Differences in nature of electrical conductions among Bi$_4$Ti$_3$O$_{12}$-based ferroelectric polycrystalline ceramics

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Bismuth titanate Bi$_4$Ti$_3$O$_{12}$ (BiT), was one of the most promising lead-free high-temperature piezoelectric materials, due to high Curie temperature (675 °C) and large spontaneous polarization (50 $\mu$C/cm$^2$); however, extensive studies had revealed that high leakage conductivity interferes with the poling process, hindering its practical applications. In this paper, an electrically insulating property was achieved by a low level Nb donor substitution to suppress a high level of holes associated with high oxygen vacancy concentration. Bi$_4$Ti$_{2.97}$Nb$_{0.03}$O$_{12}$ ceramic showed significant enhancements of electrical resistivity by more than three orders of magnitude and activity energy with value $>1.2$ eV, which are significant for piezoelectric applications of BiT-based materials. However, pure and A$_2$O$_3$-excess (A = Bi, La and Nd; 3 at %) BiT ceramics, were mixed hole and oxygen ion conductors. Schottky barriers were both formed at grain boundary region and the sample-electrode interface, because of the existence of semiconducting bulk. Interestingly, the electron conduction could be suppressed in N$_2$, as a consequence, they became oxide ion conductors with conductivity of about $4 \times 10^{-4}$ S cm$^{-1}$ at 600 °C.

Bismuth titanate Bi$_4$Ti$_3$O$_{12}$ (BiT), has been widely studied as one of most important bismuth-layer-structured ferroelectrics (BLSFs), which consists of three-layer pseudo-perovskite (Bi$_4$Ti$_3$O$_{12}$)$^{2-}$ units sandwiched between (Bi$_2$O$_3$)$^{2+}$ layers along the $c$ axis$^{1-5}$. BiT shows a high Curie point ($T_c$) of 675 °C and a large spontaneous polarization ($P_s$) of about 50 $\mu$C/cm$^2$.$^6,7$. It is well known that Bi$_2$O$_3$ vaporization with generations of VBi$^{‴}$ (bismuth vacancy) and VO$^{‴}$ (oxygen vacancy) is a severe problem in the preparation of BiT-based materials, which largely affect electrical properties of them. High leakage conductivity closely related to the existence of VO$^{‴}$ and VO$^{‴}$ excess ($A = Bi, La$ and Nd; 3 at %) BiT ceramics, were mixed hole and oxygen ion conductors. Schottky barriers were both formed at grain boundary region and the sample-electrode interface, because of the existence of semiconducting bulk. Interestingly, the electron conduction could be suppressed in N$_2$, as a consequence, they became oxide ion conductors with conductivity of about $4 \times 10^{-4}$ S cm$^{-1}$ at 600 °C.

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It is distinct that a problem that must be addressed in the development of BiT-based sensors is the origin of high leakage conductivity of materials. Takahashi et al. revealed that BiT single crystals were oxide ionic and $p$-type mixed conductors$^{31}$. They suggested that VO$^{‴}$ and VO$^{‴}$ preferentially existed in the perovskite layers, which could be effectively suppressed by the A-site La or the B-site donor substitution; thus the decreases in electronic and ionic conductivities were achieved, along the $ab$ axis in BiT single crystals$^{31-33}$. But for ceramics, the grain boundary is likely to act as a source or sink for defects (oxygen vacancies)$^{34-38}$. Consequently the ceramics

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other than single crystals, are often electrically heterogeneous. BiT ceramics also showed oxide ionic and $p$-type mixed conduction, where the electrical properties of the boundaries were pronounced $^{39,40}$. Impedance spectroscopy has been widely used to investigate AC conduction behaviors of crystalline, polycrystalline and amorphous materials $^{41}$. Commonly, electrode, grain boundary and grain components together contribute to the conductions of polycrystalline materials $^{41-43}$. In this paper, impedance data of BiT-based ceramics including BiT, BiT-A (3 at. % excess A$_2$O$_3$; A = Bi, La and Nd), BLT (Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$) and BiT-Nb (Bi$_{4}$Ti$_{2.97}$Nb$_{0.03}$O$_{12}$), were studied systematically, to investigate the effects of different modifications on heterogeneous structure and electrical conductivity. Also, electrical conduction behaviors of them as functions of temperature and atmosphere were elaborated.

### Results

#### Structure and compositional analysis.

Powder diffraction refinement with a Le-Bail fit (GSAS-EXPGUI program) $^{44,45}$ was carried out to characterize crystal structures of the prepared oxides, as shown in Fig. 1. The orthorhombic Aba2 (ICSD #240210) transformed from B2cb (Aba2: abc = B2cb: b’c’a’) was used as an initial structural model. For each composition, the calculated data well agrees with the experimental ones, and the reliability factors ($R_{wp}$, $R_p$ and reduced $\chi^2$; Table 1) are reasonable. However, the refined results reveal small amounts

| Composition | BiT | BiT-Bi | BiT-La | BiT-Nd | BiT-Nb |
|-------------|-----|--------|--------|--------|--------|
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | Aba2 | Aba2 | Aba2 | Aba2 | Aba2 |
| T (K) | 298 | 298 | 298 | 298 | 298 |
| a (Å) | 5.40949(13) | 5.40986(23) | 5.41282(21) | 5.40957(22) | 5.41134(15) |
| b (Å) | 32.81958(21) | 32.81764(16) | 32.82626(20) | 32.82428(23) | 32.82782(31) |
| c (Å) | 5.44826(16) | 5.44907(30) | 5.44637(28) | 5.44575(25) | 5.44841(16) |
| V (Å$^3$) | 967.27(4) | 967.48(7) | 967.72(6) | 966.98(6) | 967.87(4) |
| Orthorhombicity | 7.15 × 10$^{-3}$ | 7.22 × 10$^{-3}$ | 6.17 × 10$^{-3}$ | 6.66 × 10$^{-3}$ | 6.83 × 10$^{-3}$ |
| Degree of Texture | 89% | 91% | 89% | 82.5% | 54% |
of Bi$_2$O$_3$ in BiT-A (e.g., BiT-Bi and BiT-La), corresponding to the small diffraction peak at $2\theta = \sim 28^\circ$ (insets of Fig. 1b and c). In addition, the (00$l$) diffraction peaks in BiT, BiT-Bi and BiT-La, e.g., (060), (080) and (0140), are abnormally intensive, while the major peak (171) is severely suppressed (Fig. 1a–c). Absolutely, they were highly textured in the $c$ axis direction. However, the texture is not pronounced in BiT-Nb (Fig. 1d). The degree of texture can be expressed by using Lotgering orientation factor (LOF), $f$. For (00$l$) preferred orientation, $f$ is defined as following equations:

$$f = \frac{P - P_0}{1 - P_0}$$

where $P = \sum I_{(00l)}/\sum I_{(00l)}$ (target sample) and $P_0 = \sum I_{(00l)}/\sum I_{(00l)}$ (standard random sample, PDF#35–0795). For BiT and BiT-A, highly c-oriented structure results in high $f$ value, being around 0.9, much higher than that for BiT-Nb (0.54). Table 1 lists refined lattice parameters of BiT, BiT-A and BiT-Nb. BiT-Nb shows larger lattice parameters ($a$, $b$ and $c$) and unit cell volume ($V$) than BiT, which should be the results of incorporation of Nb$^{5+}$ with larger size at B site (Nb$^{5+}$: N0.64 Å, Ti$^{4+}$: 0.605 Å; 6 CN)$^{47}$. BiT-Bi and BiT-La show increased $V$, however, this value for BiT-Nd decreases.

As indicated by surface SEM (scanning electron microscope) images (Fig. S1a–c; Supplementary Information), the great majority of grains in BiT-A are overlarge and laminated. The aspect ratio $L/t$ (length/thickness) of the laminated grains ranges from 10 to 30. Probably, that stacking and laminating a few such grains leads to high degree of texture in them. In contrast, BiT-Nb shows size-smaller grains, which is consistent with the results of the Ta/Nb substituted BiT ceramics$^{35}$. And no pores are found within grains, which are visible in BiT-A (cross-section SEM images; insets of Fig. S1a–d, Supplementary Information). It is presumed that the incorporation of Nb$^{5+}$ into the lattices leads to a lower grain-growth rate in the $a$-$b$ plane due to low V$_{O^{2-}}$ concentration ([V$_{O^{2-}}$]) in the perovskite layers. Figure 2a and b show microstructure of the grain boundary region of the polished BiT-Bi and BiT-La samples, respectively. It is clear that heterogeneous structure is observed at the grain boundaries.
indicated by EDS (energy-dispersive x-ray spectroscopy) line scans, BiT-Bi and BiT-La show no obvious variation in Bi and Ti intensities along the line 1 → 3, whereas a composition deviation with respect to oxygen is observed at the position 2 of grain boundary (Fig. 2c and d). This position may correspond to the grain-boundary surface layer, which is possibly created by the accumulation of space charges. In addition, grain composition for them is analyzed by EDS surface scans of five entire grains, and the average atomic ratios are normalized and listed in Table 2. The measured compositions of BiT-Bi and BiT-La are close to the theoretical ratios in BiT within instrument resolution and standard deviations. However, stoichiometric composition shows somewhat deviation at the position 2 of grain boundary, where the O concentration and the ratio of \(2[O]/(3[Bi] + 4[Ti] + 3[La])\) are both higher than those in grain (about 63% and 1, respectively). The experiments also reveal about 0.55 at. % La in the bulk phase, close to nominally excess level (0.62 at. %). Presumably, these nonstoichiometric compositions at the grain boundary regions are not associated with Bi\(_2\)O\(_3\) or La\(_2\)O\(_3\). TEM (Transmission electron microscopy) image reveals an evidence of some Bi-rich regions at the triple points in BiT-Bi, as shown in Fig. 3a. The relevant EDS line scan reveals the absence of element Ti in Bi-rich phase (Fig. 3b), which is likely ascribed to be Bi\(_2\)O\(_3\).

| Sample          | elements | grain     | Point 2 at grain boundary | theoretical composition |
|-----------------|----------|-----------|---------------------------|-------------------------|
| BiT-Bi (Bi\(_4\)Ti\(_3\)O\(_12\) • 0.06Bi\(_2\)O\(_3\)) | O (at. %) | 63.44(0.38) | 66.77                     | 63.11                   |
|                 | Bi (at. %) | 21.36(0.41) | 20.15                     | 21.35                   |
|                 | Ti (at. %) | 15.20(0.46) | 13.08                     | 15.54                   |
| BiT-La (Bi\(_4\)Ti\(_3\)O\(_12\) • 0.06La\(_2\)O\(_3\)) | O (at. %) | 63.34(0.45) | 65.24                     | 63.11                   |
|                 | Bi (at. %) | 20.83(0.32) | 20.55                     | 20.73                   |
|                 | Ti (at. %) | 15.28(0.42) | 13.79                     | 15.54                   |
|                 | La (at. %) | 00.55(0.21) | 00.43                     | 0.62                    |

Table 2. Composition analyses for BiT-Bi and BiT-La. EDS data for grain composition were obtained by surface scans on five entire grains, and the mean value and standard deviation were listed. Point 2 at grain boundary was shown in Fig. 2a and b.

