = 0.01, 0.02$) does not change the values of relative dielectric constant (ϵ'_r) of BIT at high frequency as shown in Fig. 3(a), and the values of ϵ'_r are ~120. For the SrBi₈Ti₇O₂₇ sample, the value of ϵ'_r is ~150. The low-frequency dielectric dispersion is generally attributed to the polarization of space charges [20,21]. The depression of dielectric dispersion by Sr doping suggests that Sr dopants decrease the number of activated space charges in samples at RT. At 250 °C, the dielectric relaxation is clearly observed in the samples. The relaxation frequency of BIT is lower than those of 1%Sr and 2%Sr samples as marked by arrows in Fig. 3(b). The ϵ''_r value of the 1%Sr sample is less than that of BIT at low frequency but larger at high frequency. At 450 °C, the ϵ''_r value of 1%Sr sample is larger than that of BIT approximately in all frequency range. The $\log \epsilon''_r$ vs. $\log f$ plots of the samples show a linear relation at low frequency with slope nearly equal to 1 as shown in Fig. 3(c), which suggests the dominance of DC conductivity in the corresponding frequency. The temperature spectra of ϵ'_r in Fig. 3(d) indicate the significant increase of the polarization of space charges with increasing temperature. Dielectric peaks are observed at 681 °C for BIT, 663 °C for 1%Sr, 640 °C for 2%Sr, 638 °C for 5%Sr, and 624 °C for SrBi₈Ti₇O₂₇. The peak temperatures of BIT and SrBi₈Ti₇O₂₇ are consistent with the T_c values of BIT (675 °C) and SrBi₈Ti₇O₂₇ (620 °C) reported in Refs. [11,22], confirming that the dielectric anomalies correspond to the ferroelectric transition. It indicates that the Sr dopants decrease T_c of BIT.

Fig. 3 Frequency spectra of ε'_r and ε''_r of SBIT ceramics at various temperatures: (a) room temperature, (b) 250 °C, (c) 450 °C; (d) temperature spectra at 1 MHz.

The decrease of T_c induced by Sr dopants can be reasonably understood considering the possible effects of Sr dopants on the crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. It is believed that the T_c of Aurivillius compounds is closely related with the perovskite tolerance factor ($\tau = (r_A + r_O) / [\sqrt{2}(r_B + r_O)]$), where r_A , r_B , and r_O are the average effective ionic radii of the A and B cations and oxygen anion in ABO_3 perovskite compounds, respectively) [23]. A smaller value of τ (for the case of $\tau < 1$) indicates heavier structural distortion, consequently increasing the T_c of Aurivillius compounds [23]. The larger size of Sr^{2+} ions increases the τ value of perovskite units, which should result in the decrease of T_c . In addition, Sr dopants can weaken the covalent hybridization of the Bi 6s and O 2s/p orbits which is believed to result in the ferroelectric distortion of Bi-containing perovskite compounds [24]. Therefore, the decrease of T_c in Sr-doped samples with respect to the undoped sample is reasonable.

To clarify the conduction characteristics and understand the dielectric differences between BIT and 1%Sr-doped BIT at different temperatures, the impedance analysis was carried out. Figure 4 shows the Nyquist plots of complex impedance (Z' vs. Z'') of BIT and 1%Sr samples at several characteristic temperatures. At

50 °C, impedance curve of 1%Sr is closer to the imaginary axis than that of BIT, indicating higher resistivity of 1%Sr than that of BIT. With increasing temperature, the curves gradually bend toward the real axis, which indicates the decrease of resistivity with temperature. At 110 °C, a relaxation semicircular arc is clearly observed in the 1%Sr sample. Increasing temperature to 190 °C, the BIT sample also exhibits a relaxation arc at high frequency. It is known that the intercept of the impedance semicircular arc on the real axis marks out the resistance of the corresponding microstructural components, such as grains, grain boundaries, and electrode interfaces [25]. Therefore, the resistance of the high-frequency microstructural component of the 1%Sr sample is lower than that of the BIT sample as shown in Fig. 4(c). However, the slope of the curve of BIT at low frequency is less than that of the 1%Sr sample, indicating that the 1%Sr sample is more resistive than the BIT sample at 190 °C. The Nyquist diagrams at 250 °C reflect the similar properties as those at 190 °C except that the curves bend closer to the real axis, namely the resistances become lower. At 310 °C, nearly whole semicircular arcs at low frequencies are observed as well as the high-frequency arcs, showing the corresponding resistance

Fig. 4 Nyquist plots of complex impedance (Z' vs. Z'') of BIT and 1%Sr samples at several temperatures: (a) 50 °C, (b) 110 °C, (c) 190 °C, (d) 250 °C, (e) 310 °C, (f) 450 °C.

