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

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Abstract: Bi$_4$Ti$_3$O$_{12}$ is an important lead-free ferroelectric material. Doping modification of Bi$_4$Ti$_3$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 Bi$_4$Ti$_3$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 Bi$_4$Ti$_3$O$_{12}$ ceramic at room temperature, and resulted in different effects on the conductivity of grains and grain boundaries. The conductivity of grains in Bi$_4$Ti$_3$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 Bi$_4$Ti$_3$O$_{12}$ exhibited lower conductivity than pure Bi$_4$Ti$_3$O$_{12}$ below ~380 °C and higher conductivity above ~380 °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 $(A_{n-1}B_nO_{3n+1})^2$ $(B_2O_2)^{2+}$, 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 $(A_{n-1}B_nO_{3n+1})^2$ and fluorite structure layers $(B_2O_2)^{2+}$ 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]. Bi$_4$Ti$_3$O$_{12}$ (BIT) is a typical 3-layered Aurivillius compound with $T_c = 675$ °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 Bi$_4$Ti$_3$O$_{12}$-based compounds have been developed, such as Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ [13], Sr$_{4}$Bi$_5$Ti$_6$O$_{27}$ [14], SrBi$_3$Ti$_4$O$_{15}$ [15], and La$_{0.75}$Bi$_3$Ti$_3$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...
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 Bi$_4$Ti$_3$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 (Bi$_{1-x}$Sr$_x$)$_4$Ti$_3$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 SrBi$_8$Ti$_7$O$_{27}$ sample was also prepared. Stoichiometric amounts of Bi$_2$O$_3$, 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-calced 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 Ka, 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 Bi$_4$Ti$_3$O$_{12}$ (JCPDS No. 35-0795); however, the sample of $x = 0.05$ fits with two phases of Bi$_4$Ti$_3$O$_{12}$ and SrBi$_8$Ti$_7$O$_{27}$ (JCPDS No. 31-1342). The enlarged parts of XRD patterns clearly show that the single peaks at ~16.2° and ~30° 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 ~16.2° 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 (Bi$_{20}$TiO$_{32}$) is observed in the samples of $x = 0.05$ and SrBi$_8$Ti$_7$O$_{27}$, which is evidenced by the weak peak at ~28°. The XRD patterns of $x = 0, 0.01$, and 0.02 are well indexed with the monoclinic structure $B2\overline{2}c$. 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 ($r = 1.26$ Å, coordination number CN = 8) than Bi$^{3+}$ ions ($r = 1.17$ Å, 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 (Bi$_{1-x}$Sr$_x$)$_4$Ti$_3$O$_{12}$ is less than 0.02 according to the experimental results.
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 ($\varepsilon'_r$) and imaginary part ($\varepsilon''_r$) 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 frequency, and much larger $\varepsilon''_r$ 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 ($\varepsilon'_r$) of BIT at high frequency as shown in Fig. 3(a), and the values of $\varepsilon'_r$ are ~120. For the SrBi$_8$Ti$_7$O$_{27}$ sample, the value of $\varepsilon'_r$ 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 $\varepsilon'_r$ value of the 1%Sr sample is lower than that of BIT at low frequency but larger at high frequency. At 450 °C, the $\varepsilon'_r$ value of 1%Sr sample is larger than that of BIT approximately in all frequency range. The log $\varepsilon'_r$ 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 $\varepsilon'_r$ 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 SrBi$_8$Ti$_7$O$_{27}$. The peak temperatures of BIT and SrBi$_8$Ti$_7$O$_{27}$ are consistent with the $T_c$ values of BIT (675 °C) and SrBi$_8$Ti$_7$O$_{27}$ (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.

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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 Bi\(_4\)Ti\(_3\)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 \( \tau \) (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 \( \tau \) 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
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 $\log M^*/j\omega$.