Figure 3. HAADF Z-contrast image showing Bi-rich phase (arrowed light areas) at the triple points in BiT-Bi. (b) EDS line scan across the Bi-rich phase in BiT-Bi.
Impedance spectra and component response. Figure 4 demonstrates variable-temperature impedance diagrams of the air-, O₂- and N₂-processed BiT-Bi samples. For the three samples, two complete arcs at high and medium frequencies and, an incomplete one at low frequencies (0.1–1 Hz) due to the limited measurement range of the instrument, are observed in the 250°C diagrams (Fig. 4a). The 250°C capacitance ($C'$) plots of BiT-Bi show a plateau with capacitance values of $\sim$5 nF/cm at low frequencies (Fig. 5). Therefore, the incomplete arc can be ascribed to a grain boundary (GB) response[8]. Previously, BiT single crystals showed two resolved impedance...
semicircles, which were considered as the results of the effects of crystalline plate (CP) and plate boundary (PB), respectively 43. In this study, BiT-Bi ceramic also presents mica-like grains, where CP and PB are visible (inset of Fig. S1a; Supplementary Information). Therefore, the two complete arcs as mentioned above are likely to be associated with the responses of CP and PB, respectively. As indicated by inset of Fig. 4a and the frame inside Fig. 4e, two component parts are observed at the CP region. In BiT-Bi, the electrical properties of the (Bi₂O₂)₂⁺ layers should be pronounced due to high degree of texture in the c axis direction. Therefore, it is likely that they correspond to the AC responses of the (Bi₂O₂)₂⁺ layers (higher frequency) and the pseudo-perovskite blocks (lower frequency), respectively 49. It is reasonable that the former has a lower electrical capacitance than the latter, because of the polarization vector of BiT along the crystallographic a-axis (within the pseudo-perovskite blocks).

When temperature is elevated, the grain boundary arc becomes complete, and another arc (the 4th arc; inset of Fig. 4b) is visible in the 400 °C air/O₂ impedance diagrams, at low frequencies (Fig. 4b). The same data presented as Z″ plots (Fig. 4f) also exhibit an additional peak at low frequencies. The 400 °C C′ plot of the O₂ sample shows a high capacitance plateau (10⁻⁷–10⁻⁶ F/cm) in the same frequency range (Fig. 5a). These experiments suggest that the most likely origin of the 4th arc is ascribed to the electrode effect (discussed later) 38, 42. However, a clear Warburg impedance contribution can be observed below 1 Hz in the 400 °C Z′ plot of the N₂ sample (Fig. 4b). To further increasing temperature, such a Warburg response presents an intensive inclined spike at 550 °C and 700 °C (Fig. 4c and d), due to limited ionic diffusion into a partially blocking electrodes 42, 50. This, combined with steeply increased capacitance at low frequencies (Fig. 5b), indicates that the N₂ sample shows prominent ionic conduction, and the principal conducting species could be O₂⁻ ions 51. In contrast, the air/O₂ samples only show a tail associated with a weak trace of Warburg impedance at the lowest frequencies, due to significantly enhanced electronic conduction 53, 54. The ionic transference number (t_ion) can be evaluated from these Warburg impedances in the case of ion blocking electrode condition, which was described in the literature 52–54. t_ion in N₂ is roughly evaluated to be about 0.85 at 550 °C, which are much higher than those in air and O₂ (<0.1). High t_ion in N₂ is apparently associated with high [VO••] in the sample.

In general, the time constant difference for relaxation of each component is large at low temperature, so one can see separated semicircles for each component (see Fig. 4a and b) 35. However, at high temperature, the time constants for different component are very close and/or relatively small for some of the components, so we normally observe two component semicircles at 700 °C. Like electrolytes and solid-state ionic conducting materials 36, 37, a modified Randles equivalent circuit was used to calculate the impedance data of the N₂ sample, as shown in Fig. 6a An equivalent circuit including several (R/CPE) elements in series (Fig. 6b) was used to calculate the impedance data of the air/O₂ samples. Here, the bulk is integrated and considered as a (R/CPE) component. The parameters and errors for the equivalent circuits are reasonable, and the calculated data well agree with the experiment ones. Similar impedance behaviors as functions of atmosphere and temperature are found for BiT-La and BiT-Nd, which are not shown here. For BiT-La with Pt and Ag electrodes, there are both four overlapping arcs in the 450 °C Z⁺ plots (Fig. S2, Supplementary Information). The resistance (the 4th arc) and the capacitance associated with the electrode effect in the low frequency range are clearly affected by the electrode materials, because of different work functions of them. However, the bulk response that dominates the high frequency data remains unchanged. These experiment results are consistent with those for CaCu₃Ti₄O₁₂ ceramics 38. Slightly affected boundary responses may be ascribed to two different preparation conditions for Ag and Pt electrodes.

In contrast, BLT and BiT-Nb show dissimilar AC responses, as shown in Fig. 7. In Fig. 7a, the N₂-processed BLT sample shows a small inclined spike at 400 °C, which turns into a distorted arc at 750 °C (inset of Fig. 7a).
While no obvious Warburg characteristic is found in BiT-Nb at both 550 °C and 750 °C (Fig. 7c and inset of Fig. 7c), which is an indication of a very small contribution of ion conduction to the electrical conduction. This could be related to low $[V_{\text{O}}^{\bullet\bullet}]$ and highly stabilized oxygen ion in it. In addition, two principal semicircles are
observed in the complex $Z''$ plots of BLT and BiT-Nb under O$_2$ and N$_2$. The same data presented as $C'$ (Fig. 7b and d) and $Z''$ (insets of Fig. 7b and d) plots show two capacitance plateaus and two $Z''$ peaks, respectively. It means that the resistances and the capacitances of BLT and BiT-Nb are principally derived from two regions, i.e., grain (high frequency) and GB (low frequency), respectively.

$pO_2$ dependences of resistivity ($\rho$) and conductivity ($\sigma$). Figure 8 shows $\rho_{\text{bulk}}$ (bulk resistivity) and $\rho_{\text{GB}}$ (GB resistivity) Arrhenius plots for the air-, O$_2$- and N$_2$-processed BiT-Bi, BLT and BiT-Nb samples.

Figure 8. (a) $\rho_{\text{bulk}}$ and (b) $\rho_{\text{GB}}$ Arrhenius plots for the air-, O$_2$- and N$_2$-processed BiT-Bi, BLT and BiT-Nb samples.

