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# Dramatic impact of the TiO<sub>2</sub> polymorph on the electrical properties of 'stoichiometric' Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> ceramics prepared by solid-state reaction

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Fan Yang<sup>a,\*,#</sup>, Yidong Hu<sup>b,#</sup>, Qiaodan Hu<sup>b,\*</sup>, Sebastian Steiner<sup>c</sup>, Till Frömling<sup>c,\*</sup>, Linhao Li<sup>d</sup>, Patrick Wu<sup>d</sup>, Emilio Pradal-Velázquez<sup>d</sup> and Derek C Sinclair<sup>d,\*</sup>

Bulk conductivity ( $\sigma_b$ ) values of nominally stoichiometric Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT) prepared by solid-state reaction collated from literature show random variation between 10<sup>-6</sup>–10<sup>-3</sup> S cm<sup>-1</sup> (at 600 °C). This makes it challenging to obtain reliable and reproducible performances of NBT-based devices, especially as the underlying reason(s) for this variance are not fully understood. Here we report the dramatic impact of the TiO<sub>2</sub> reagent, in particular, the polymorphic form of TiO<sub>2</sub> on the electrical conductivity and conduction mechanism of NBT. Based on our solid-state processing route, NBT ceramics prepared by rutile TiO<sub>2</sub> are ionically conductive, and those prepared by anatase TiO<sub>2</sub> are insulating. The dramatic difference in electrical properties of NBT prepared using rutile and anatase TiO<sub>2</sub> is related to the NBT formation process: the intermediate phase Bi<sub>12</sub>Ti<sub>20</sub> is more stable during formation of NBT in the case of anatase TiO<sub>2</sub>, which reduces the volatility of Bi<sub>2</sub>O<sub>3</sub> during solid-state reaction. These results give plausible explanations for the large variation of  $\sigma_b$  reported in the literature and highlight the importance of selecting an appropriate TiO<sub>2</sub> reagent when targeting controllable  $\sigma_b$  in NBT-based ceramics. For ion-conducting applications (such as in intermediate-temperature solid oxide fuel cells, IT-SOFCs), rutile TiO<sub>2</sub> should be used, and for dielectric applications (such as in multilayer ceramic capacitors, MLCC) anatase TiO<sub>2</sub> should be used.

## Introduction

Sodium bismuth titanate (Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>, NBT) has been long considered as a promising lead-free piezoelectric/ferroelectric material to replace lead zirconate titanate (PZT)<sup>1,2</sup>, and therefore has potential applications in sensors, actuators, and multi-layer ceramic capacitors<sup>3</sup>. It is also a recently discovered oxide-ion conductor, which shows great potential as an electrolyte material for intermediate-temperature solid oxide fuel cells (IT-SOFCs)<sup>4,5</sup>. Different applications require totally different electrical properties of NBT. For example, for dielectric/ferroelectric applications, a low bulk electrical conductivity ( $\sigma_b$ ) is essential to reduce the leakage current and dielectric loss. In contrast, for IT-SOFCs applications, a high  $\sigma_b$  is required to reduce the ohmic polarization. However,  $\sigma_b$  of NBT is highly sensitive to small compositional variations such that very low levels of Na or Bi non-stoichiometry can lead to significant changes in  $\sigma_b$ <sup>4, 5</sup>.  $\sigma_b$  of NBT, in particular, the nominally stoichiometric NBT (NB<sub>0.50</sub>T) reported by different research groups can vary several orders of magnitude, i.e.,  $\sigma_b$  < 10<sup>-6</sup> S cm<sup>-1</sup> (600 °C) by Khatua *et al.*<sup>6</sup>

and  $\sigma_b \sim 10^{-3}$  S cm<sup>-1</sup> (600 °C) by Li *et al.*<sup>4</sup>. A summary of values for NBT collated from the literature<sup>4-13</sup> is plotted in Fig.1, where significant scattering of  $\sigma_b$  can be observed. This variance of  $\sigma_b$  makes it challenging to obtain reliable and reproducible performances of NBT-based devices.