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

$M''_{\text{max}}$ and $\log Z'' / Z''_{\text{max}}$ curves at 450 ℃. Both $\log Z'' / Z''_{\text{max}}$ and $\log M'' / M''_{\text{max}}$ curves show two peaks at low frequency and high frequency, respectively, in accordance with the $Z'' = Z'$ plots. While the low-frequency $\log M'' / M''_{\text{max}}$ 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 ℃, and changes to be lower above ~380 ℃ 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 ($\sigma_{\text{ac}}$) which is calculated from the dielectric data using the relation $\sigma_{\text{ac}} = \omega \varepsilon \varepsilon_0$, where $\omega$ is angular frequency and $\varepsilon_0$ 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, $\sigma_{\text{ac}}$ 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 $\sigma_{\text{ac}}$ departs from the linear region in Fig. 6 are consistent with the low-frequency relaxation frequencies in Fig. 5, indicating the departure of $\sigma_{\text{ac}}$ from DC dominance is caused by the capacitance impedance contribution.

![Fig. 6](http://www.springer.com/journal/40145)

Fig. 6 Frequency dependence of $\sigma_{\text{ac}}$ of (a) BIT and (b) 1%Sr ceramics at different temperatures. The inset shows $\log \sigma_{\text{ac}}$ as a function of $10^3/T$.
of grain boundaries. The DC conductivities ($\sigma_{dc}$) of the samples are obtained by extrapolating the frequency independent $\sigma_{ac}$ 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 ($E_a^{ac}$) 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.

The high-temperature linear relation of $\ln(\sigma_{dc})-1/T$ 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 7(a) shows $\log(\sigma_{ac})$ as a function of $10^3/T$ for BIT, 1%Sr, 2%Sr, 5%Sr, and SrBi$_8$Ti$_7$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 SrBi$_8$Ti$_7$O$_{27}$ ceramic show the apparent ferroelectric polarization characteristics with the sharper mouths of

![Fig. 7](image-url)  (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](image-url)  $P-E$ loop of Sr-doped ceramics: (a) BIT, (b) 1%Sr, (c) 2%Sr, (d) 5%Sr, (e) SrBi$_8$Ti$_7$O$_{27}$; (f) $P-E$ loop of all the Sr-doped ceramics at 60 kV/cm.
hysteresis loops. Both of BIT and SrBi$_5$Ti$_4$O$_{17}$ 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 SrBi$_5$Ti$_4$O$_{17}$ 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]:

\[ \text{Vo} \leftrightarrow \text{Vo}^- + e^- \quad \text{Vo} \leftrightarrow \text{Vo}^{2-} + 2e^- \quad (1) \]

where \( \text{Vo} \) and \( \text{Vo}^- \) 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 carries 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 doubly-ionized oxygen vacancies in SrTiO$_3$ crystal is 0.98 eV. The conduction activation energies for doubly ionized oxygen vacancies in (Sr$_{1-1.5x}$Bi$_x$)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 \( \text{Vo}^{2-} \).

The activation energy of conduction \( E_a^\text{ac} \) 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]:

\[ 2\text{SrO} \rightarrow \text{Bi}_{2-x}\text{Sr}_x\text{Ti}_4\text{O}_{12} \rightarrow 2\text{Sr}^{2+} + 2\text{O} + \text{Vo}^{2-} \quad (2) \]

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 vaporization 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]:

$$V_0^+ + \frac{1}{2}O_2 \rightarrow O_0 + 2h^+ \quad (3)$$

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

$$2SrO \rightarrow Bi_2Ti_3O_{12} \rightarrow 2SrBi_2O_3 + O_2 + O + 2h^+ \quad (4)$$

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 (O₂). When the
temperature rises up to the range where the conduction
is dominated by the motion of charged oxygen
vacancies (V_0^+), the reaction (2) would take effect and
induce more oxygen vacancies in grain boundaries.
This results in 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 SrBi₈Ti₆O₂₇
ceramic is highly resistive.

4 Conclusions

Bi₄Ti₃O₁₂ 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 Bi₄Ti₃O₁₂ were more
resistive than pure Bi₄Ti₃O₁₂ below ~380 °C while
more conductive above ~380 °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 Bi₄Ti₃O₁₂ related ceramics.