Each $V_{0}^{**}$ is compensated by two holes ($h^+$) to satisfy the electroneutrality condition, and consequently the sample presents $p$-type conduction. When the reaction by Eq. 2 is dominant, Takahashi, et al. suggested that hole conductivity (or hole concentration $[h^+]$) follows the 1/6 power dependence of $pO_2$. The $\rho_{\text{GB}}$ nearly proportional to $pO_2^{1/6}$ in the measured $pO_2$ range at 500 °C, implies that $p$-type conduction is predominant at the GB of BiT-Nb.
However at 750 °C, the two conductivities both increase with decreasing $pO_2$, which is directly opposite to the experiments exhibited at 500 °C. This change is consistent with the results of YMnO$_3$ ceramics$^{58}$. It is presumed that BiT-Nb above $T_c$ is an oxide ionic and $n$-type mixed conductor. Under reducing conditions the required electrons ($\epsilon'$) are created through the release of oxygen from the lattices, expressed by the following equation.

$$O_2 \rightarrow V_{O}^{**} + 2\epsilon' + \frac{1}{2}O_2$$

(3)

The reduction of Ti$^{4+}$ to Ti$^{3+}$ is likely to be the source of conduction. And the electrons are probably trapped by the donor defects such $V_{O}^{**}$ and Nb$^{4+}$, leading to high $E_c$ ($>2.0$ eV) for the N$_2$ sample in the high temperature range (see Fig. 8). In addition, good fittings for the $\sigma_{bulk}$ and $\sigma_{GB}$ of BiT-Nb at 750 °C can be obtained by an equation of $\sigma_{bulk} = \sigma_{bulk} + \sigma_{electronic} (pO_2)^m$ ($m = -1/6$). In the case of both 500 °C (BiT-Nb) and 600 °C (BiT-Bi), the exponent $m$ is equal to 1/6. For the O$_2$ processed BiT-Bi sample at 600 °C ($pO_2 = 1$ atm), the calculated $\sigma_{bulk}$ and $\sigma_{electronic}$ (hole) in the bulk are 3.02 $\times$ 10$^{-4}$ and 2.21 $\times$ 10$^{-4}$ S cm$^{-1}$, respectively, and they are estimated to be 0.68 $\times$ 10$^{-3}$ and 1.64 $\times$ 10$^{-3}$ S cm$^{-1}$ at the GB region, respectively.

**Phase transition and dielectric relaxation.** Figure 10a shows temperature dependence of dielectric permittivity ($\varepsilon'$) at several frequencies for the air-, O$_2$- and N$_2$-processed BiT samples. High-and-sharp dielectric permittivity peak corresponds to ferroelectric-to-paraelectric phase transition. It is observed that the atmosphere has no influence on $T_c$ of BiT, which is around 673 °C and the same as those reported in the literature$^{6,40}$. Notably, an anomaly associated with two primarily high permittivity regions is detected below $T_c$, which agrees with the results of Shulman et al.$^{15}$. Also, there are several peaks observed in the tan $\delta$-T plots (Fig. 10b), corresponding to the steep increases of dielectric permittivities in the $\varepsilon'$ vs. $T$ plots (Fig. 10a), which all move toward higher temperature with increasing frequency. The dielectric relaxation and the loss peak in the low temperature range (region I) are not almost affected by altering $pO_2$, indicating an intrinsically physical nature, i.e., the bulk response. In contrast, the medium- and high-temperature dielectric relaxations in regions II and III, respectively, are strongly affected. They are likely in response to the boundary capacitance and the electrode capacitance, respectively, being referred to the results of Fig. 4 and ref. 38. The notable peak between 450 and 550 °C in the dielectric loss tangent (inset of Fig. 10b) for the air/O$_2$ samples seems to be attributed to the conduction loss.

As shown in Fig. 10c and d, the Nb donor substitution suppresses the loss and the relaxation process dramatically, and a sharp transition peak is observed at $T_c$. However, the A$_x$O$_3$ additions are not critical to the dielectric data. In addition, the $T_c$ of BiT-Bi and BiT-Nb is close to that of BiT, while the $T_c$ of BiT-La and BiT-Nd decreases to 638 °C and 647 °C, respectively (Fig. 10c). For A-site bismuth-containing Aurivillius compounds, the polarity Bi$^{3+}$ with 6 $s^2$ lone pair electrons causes the deformation from the prototype structure$^{39}$. Therefore, it is presumably that non-polarity La$^{3+}$ and Nd$^{3+}$ were incorporated into the lattices by replace the A-site Bi$^{4+}$, and thus the $T_c$ of BiT-La and BiT-Nd decreases significantly. Newnham et al.$^{1}$ proposed that $T_c$ vs. $x$ in Bi$_{4-x}$RE$_x$Ti$_3$O$_{12}$ follows a linear relationship$^{60}$. In this study, the substitution content $x$ in BiT-La and BiT-Nd is roughly estimated to be about 0.1 (Fig. S3; Supplementary Information), close to nominal A-site excess level (Bi$_{4}$A$_{0.12}$Ti$_3$O$_{12}$). Furthermore, the change trend of $T_c$ is in accord with that of structural orthorhombicity (see Table 1), and higher $T_c$ corresponds to higher orthorhombicity value.