Previous studies<sup>4, 5</sup> have revealed the significant change in  $\sigma_b$  induced by low levels of Na or Bi non-stoichiometry (<1 at.%) as being related to a switch between electronic and oxide-ion conduction. Similar behavior can be observed using varying concentrations of acceptor dopants<sup>9, 14</sup>. The presence of a small number of oxygen vacancies can change the predominant intrinsic electronic conduction behavior of NBT based on a d<sup>0</sup> insulator to predominant oxide-ion conduction due to the high mobility of oxygen ions in the NBT lattice<sup>15</sup>. Dense NBT ceramics are usually prepared by the conventional solid-state reaction method using Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> as reagents. Although different researchers may employ a different procedure, a general route for solid-state reaction synthesis involves pre-drying, weighing, milling, calcination, cold pressing, and sintering. Many steps in this process can cause low-level compositional variations and thus influence the oxygen vacancy level and therefore alter the  $\sigma_b$  of NBT. Over several years, we have conducted careful investigations to probe the relationships between the solid-state processing procedure and the electrical behaviour of NBT and have established a "standard" route to minimize the impact from sample preparation to obtain controllable  $\sigma_b$ . Under our "standard" route,  $\sigma_b$  and the conduction mechanism can be flexibly tuned by varying the A-site Na/Bi ratio of the starting composition. When Na/Bi ≥ 1, i.e., Na-excess or Bi-deficient, NBT exhibits high  $\sigma_b$

<sup>a</sup> Institute of Fuel Cells, School of Mechanical Engineering, Shanghai Jiao Tong University, 200240, Shanghai, China. Email: [fanyang\\_0123@sjtu.edu.cn](mailto:fanyang_0123@sjtu.edu.cn);

<sup>b</sup> School of Materials Science and Engineering, Shanghai Jiao Tong University, 200240, Shanghai, China. Email: [gdhu@sjtu.edu.cn](mailto:gdhu@sjtu.edu.cn);

<sup>c</sup> Department of Materials and Earth Science, Technical University of Darmstadt, FB Nichtmetallisch-Anorganische Werkstoffe, Alarich-Weiss-Straße 2, D-64287 Darmstadt, Germany. Email: [froemling@ceramics.tu-darmstadt.de](mailto:froemling@ceramics.tu-darmstadt.de);

<sup>d</sup> Department of Materials Science and Engineering, University of Sheffield, S1 3JD, UK. Email: [d.c.sinclair@sheffield.ac.uk](mailto:d.c.sinclair@sheffield.ac.uk)

<sup>#</sup> These authors contribute equally.

with an oxide-ion transport number,  $t_{\text{ion}}$  close to unity at  $\geq 600$  °C. When Na/Bi < 1, i.e., Na-deficient or Bi-excess, NBT shows very low  $\sigma_b$  with  $t_{\text{ion}}$  close to zero at  $\geq 600$  °C. A detailed discussion on the defect chemistry mechanisms induced by A-site Na or Bi non-stoichiometry and how they affect the electrical properties of NBT can be found in Ref. 16.

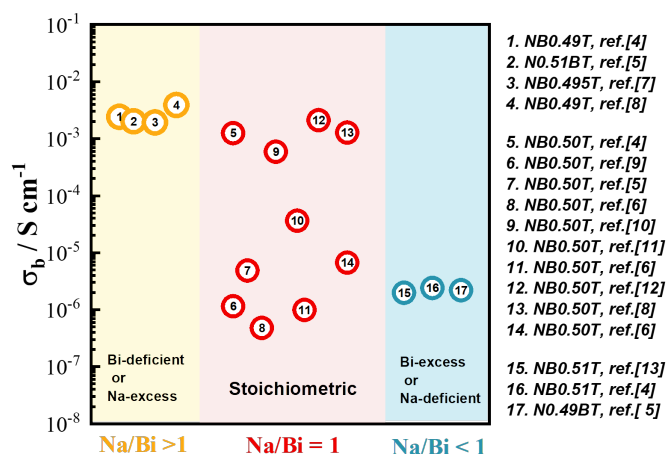


Fig.1 Summary of  $\sigma_b$  for NBT ceramics based on various Na/Bi ratios. Data are collated from the literature.