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Electronic Supplementary Material

Supplementary material (Nyquist plots of BIT and 1%Sr
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s40145-018-0277-1.

References

[1] Aurivillius B. Mixed bismuth oxides with layer lattices.
Arkiv Kemi 1949, 1: 463–480, 499–512.
[2] Subbarao EC. A family of ferroelectric bismuth compounds.
J Phys Chem Solids 1962, 23: 665–676.
[3] Zhao Y, Fan H, Ren X, et al. Lead-free Bi₅₋ₓLaxTi₃FeO₁₅ (x =
0, 1) nanofibers toward wool keratin-based biocompatible
piezoelectric nanogenerators. J Mater Chem C 2016, 4:
7324–7331.
[4] Zhao Y, Fan H, Liu G, et al. Ferroelectric, piezoelectric
properties and magnetoelectric coupling behavior in
aurivillius Bi₅Ti₃FeO₁₅ multiferroic nanofibers by
electrospinning. J Alloys Compd 2016, 675: 441–447.
[5] Kendall KR, Thomas JK, Loe H-C. Synthesis and ionic
conductivity of a new series of modified Aurivillius phases.

www.springer.com/journal/40145
Goodenough JB. Oxide-ion electrolytes. **Ann Rev Mater Res** 2003, **33**: 91–128.

Park BH, Kang BS, Bu SD, *et al.* Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature* 1999, **401**: 682–684.

Cheng C, Tang M, Ye Z, *et al.* Microstructure and ferroelectric properties of dysprosium-doped bismuth titanate thin films. *Mater Lett* 2007, **61**: 4117–4120.

De Araujo CA-P, Cuchiaro JD, McMellan LD, *et al.* Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature* 1995, **374**: 627–629.

Fang P, Fan H, Xi Z, *et al.* Studies of structural and electrical properties on four-layers Aurivillius phase BaBi$_4$Ti$_4$O$_{15}$. *Solid State Commun* 2012, **152**: 979–983.

Subohi O, Kumar GS, Malik MM, *et al.* Dielectric properties of bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) synthesized using solution combustion route. *Physica B* 2012, **407**: 3813–3817.

Chang Q, Fan H, Long C. Effect of isovalent lanthanide cations compensation for volatilized A-site bismuth in Aurivillius ferroelectric bismuth titanate. *J Mater Sci Mater El* 2017, **28**: 4637–4646.

Takenaka T, Sakata K, Toda K. Piezoelectric properties of bismuth layer-structured ferroelectric Na$_{0.5}$Bi$_4$Ti$_4$O$_{15}$ ceramic. *Jpn J Appl Phys* 1985, **24**: 730.

Gelfuso MV, Thomazini D, Eiras JA. Synthesis and structural, ferroelectric, and piezoelectric properties of SrBi$_4$Ti$_4$O$_{15}$ ceramics. *J Am Ceram Soc* 1999, **82**: 2368–2372.

Kharitonova EP, Voronkova VI. Synthesis and electrical properties of mixed-layer Aurivillius phases. *Inorg Mater* 2007, **43**: 1340–1344.

Park BH, Kang BS, Bu SD, *et al.* Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature* 1999, **401**: 682–684.

Speight JG. *Lange’s Handbook of Chemistry*. McGraw-Hill, 2005.

Rodriguez-Carvajal J. Fullprof: A program for Rietveld refinement and pattern matching analysis. In *Proceedings of the Satellite Meeting on Powder Diffraction of the XV congress of the IUCr*, 1990: 127.

Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst* 1976, **A32**: 751–767.

Jonsher AK. A new understanding of the dielectric relaxation of solids. *J Mater Sci* 1981, **16**: 2037–2060.

Saha S, Sinha TP. Dielectric relaxation in SrFe$_{12}$Nb$_2$O$_{39}$. *J Appl Phys* 2006, **99**: 014109.