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Figure 9. $pO_2$ dependences of $\sigma_{bulk}$ and $\sigma_{GB}$ of BiT-Bi and BiT-Nb. (a) BiT-Bi at 600 °C, (b) BiT-Nb at 500 °C and 750 °C.
Discussion

Commonly, Schottky barriers can form in electrically heterogeneous ceramics at insulating grain boundaries between semiconducting grains, which is referred to as an internal barrier layer capacitor (IBLC) effect61. Also, Schottky barriers can occur between “leaky” or semiconducting ceramics and metal electrodes, acting as a non-ohmic electrode effect62. The formation of these barriers can be ascribed to compositional variations and/or a mismatch between Fermi energy levels between the two materials that meet at the interface38, 48. Polarization effects at these barrier layers can generate nonintrinsic and colossal dielectric permittivities in ceramics such as CaCu3Ti4O12 (CCTO) 38. In this study, the bulks of BiT-A clearly are semiconducting, whose resistivity are lower than 105 Ω cm above 300 °C (Fig. 8a). Thus the Schottky barriers are possibly generated at the grain boundary regions in them, which is consistent with the results of CCTO and Pb(Fe 1/2Nb 1/2)O 3 ceramics37, 38. The results of Figs 8 and 9 indicate that BiT-Bi is an oxygen ion and hole mixed conductor. It is presumed that the bulk of BiT-Bi is dominated by positive defects (h• and VO••), which can be charge-compensated by grain boundary acceptor surface charges. Such a barrier layer may be associated with the depletion of VO•• at the grain boundary region during oxidative cooling63, as sketched in Fig. 11a.

Figure 10. (a) Log ε′ vs. T and (b) log tanδ vs. T plots for the air-, O2-, and N2-processed BiT samples, and tanδ vs. T plots for the air-, O2- and N2-processed BiT as an inset in (b). (c) ε′ vs. T and (d) tanδ vs. T plots for the air-processed BiT, BiT-A, BLT and BiT-Nb samples, with an inset showing regionally enlarged drawing for ε′ vs. T plots in (c).

It is possible that the electrodes nominally "blocking" for ions, allow for a certain ionic leakage, while the electrodes nominally “reversible” for electrons, still represent a certain interfacial resistance52, 64. In the case of the air/O2 BiT-Bi samples, it is believed that weak Warburg impedance at the lowest frequencies corresponds to the limited ionic diffusion into a partially blocking electrode (see Fig. 4). Two types of electrode effects together with the boundary barrier effects that dominate the intermediate frequency data, induce two high dielectric permittivity regions for BiT-A. Therefore, the following successions of layers starting from the inside are possibly: bulk/plate boundary/grain boundary/electrode.

One can speculate that oxide ion conduction may be a common feature of perovskite materials with a high [VO••*]. Furthermore, high oxygen ion conductivity has been recorded in the literature for intergrowths of Aurivillius with Brownmillerite structure, and cubic δ-Bi3O5 is known as a fast ion oxygen conductor11, 65, 66. For BiT-A, it is reasonable that predominant ionic conduction in the bulk is associated with the textured structure along the c-axis direction, in addition to high [VO••*] in the perovskite blocks. However, hole conduction is dominant at the boundaries, and thus the ρGB or σGB is apparently dependent of pO2 (see Figs 8b and 9a). A detailed structure analysis for pure BiT showed that some Bi ions in the perovskite layers are overbonded with a valence state of >3+467. A Pb2+ → Pb3+ hopping conduction has been proposed in PZT perovskite68. Presumably in BiT-Bi, hole conduction is associated with oxidation of Bi3+ to Bi4+, and the relevant Ea is probably close to that for the trapping of holes by Pb3+ ions, 0.26–0.3 eV11, 68, 69. The reported Ea for the mobility of VO•• is about 1.0 eV70, 71.
The $E_a$ of about 0.6 eV for the bulk of BiT and BiT-A can be attributed to a compromise of oxide ion conduction and hole conduction. Higher $E_a$ (1.0–1.2 eV) for the boundary barriers may be attributed to trapping of holes ($h^*$) by the grain-boundary acceptor surface charges ($A^+$)\(^4\).

In order to achieve predominant oxygen ion conduction, it is necessary to avoid samples picking up oxygen from high $pO_2$ environments. Otherwise, the rich-oxygen atmosphere encourages the incorporation of foreign oxygen into the lattices (Eq. 1); as a consequence, the samples transform into $p$-type electronic conductors with higher conductivity and lower activation energy. As indicated by the XPS (X-ray photoelectron spectroscopy) results (Fig. 12a), the increased $pO_2$ leads to the increases in the nominal valence states of Bi and Ti, which is related to both a decrease in $[VO^{\cdot\cdot\cdot}]$ and an increase in $[h^*]$\(^7\). Therefore, BiT-A show a transition from the dominant oxide ion conduction to the dominant $p$-type semiconduction with increasing $pO_2$.

As shown in Fig. S4 (Supplementary Information), BiT shows similar conduction behaviors as functions of atmosphere and temperature. BiT-A relative to BiT shows slightly increased $p_{\text{bulk}}$, and the variations in $p_{\text{PB}}$ (PB resistivity) and $p_{\text{GB}}$ are slight and irregular (Fig. S5; Supplementary Information). This, combined with the evolutions in $V$ and $T_c$ (see Table 1 and Fig. 10c), indicates that $A^{3+}$ could be mainly diffused into the lattices by substituting the A-site Bi\(^{3+}\), which limited the predicted compensation effect of excess A\(_2\)O\(_3\) on the V\(_{Bi}^{\cdot\cdot\cdot}\) and VO\(_{n}^{\cdot\cdot\cdot}\) sites. Excess or substituted bismuth (in fact, Bi\(_2\)O\(_3\)), should act as sintering aids because of low melting point (about 830°C), and consequently BiT-A and BiT show comparable grains and texture factor values. La isovalent substitution with a high concentration can induce an increase in the formation energy of VO\(_{n}^{\cdot\cdot\cdot}\) in the perovskite blocks, where the decreases in $[VO^{\cdot\cdot\cdot}]$ and $[h^*]$ are induced\(^3\). Thus in BLT, hole conduction and oxygen ion conduction are both suppressed. As sketched in Fig. 11b, BiT-Nb relative to BiT-Bi becomes rather more insulating. Two situations can be considered by the Nb substitution for the Ti site (B site), as expressed by the following equations.