of the 1%Sr sample is close to that of BIT. As temperature rises up to 450 °C, the whole low-frequency semicircular arcs are obtained. Both the low-frequency and high-frequency resistances of the 1%Sr sample are lower than those of BIT. The critical temperature at which the resistances of two samples are nearly equal is about 380 °C as shown in Fig. S1 in the Electronic Supplementary Material (ESM). An equivalent circuit containing a series combination of two parallel (QR) circuit elements gives a good fitting of the complex impedances as shown in Fig. 4(f),

where R is the resistance and Q is the constant phase element (CPE). The high-frequency and low-frequency impedance arcs are attributed to the contributions from grains and grain boundaries respectively, which are determined by the capacitance criterion, $C_{hf} < C_{lf}$, based on the fact that the much thinner boundaries result in much larger capacitance (C) of grain boundaries than that of grains. To obtain a more intuitive comparison of C_{hf} and C_{lf} , the frequency dependence of electric modulus (M^*) is plotted. Figure 5 shows the frequency dependence of $\log M'' /$

Fig. 5 Frequency dependence of $\log M''/M''_{\max}$ and $\log Z''/Z''_{\max}$ of BIT and 1%Sr samples at 450 °C.

$M''_{\max}$ and $\log Z''/Z''_{\max}$ curves at 450 °C. Both $\log Z''/Z''_{\max}$ and $\log M''/M''_{\max}$ curves show two peaks at low frequency and high frequency, respectively, in accordance with the $Z''-Z'$ plots. While the low-frequency $\log M''/M''_{\max}$ peaks are so weak that the logarithmic plot is required to make them observable. It is known that the M'' value is proportional to the inverse of capacitance [26,27], so the low-frequency peaks of M'' correspond to more capacitive components than the high-frequency peaks. Therefore, the two relaxations are distinguished: the low-frequency one originates from grain boundaries and the high-frequency one results from grains. The BIT sample has lower relaxation frequencies than the 1%Sr sample, in consistent with the dielectric data displayed in Fig. 3.

The electrical properties of microstructural components

are qualitatively assessed according to the dielectric and impedance analysis. For both samples of BIT and 1%Sr, the resistances are dominated by grain boundaries as evidenced by the much larger diameters of the impedance semicircular arcs at low frequencies than those at high frequencies as shown in Fig. 4. Doping Sr in BIT dramatically decreases the resistivity of grains (i.e., the compound), however, brings about different effects on the resistance of grain boundaries depending on temperature. The resistance of grain boundaries of the 1%Sr sample is larger than that of the BIT sample below ~380 °C, and changes to be lower above ~380 °C as shown in Fig. S1 in the ESM.

To understand the temperature dependent conductivities of the samples, the kinetic analysis of conduction is performed. Figure 6 shows the frequency dependence of AC conductivity (σ_{ac}) which is calculated from the dielectric data using the relation $\sigma_{ac} = \omega \epsilon_0 \epsilon''$, where ω is angular frequency and ϵ_0 is the permittivity of free space. It is observed that the AC conductivity of the ceramics increases with increasing temperature. The frequency independent plateau (region I) is observed at low frequency and high temperature, indicating the dominance of DC conductivity in the region I, which is consistent with the linear region with slope ~1 in Fig. 3(c). With increasing frequency, σ_{ac} changes to frequency dependent as the frequency is beyond a certain value due to the capacitance impedance contribution. Comparing with the $Z''-\log f$ and $M''-\log f$ plots in Fig. 5, the frequencies when σ_{ac} departs from the linear region in Fig. 6 are consistent with the low-frequency relaxation frequencies in Fig. 5, indicating the departure of σ_{ac} from DC dominance is caused by the capacitance impedance contribution

Fig. 6 Frequency dependence of σ_{ac} of (a) BIT and (b) 1%Sr ceramics at different temperatures. The inset shows $\log \sigma_{dc}$ as a function of $10^3/T$.

of grain boundaries. The DC conductivities (σ_{dc}) of the samples are obtained by extrapolating the frequency independent σ_{ac} to $f = 0$ and plotted versus $10^3/T$ as shown in the inset of Fig. 6. The $\ln\sigma_{dc}-1/T$ plots show a linear relation in the temperature range from 270 to 600 °C for the 1%Sr sample and from 310 to 600 °C for BIT, obeying the Arrhenius-type thermal activation behavior ($\sigma = \sigma_0 \exp(-E_a / k_B T)$). The conduction activation energies (E_a^{dc}) of the materials are calculated with the Arrhenius relation, and the calculated E_a^{dc} values are 0.91 and 1.01 eV for BIT and 1%Sr samples, respectively.