Noguchi Y, Miyayama M, Kudo T. Ferroelectric properties of intergrowth Bi$_3$Ti$_4$O$_{12}$–SrBi$_4$Ti$_4$O$_{15}$ ceramics. *Appl Phys Lett* 2000, **77**: 3639–3641.

Suárez DY, Reaney IM, Lee WE. Relation between tolerance factor and $T_c$ in Aurivillius compounds. *J Mater Res* 2001, **16**: 3139–3149.

Ravindran P, Vidyra R, Kjekshus A, *et al.* Theoretical investigation of magnetoelectric behavior in BiFeO$_3$. *Phys Rev B* 2006, **74**: 224412.

Rehman F, Li J-B, Zhang J-S, *et al.* Grains and grain boundaries contribution to dielectric relaxations and conduction of Bi$_5$Ti$_3$FeO$_{15}$. *J Appl Phys* 2015, **118**: 214101.

Wong YJ, Hassan J, Hashim M. Dielectric properties, impedance analysis and modulus behavior of CaTiO$_3$ ceramic prepared by solid state reaction. *J Alloys Compd* 2013, **571**: 138–144.

Morrison FD, Sinclair DC, West AR. Characterization of lanthanum-doped barium titanate ceramics using impedance spectroscopy. *J Am Ceram Soc* 2001, **84**: 531–538.

Rojac T, Bencan A, Drazic G, *et al.* Piezoelectric nonlinearity and frequency dispersion of the direct piezoelectric response of BiFeO$_3$ ceramics. *J Appl Phys* 2012, **112**: 064114.

Ginsberg DM. *Physical Properties of High Temperature Superconductors I*. World Scientific, 1998.

Schooler JF, Hosler WR, Cohen ML. Superconductivity in Semiconducting SrTiO$_3$. *Phys Rev Lett* 1964, **12**: 474.

Rehman F, Li J-B, Cao M-S, *et al.* Contribution of grains and grain boundaries to dielectric relaxations and conduction of Aurivillius Bi$_3$Ti$_3$Fe$_{0.5}$Nb$_{0.5}$O$_{12}$ ceramics. *Ceram Int* 2015, **41**: 14652–14659.

Nagata H. Electrical properties and tracer diffusion of oxygen in some Bi-based lead-free piezoelectric ceramics. *J Ceram Soc Jpn* 2008, **116**: 271–277.

Bidault O, Goux P, Chikichek M, *et al.* Space-charge polarization in perovskites. *Phys Rev B* 1994, **49**: 7868.

Dwivedi RK, Kumar D, Parkash O. Dielectric relaxation in valence compensated solid solution Sr$_{0.65}$La$_{0.35}$Ti$_{0.65}$Co$_{0.35}$O$_3$. *J Phys D: Appl Phys* 2000, **33**: 88.

Paladino AE. Oxidation kinetics of single-crystal SrTiO$_3$. *J Am Ceram Soc* 1965, **48**: 476–478.

Ang C, Yu Z, Cross LE. Oxygen-vacancy-related low-frequency dielectric relaxation and electrical conduction in Bi$_2$SrTiO$_5$. *Phys Rev B* 2000, **62**: 228.

Waser R, Baiatu T, Härndtl K-H. dc electrical degradation of perovskite-type titanates: I. ceramics. *J Am Ceram Soc* 1990, **73**: 1645–1653.

Subohi O, Shastri L, Kumar GS, *et al.* Study of Maxwell–Wagner (M–W) relaxation behavior and hysteresis observed in bismuth titanate layered structure obtained by solution combustion synthesis using dextrose as fuel. *Matier Res Bull* 2014, **49**: 651–656.

Hervoches CH, Snedden A, Riggs R, *et al.* Structural behavior of the four-layer Aurivillius-phase ferroelectrics SrBi$_4$Ti$_4$O$_{15}$ and Bi$_5$Ti$_3$Fe$_{0.5}$O$_{12}$. *J Solid State Chem* 2002, **164**: 280–291.

Smyth DM. *The Defect Chemistry of Metal Oxides*. Oxford University Press, 2000.

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