Figure 11. Schematic illustrations of (a) formation of the barrier layer at the grain boundary region (b) electrical microscopes of BiT-Bi and BiT-Nb.
Clearly the Nb\(^{5+}\) donor substitution can decrease efficiently [\(h^+\)] and [\(V^\bullet\bullet\)] in the perovskite blocks, which supports significantly increased \(\rho_{\text{bulk}}\) of BiT-Nb (see Fig. 9). As indicted by the results of Figs 8 and 9, for BiT-Bi (>350 °C) and BiT-Nb, the grain resistivity of is lower than the grain resistivity. However, it does not mean that grain boundaries are electrically more conduction than bulk grains. In fact, grain boundaries in this study are electrically more insulating as shown in Fig. 11b, because the thicknesses of them are far smaller than the grain sizes of samples. This is consistent with the results of other electroceramics\(^{73}\). The XPS results of Fig. 12b indicates that BiT-Nb shows lower [\(V^\bullet\bullet\)] and stronger Ti-O band than BiT-Bi, in the perovskite blocks. In addition, the donor centrals (Nb\(^{5+}\)) may affect the movement of \(V^\bullet\bullet\)\(^{11,12}\). This combined with low [\(V^\bullet\bullet\)], should result in much higher potential barrier energy for the jump of \(V^\bullet\bullet\) in BiT-Nb than those in BiT and BiT-A, as sketched in Fig. 13. Therefore, the oxygen ion conduction is weak in BiT-Nb, of which the electrical conduction is primarily attributed to an electronic mechanism. Previous researches revealed that additional polarization associated with the electrode-sample interface was readily observed for CCTO ceramics with relatively low \(\rho_{\text{GB}}\)\(^{38}\). If \(\rho_{\text{GB}}\) was large, the electrode polarization was obscured by sample-related effects. Thus, the absence of the electrode effect in BLT and BiT-Nb may be associated with high \(\rho_{\text{GB}}\) of them, which are much higher than those of BiT and BiT-A (see Fig. 8b).

\[
\text{Nb}_2\text{O}_5 + V^\bullet\bullet_{\text{O}} \rightarrow 2\text{Nb}\_5^+ + 5\text{O}^2_\text{O} \\
\text{(4)}
\]

\[
\text{Nb}_2\text{O}_5 + 2h^+ + 2\text{O}^\bullet\bullet_{\text{O}} \rightarrow 2\text{Nb}\_5^+ + 4\text{O}^2_\text{O} + 0.5\text{O}_2 \\
\text{(5)}
\]

Conclusions

Structure and electrical properties of modified BiT-based ceramics could be tailored readily by changing chemical compositions, including the perovskite A and B sites. As a consequence, different electrical conductions and dielectric properties among them were found. Excess A\(_2\)O\(_3\) had no obvious effects on electrical resistivity and conduction mechanism. BiT and BiT-A all showed prominent oxide ion conduction under N\(_2\), which was likely associated with high [\(V^\bullet\bullet\)] in the perovskite blocks and the pronounced texture in the c-axis direction.
However, the hole conduction was prominent in the air/O₂ samples, because of the absorption of oxygen by them. In addition to the semiconducting bulk, impedance data revealed that Schottky barriers had been formed both at grain boundary and at the sample-electrode interface in heterogeneous BiT and BiT-A, which contributed to two abnormally high ε’ regions below Tc. BLT with 0.75 La substitution at A site and BiT-Nb with 0.03 Nb substitution at B site, both showed a suppression in electrical conduction including ionic and electronic. Especially, a low level of Nb donor substitution led to the significant decreases in [Vo] and [Ih]; thus BiT-Nb showed much higher ρ and Eₜ than BiT and BIT-A. The results in this study are significant for BiT-base high-temperature piezoelectric sensors in solving the origin of high leakage conductivity. Also, they provided some probability for the future work that BiT-based ceramics are considered as new oxide ion conductors by adjusting appropriately chemical compositions.

## Methods

### Materials

BiT-based ceramics, BiT, BiT-A (A = Bi, La and Nd), BLT and BiT-Nb, were prepared by using traditional solid state reaction. Appropriate amounts of starting materials [Bi₂O₃ (99.5%), TiO₂ (99.99%), La₂O₃ (99.99%), Nd₂O₃ (99.99%), and Nb₂O₅ (99.99%); Sinopharm Chemical Reagent Co., Ltd, CN] were mixed and milled in ethanol for 24 h. The mixtures were dried and then calcined at 800 °C for 4 h. The calcined powders were remilled in ethanol for 24 h, dried, ground and cold isostatically pressed into pellets at 300 MPa. The pressed pellets were then sintered at 980–1000 °C for 2 h.

### Characterization and measurements

XRD data were collected by using an automated diffractometer (X’Pert PRO MPD, Philips, Eindhoven, The Netherlands) with a nickel filter (Cu Kα radiation) at room temperature. SEM images were observed by using a field-emission scanning electron microscopy (JEOL-6700F, Japan) instrument equipped with an EDS system, at room temperature. TEM image and compositional analysis were performed by using a transmission electron microscopy (Tecnai F30, FEI, Hillsboro, OR, USA) instrument equipped with an EDS system, at room temperature. XPS data were performed with a spectrometer (VG ESCALAB220i-XL, Thermo Scientific, Surrey, UK) with Al Kα (E = 1486.6 eV) radiation, at room temperature. Temperature dependences of dielectric permittivity and dielectric loss were measured by using an LCR meter (4284 A, Agilent, CA, USA). Impedance data were performed by using an impedance analyzer (Solartron, SI 1260, Hampshire, UK) with Al Kα radiation, at room temperature. Temperature dependences of dielectric permittivity and dielectric loss were measured by using a zirconia oxygen sensor. Ag and Pt electrodes for the measurements of the electrical properties were made of fired-on silver paste at 850 °C and sputtered at room temperature (after removing Ag), respectively.