Figure 7(a) shows $\log\sigma_{ac}$ as a function of $10^3/T$ for BIT, 1%Sr, 2%Sr, 5%Sr, and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ceramics at 100 Hz. The plots show two linear regimes. The

high-temperature linear relation of $\ln\sigma_{ac}-1/T$ is frequency independent, and the conduction activation energies (E_a^{ac}) are calculated to be 0.91 and 1.01 eV for BIT and 1%Sr-doped samples respectively, as shown in Figs. 7(b) and 7(c). The E_a^{ac} values calculated from the low-temperature linear relations are 0.54 eV for BIT and 0.56 eV for the 1%Sr sample.

Figure 8 depicts the polarization versus electric field ($P-E$) hysteresis loop of Sr-doped bismuth titanate ceramics. Although all of the $P-E$ loops are not saturated, they can provide some useful information for understanding the conduction of doped ceramics. As can be seen, the undoped BIT ceramic and the $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ceramic show the apparent ferroelectric polarization characteristics with the sharper mouths of

Fig. 7 (a) $\log\sigma_{ac}$ as a function of $10^3/T$ for different compositions at 100 Hz; (b) $\log\sigma_{ac}$ of BIT ceramic at 100 Hz and 1 kHz; (c) $\log\sigma_{ac}$ of 1%Sr ceramic at 100 Hz and 1 kHz.

Fig. 8 $P-E$ loop of Sr-doped ceramics: (a) BIT, (b) 1%Sr, (c) 2%Sr, (d) 5%Sr, (e) $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$; (f) $P-E$ loop of all the Sr-doped ceramics at 60 kV/cm.

hysteresis loops. Both of BIT and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ceramics can withstand about 100 kV voltage. However, the 1%Sr and 2%Sr doped ceramics can only bear a voltage of ~ 80 kV because the Sr dopants increase the conductivity of grains as discussed below. The 5%Sr sample exhibits a plump loop, which may be attributed to the mixed microstructure of large leakage Sr-doped phase and insulated $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ phase. The mixed microstructure forms a complicated capacitance structure, leading to the plump loop but not from the intrinsic ferroelectric polarization. It should be noted that the BIT ceramic displays a necking P – E loop, which may result from pinning by defects, probably acceptor–oxygen-vacancy defect complexes [28].

4 Discussion

The impedance analysis indicates that the resistance of grain boundaries is higher than that of grains in the prepared ceramics. This phenomenon would be caused by the re-oxidation of grain boundaries during cooling from sintering temperature. It is generally accepted that the dielectric properties and conduction behaviors of perovskite-related oxides are closely related to the oxygen vacancies [29,30]. Our previous work of oxidation/reduction annealing on BIT-based ceramics also confirms the above conclusion [31]. It is believed that the oxygen vacancies are induced by the evaporation of Bi at sintering temperature [32]. The ionization of oxygen vacancies creates electrons and charged oxygen vacancies with the Kroger–Vink notation [33]:

where $\text{V}_\text{O}^\bullet$ and $\text{V}_\text{O}^{\bullet\bullet}$ are the single and double-ionized oxygen vacancies, respectively. The long-range migrations of these oxygen-vacancy-related carriers result in conduction, and the localized reorientation hopping of these carriers contributes to the polarization and dielectric relaxations. During cooling down from sintering temperature, the samples are re-oxidized, but the re-oxidation takes place mainly at grain boundaries because the oxidation is controlled by oxygen diffusion [34]. Therefore, the grain boundaries of the prepared ceramics are more resistive than grains.

In this work, the 1%Sr dopants suppress the low-temperature conduction of BIT while increase the high-temperature conduction, and lead to different effects on the conduction of grains and grain boundaries. To understand these phenomena, it requires an insight

to the mechanism of conduction. The conduction activation energy of BIT and Sr-doped samples at high temperatures is ranging from 0.91 to 1.01 eV, close to the reported values of charged oxygen vacancies in perovskite oxides [33,35–38]. Paladino [35] reported that the activation energy for diffusion of the double-ionized oxygen vacancies in SrTiO_3 crystal is 0.98 eV. The conduction activation energies for doubly ionized oxygen vacancies in $(\text{Sr}_{1-1.5x}, \text{Bi}_x)\text{TiO}_3$ is 0.99–1.12 eV [36]. Waser *et al.* [37] reported that the conduction activation energy of oxygen vacancy is 1.005–1.093 eV in Fe-doped SrTiO_3 . This is a good agreement with the experimental results of the conduction activation energy (0.91–1.01 eV) obtained in the present paper. Hereby, the conduction above 270 °C for the 1%Sr sample and above 310 °C for BIT very likely arises from the movement of $\text{V}_\text{O}^{\bullet\bullet}$.