It should be noted that the above-mentioned empirical relationship between  $\sigma_b$  and Na/Bi ratio is established based on using the same  $\text{Na}_2\text{CO}_3$  (99.5%),  $\text{Bi}_2\text{O}_3$  (99.9%), and  $\text{TiO}_2$  (99.9%, rutile) reagents. The high sensitivity of  $\sigma_b$  to compositional variations highlights the possibility that reagents with different purity grades, types of impurity, or those from different suppliers (or different batches from the same supplier), may also have a significant impact on  $\sigma_b$  of NBT. Such concerns are not unfounded as low levels of impurities have been proven to have dramatic effects on the electrical properties of many perovskite-type materials such as  $\text{BaTiO}_3$ <sup>17</sup> and  $\text{LaFeO}_3$ <sup>18</sup>. Furthermore, the common polymorphic phase of the  $\text{TiO}_2$  reagent, i.e., rutile or anatase, may also have an impact on  $\sigma_b$  of NBT. This has been overlooked previously because the anatase to rutile phase transition of undoped  $\text{TiO}_2$  usually occurs between 600–700 °C<sup>19</sup>. In our “standard” solid-state processing procedure,  $\text{TiO}_2$  powder is subjected to pre-treatment overnight drying at 900 °C prior to weighing and batching. It is considered to have fully transformed to the rutile form after pre-drying; however, the  $\text{TiO}_2$  polymorphic phase transition temperature can vary over a wide temperature range  $\sim 400$ –1200 °C depending on variables such as impurities, dopants, particle morphology, and synthesis method<sup>20</sup>. It is possible that anatase  $\text{TiO}_2$  can be retained after pre-drying at 900 °C. Recently, Goutham *et al.*<sup>21</sup> reported the significantly dissimilar microstructural and dielectric/ferroelectric properties of NBT synthesized with anatase and rutile  $\text{TiO}_2$  via a hydrothermal technique. Whether and how different phases of  $\text{TiO}_2$  impact the electrical conductivity of NBT prepared by solid-state reaction has yet to be explored.

Here we investigate the effect of raw starting materials on the electrical properties of NBT ceramics prepared by solid-state reaction. Raw reagents from different suppliers with reasonable

grade purity (> 99.5%) were selected to prepare nominally stoichiometric  $\text{NB}_{0.50}\text{T}$  ceramics by our “standard” route. We show the polymorphic form of the  $\text{TiO}_2$  source has a dramatic impact on the electrical properties of  $\text{NB}_{0.50}\text{T}$ . The possible reasons for the significantly different electrical conductivity behaviour of  $\text{NB}_{0.50}\text{T}$  prepared by anatase and rutile  $\text{TiO}_2$  are investigated and discussed. This work provides a plausible explanation for the large variance within the literature regarding the reported electrical properties of NBT-based materials prepared by the solid-state reaction method. This suggests that anatase should be used as the pre-dried  $\text{TiO}_2$  reagent to prepare NBT ceramics via solid-state synthesis for piezo/ferroelectric applications, and rutile  $\text{TiO}_2$  to prepare NBT for ion-conducting applications, i.e., as electrolyte material for IT-SOFCs.

## Experimental

### Raw materials

Nominally stoichiometric NBT ( $\text{NB}_{0.50}\text{T}$ ) ceramics were prepared by the conventional solid-state reaction method using  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  as starting materials. Raw materials with reasonable purity levels from various suppliers were used to evaluate the impact of different reagents. Detailed information on the raw reagents used is listed in Table 1.