## References

1. Aurivillius, B. Mixed Bismuth Oxides with Layer Lattices: I. Ark. Kemi. 1, 463–471 (1949).
2. Aurivillius, B. Mixed Bismuth Oxides with Layer Lattices: II. Ark. Kemi. 1, 499 (1950).
3. Park, B. H. et al. Lanthanum-Substituted Bismuth Titanate for Use in Non-volatile Memories. Nature 401, 682 (1999).
4. Damjanovic, D. Ferroelectric, Dielectric and Piezoelectric Properties of Ferroelectric Thin Films and Ceramics. Rep. Prog. Phys. 61, 1267 (1998).
5. Damjanovic, D. Materials for High Temperature Piezoelectric Transducers. Curr. Opin. Solid State Mater. Sci. 3, 469 (1998).
6. Yan, H. X., Zhang, H. T., Reece, M. J. & Dong, X. L. Thermal Depoling of High Curie Point Aurivillius Phase Ferroelectric Ceramics. Appl. Phys. Lett. 87, 082911 (2005).
7. Cummins, S. E. & Cross, L. E. Electric and Optical Properties of Ferroelectric Bi₃Ti₅O₁₅ Single Crystals. J. Appl. Phys. 39, 2268 (1968).
8. Irie, H., Saito, H., Ohkoshi, S. & Hashimoto, K. Enhanced Ferroelectric Properties of Nitrogen-Doped Bi₅Ti₃O₁₁ Thin Films. Adv. Mater. 17, 491–494 (2005).
9. Takahashi, R. et al. Perfect Bi₃Ti₅O₁₅ Single-Crystal Films via Flux-Mediated Epitaxy. Adv. Funct. Mater 16, 485–491 (2006).
10. Noguchi, Y., Yamamoto, K., Kitanaka, Y. Z. & Miyayama, M. Effects of Mn doping on the polarization and leakage current properties in Bi₅Ti₃O₁₁ single crystals. J. Eur. Ceram. Soc. 27(13–15), 4081 (2007).
11. Shulman, H. S., Testorf, M., Damjanovic, D. & Setter, N. Microstructure, Electrical Conductivity, and Piezoelectric Properties of Bismuth Titanate. J. Am. Ceram. Soc. 79, 3124–3128 (1996).
48. Li, M. & Sinclair, D. C. The extrinsic Origins of High Permittivity and its Temperature and Frequency Dependence in Y0.5Ca0.5MnO3
47. Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides.
46. Lotgering, F. K. Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures.
45. Toby, B. H. EXPGUI, a graphical user interface for GSAS.
44. Larson, A. C. & Von Dreele, R. B. 
36. Krohns, S., Lunkenheimer, P., Ebbinghaus, S. G. & Loidl, A. Colossal Dielectric Constants in Single-Crystalline and Ceramic
31. Takahashi, M., Nguchi, Y. & Miyayama, M. Electrical Conduction Mechanism in Bi4Ti3O12 Single Crystal.
32. Takahashi, M., Nguchi, Y. & Miyayama, M. Effects of V-Doping on Mixed Conduction Properties of Bismuth Titanate Single
30. Raymond, M. V. & Smyth, D. M. Defects and charge transport in perovskite ferroelectrics. J. Phys. Chem. Solids 57, 1507–1511
29. Wang, C. M. et al. Cerium-Modified Aurivillius-Type Sodium Lanthanum Bismuth Titanate with Enhanced Piezoactivities. Mater.
28. Wang, C. M., Wang, J. F. & Gai, Z. G. Enhancement of Dielectric and Piezoelectric Properties of M2−xBixTi4O15 (M = Na, K, Li)
27. Takahashi, M., Nguchi, Y. & Miyayama, M. Electrical conduction properties of La-substituted bismuth titanate single crystals. Journal of Ceramic Processing Research 6, 281–285 (2005).
26. Smyth, D. M. Defect structure in perovskite titanates. Curr. Opin. Solid-State Mater. Sci 1, 692–697 (1996).
25. Hou, J. G., Kumar, R. V., Qu, Y. F. & Krsmanovic, D. B-site Doping Effect on Electrical Properties of Bi4Ti3O12. J. Appl. Phys.
24. Cheng, H. F. Modeling of Electrical Response for Semiconducting Ferrite. J. Am. Ceram. Soc. 83, 3253–3259 (1998).
23. Nagata, M., Nguchi, Y. & Miyayama, M. Estimation of ionic and hole conductivity in bismuth titanate polycrystals at high temperatures. Jpn. J. Appl. Phys. 38, 104106 (1999).
22. Du, H. C., Wohlrab, S. & Kaskel, S. Synthesis, Structure, and Properties of Bi3.25Pr0.75Ti2.97V0.03O12 Ferroelectric Ceramics. J. Eur. Ceram. Soc. 20, 1789–1793 (2000).
21. Cheng, H. F. & Maier, J. H. Electromechanical behavior of Bi4Ti3O12 ceramics: A comparative study. J. Am. Ceram. Soc. 83, 3132–3139 (2000).
20. Yoon, S. H., Randall, C. A. & Hur, K. H. Effect of acceptor concentration on the bulk electrical conduction in acceptor Mg-doped BaTiO3. J. Phys. Appl. 80, 541006 (2009).
19. Yoon, S. H., Randall, C. A. & Hur, K. H. Difference between resistance degradation of fixed valence acceptor (Mg) and variable valence acceptor (Mn)-doped BaTiO3 ceramics. J. Appl. Phys. 108, 064101 (2010).
18. Nagata, M., Chikushu, N. & Takenaka, T. Ferroelectric Properties of Bismuth Layer-Structured Compound SrBix−2/3Tix−2/3Ta2O12 (0 < x < 2). Jpn. J. Appl. Phys. 31, 104111 (2001).
17. Du, X. F. & Chen, I. W. Ferroelectric Thin Films of Bismuth-Containing Layered Perovskites: Part I, Bi4Ti3O12. J. Am. Ceram. Soc. 81, 3253–3259 (1998).
16. Lotgering, F. K. Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures.
15. Barret, E. K. A computational study of the structural, magnetic and dielectric properties of Bi4Ti3O12. J. Phys. Chem. C. 113, 404106 (2009).
14. Scott, J. F. & Dawber, M. Oxygen-vacancy ordering as a fatigue mechanism in perovskite ferroelectrics. Adv. Mater. 15, 1320–1323 (1993).
13. Park, C. H. & Chadi, D. J. Microscopic study of oxygen-vacancy defects in ferroelectric perovskites. Phys. Rev. B 57(R13), 961 (1998).
12. Shulman, H. S., Damjanovic, D. & Setter, N. Niobium Doping and Dielectric Anomalies in Bismuth Titanate. J. Am. Ceram. Soc. 83, 528–32 (2000).
11. Scott, J. F. & Dawber, M. Oxygen-vacancy ordering as a fatigue mechanism in perovskite ferroelectrics. Appl. Phys. Lett. 76, 3801 (2000).
10. Park, B. H. et al. Differences in nature of defects between SrBi2Ta2O7 and Bi2Ta2O7. Appl. Phys. Lett. 74, 1907–1909 (1999).
9. Joshi, P. C., Krupanidhi, S. B. & Mansingh, A. Rapid Thermally Processed Ferroelectric Bi1−xSmxTiO3 Thin Films. J. Appl. Phys. 72, 5517–5519 (1992).
55. Ren, P. R., Fan, H. Q. & Wang, X. Bulk conduction and nonlinear behaviour in multiferroic YMnO₃. *Appl. Phys. Lett.* **103**, 152905 (2013).