The activation energy of conduction E_a^{ac} at low temperature is 0.54–0.56 eV. The low-temperature conduction could be attributed to the thermally activated electrons from the second-ionization of oxygen vacancies as suggested by Ang *et al.* [36]. In their work, the Bi-doped SrTiO_3 ceramics showed the conduction activation energies from 0.59 to 0.78 eV associated with the second-ionization of oxygen vacancies. Therefore, the different conduction mechanisms would exist in the experimental samples depending on temperature, the long-range motion of the double-ionized oxygen vacancies provides dominant contribution to conduction at high temperature, i.e., above ~ 270 °C for the 1%Sr sample and above ~ 310 °C for BIT; below these temperatures, the conduction mainly originates from the motion of electrons created by the ionization of oxygen vacancies.

The impedance analysis in Fig. 4 indicates that the 1%Sr dopants dramatically increase the conductivities of grains of BIT ceramics, while suppress the conductivities of grain boundaries as the temperature below ~ 380 °C and enhance the electrical conduction of grain boundaries above ~ 380 °C. These microstructure-related conduction behaviors are interpreted in term of the compensating effect of Sr dopants. The aliovalent Sr^{2+} dopants preferentially substitute Bi^{3+} in BIT because the interstitial occupancy would not be favourable due to the large ionic size of Sr^{2+} [39]. To keep the charge neutrality, the incorporation of Sr can lead to the following defect reaction [40]:

The Sr doping induces the formation of oxygen

vacancies. On the other hand, the Sr doping will suppress the evaporation of Bi and consequently decrease the oxygen vacancy concentration because the Sr–O bond has larger bond energy (454 kJ/mol) than the Bi–O bond (343 kJ/mol) [17]. In the experimental samples, the decrease of oxygen vacancies due to the suppression of Bi evaporation is apparently weaker than the inducing of oxygen vacancies by reaction (2) according to the experimental fact that the 1%Sr sample has more conductive grains than BIT. It is believed that there would be more oxygen vacancies in grains of 1%Sr sample than in BIT, which results in the higher conductivity of grains in the 1%Sr sample.

During cooling down from the sintering temperature, the re-oxidation reaction eliminates partially oxygen vacancies and produces holes, but mainly at grain boundaries [34]:

Combining equations (2) and (3), the Sr dopants work as acceptors to provide holes at grain boundaries:

The holes created by reaction (4) will compensate for the electrons resulting from the ionization of oxygen vacancies. This could be the main reason for the higher resistivity of Sr-doped samples than that of BIT at low temperature, where the conduction of samples originates from electronic carriers.

The reaction (4) implies that the amount of oxygen vacancies in grain boundaries of the Sr-doped samples is less than that of BIT at low temperature since the Sr dopants provide the lattice oxygen (O_O). When the temperature rises up to the range where the conduction is dominated by the motion of charged oxygen vacancies ($V_O^{\bullet\bullet}$), the reaction (2) would take effect and induce more oxygen vacancies in grain boundaries. This results in that the conductivity of the 1%Sr sample gradually exceeds that of BIT as shown in Fig. 4 and Fig. 7. The experimental results support well the above deduction. The other Sr-doped samples show the similar temperature dependence of conduction with the 1%Sr sample, but the conductivity is lower because they are two phase samples and the $SrBi_8Ti_7O_{27}$ ceramic is highly resistive.

4 Conclusions

$Bi_4Ti_3O_{12}$ ceramics doped with small amount Sr ions

were synthesized by conventional solid-state reaction route and investigated by temperature dependent AC impedance spectroscopy. The small amount of Sr dopants decreased grain size and suppressed the ferroelectric phase transition temperature. The impedance analysis indicated that the resistance of the prepared ceramics was controlled by grain boundary. The grain boundaries of 1 at% Sr-doped $Bi_4Ti_3O_{12}$ were more resistive than pure $Bi_4Ti_3O_{12}$ below $\sim 380^\circ C$ while more conductive above $\sim 380^\circ C$. The substitution of Sr for Bi would increase the number of intracrystalline oxygen vacancies resulting in higher intracrystalline conductivity. At low temperature, the Sr dopants play the hole-doping effect in grain boundaries and consequently result in higher resistance of Sr-doped samples than that of pure BIT. At high temperature, the Sr dopants induce more oxygen vacancies in grain boundaries to cause the higher conductivity of the 1%Sr sample than that of pure BIT. The present results provide useful information for designing and/or modifying the properties of $Bi_4Ti_3O_{12}$ related ceramics.

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Electronic Supplementary Material

Supplementary material (Nyquist plots of BIT and 1%Sr samples near critical temperature) is available in the online version of this article at <https://doi.org/10.1007/s40145-018-0277-1>.

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