56. Funabiki, A., Inaba, M. & Ogumi, Z. Ac Impedance Analysis of Electrochemical Lithium Intercalation into Highly Oriented Pyrolytic Graphite. *J. Power Sources* **68**, 227–231 (1997).

57. Stromme Mattsson, M., Niklasson, G. A. & Granqvist, C. G. Li Diffusion in Ti Oxysulfide Films: Thermal Activation Energy and Jump Length Derived From Impedance Spectroscopy. *J. Appl. Phys.* **80**(4), 2169 (1996).

58. Ren, P. R., Fan, H. Q. & Wang, X. Bulk conduction and nonlinear behaviour in multiferroic YMnO₃. *Appl. Phys. Lett.* **103**, 152905 (2013).

59. Frits, B. & Mercurio, J. P. The crystal chemistry and dielectric properties of the Aurivillius family of complex bismuth oxides with perovskite-like layered structures. *J. Alloys Comp.* **188**, 27–35 (1992).

60. Wolfe, R. W. & Newnham, R. E. Rare-earth bismuth titanates. *J. Electrochem. Soc.* **116**, 832–833 (1969).

61. Greuter, F. & Blatter, G. Electrical properties of grain boundaries in polycrystalline compound semiconductors. *Semicond. Sci. Technol.* **5**, 111 (1990).

62. Yang, C. F. An equivalent circuit for CuO modified surface barrier layer capacitors. *Ipn. J. Appl. Phys.* Part 1 **36**, 188 (1997).

63. Chiang, Y. & Takag, T. Grain-Boundary Chemistry of Barium Titanate and Strontium Titanate: II, Origin of Electrical Barriers in perovskite-like layered structures. *J. Am. Ceram. Soc.* **73**(11), 3286–3291 (1990).

64. Jamnik, J. & Maier, J. Treatment of the Impedance of Mixed Conductors: Equivalent Circuit Model and Explicit Approximate Solutions. *J. Electrochem. Soc.* **146**(11), 4183–4188 (1999).

65. Thomas, J. M., Anderson, M. E., Krause, W. E. & Loye, H. Z. Oxygen-Ion Conductivity in a New Class of Layered Bismuth Oxide Compounds. *Mater. Res. Soc. Symp. Proc.* **293**, 295–300 (1993).

66. Hapase, M. G., Tare, V. B. & Biswas, A. B. Electrical Properties and Defect Structure of Bi₂O₃. *Indian J. Pure Appl. Phys.* **5**, 401–404 (1967).

67. Withers, R. L., Thompson, J. G. & Rae, A. D. The Crystal Chemistry Underlying Ferroelectricity in Bi₄Ti₃O₁₂, Bi₃TiNbO₉ and Bi₁₅WO₃. *J. Solid State Chem.* **94**(191), 404–417.

68. Raymond, M. V. & Smyth, D. M. Science and Technology of Electroceramic Thin Films (ed. Aucrello, O. & Waser, R.) 315–325 (Kluwer 1995).

69. Prisedsky, V. V., Shishkovosky, V. I. & Klimov, V. V. High-Temperature Electrical Conductivity and Point Defects in Lead Zirconate-Titanate. *Ferroelectrics* **17**, 465 (1978).

70. Yoo, H. I., Chang, M. W. & Oh, T. S. Electrocoloration and oxygen vacancy mobility of BaTiO₃. *J. Appl. Phys.* **102**, 093701 (2007).

71. Yoo, H. I., Song, C. R. & Lee, D. K. BaTiO₃: Defect Structure, Electrical Conductivity, Chemical Diffusivity, Thermoelectric Power, and Oxygen Nonstoichiometry. *J. Electroceram* **8**, 5 (2002).

72. Park, B. H., Hyun, S. J. & Bu, S. D. Differences in nature of defects between SrBi₂Ta₂O₉ and Bi₄Ti₃O₁₂. *Appl. Phys. Lett.* **74**(13), 1907–1909 (1999).

73. Yoon, S. H. & Kim, H. Effect of donor (Nb) concentration on the bulk electrical resistivity of Nb-doped barium titanate. *J. Appl. Phys.* **92**, 1039–1047 (2002).

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Author Contributions

L.C. designed the experiments, wrote the manuscript. H.F. directed the work. H.F., L.C. and C.Q. performed the experiments and analyzed data. All authors discussed and interpreted the results and have approved the final version of the manuscript. H.F. and L.C. supervised the project.

Additional Information

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