### The “standard” solid-state reaction route

All NBT ceramics were prepared by the same solid-state reaction route. Prior to weighing, the raw powders were dried overnight at 300 °C for  $\text{Na}_2\text{CO}_3$  and  $\text{Bi}_2\text{O}_3$  and 900 °C for  $\text{TiO}_2$ . Appropriate amounts of each reagent were weighed according to the chemical formula  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  and ball-milled in isopropanol using yttria-stabilized zirconia grinding media for 6 hours. The mixture was dried overnight in an 85 °C oven, sieved, and then calcined at 800 °C for 2 h. The resultant powder was subjected to a second round of ball milling (4 h), drying, sieving, and calcination (800 °C for 2 h) and subsequently to a final, third round of ball milling (6 h) and sieving. The products were compacted into pellets either by uni-axial cold pressing followed by isostatic pressing at 200 MPa, or by uni-axial pressing with a 5 wt.% water solution of polyvinyl alcohol (PVA) as a binder. Pellets were embedded in sacrificial powder of the same composition and sintered at 1150 °C for 2 h. The heating and cooling rates for calcination and sintering were 5 °C min<sup>-1</sup>. Those with PVA binder were slowly heated to 550 °C with a heating rate of 2 °C min<sup>-1</sup> and held for 2 h to decompose the binder before sintering. The use of a binder has little influence on the electrical conductivity and conduction mechanism of NBT, as shown by Fig.S1. After sintering, pellets were removed from the sacrificial powder and ground using SiC sandpaper to obtain flat surfaces.

### Characterisations

Phase purity of NBT was examined by X-ray diffraction on the pellet surface using a Bruker D2 phaser. Ceramic microstructures were observed by scanning electron microscopy (SEM, JEOL JSM-6010LA, JEOL Ltd., Tokyo, Japan or Pheom XL, Netherlands) on thermally etched surfaces. Raman spectroscopy was performed using a Confocal Microprobe Raman system (Renishaw inVia Qontor, UK). Particle size distribution was analysed using a Mastersizer (S3500, Microtrac, USA). Atomic fractions of Na, Bi, and Ti in NBT ceramics were measured by Inductively Couple Plasma- Atomic Emission Spectroscopy (ICP-AES, Thermo Scientific™ iCAP7600, UK).

Electrical properties were measured by impedance spectroscopy using an Agilent E4980A impedance analyser (Agilent Technologies Inc., Palo-Alto, CA; frequency range 1 MHz to 20 Hz; 100 mV applied) or a Solartron 1260 system (Solartron Analytical, UK; frequency range 1 MHz to 0.01 Hz; 100 mV applied) using Au paste (fired at 850 °C for 2 h) or Pt paste (fired at 900 °C for 2 h) as electrodes. All impedance data were corrected for high frequency inductance associated with the leads and the measurement jig by performing a short circuit measurement. The corrected data were then normalised by a geometric factor (thickness/surface area) based on sample dimensions. Equivalent circuit fitting was performed using ZView software (Scribner Associates, Inc, Southern Pines, NC). Dielectric properties were measured using an LCR meter (Agilent E4980 Precision LCR Meter, Agilent Technologies) with an applied ac voltage of 100 mV. Data points were collected every 60 s from room temperature (RT) to 800 °C using a non-inductively wound tube furnace at a ramp rate of 1 °C min<sup>-1</sup>.

### Formation process of NBT

To study the formation of NBT during solid-state reaction, pre-dried Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> were weighed in the appropriate amounts and ball milled for 6 h. After drying, the mixed powders were heat treated between 400 – 800 °C (at 50 °C increments) for 2 h at each temperature. After cooling to room temperature, the resultant powder was subjected to laboratory XRD (D8 ADVANCE Da Vinci, Germany), synchrotron XRD (BL14B1 beam line station of Shanghai Synchrotron Radiation Facility, SSRF), and Raman spectroscopy (Renishaw inVia Qontor, UK) measurements to identify the reaction products. For the Synchrotron XRD experiments, a quartz capillary tube filled with calcined powder was fixed on a sample holder and aligned parallel to the X-ray beam. During measurements, an X-ray beam of 18 keV was applied to the sample with an exposure time of 20 s.

No.	Na <sub>2</sub> CO <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
1	99.5%, Fisher Chemical, UK	99.9%, Acros Organics, USA	99.9%, Sigma Aldrich, UK
2	99.5%, Alfa Aesar, Germany	99.975%, Alfa Aesar, Germany	99.6%, Alfa Aesar, Germany
3	99.8%, Aladdin, China	99.9%, Aladdin, China	99.9%, Alfa Aesar, China
4			99.99%, Aladdin, China

## Results

To identify the possible impact from different reagents, a designed experiment was conducted to prepare 5 NB<sub>0.50</sub>T ceramics using a combination of Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> reagents from the first two rows of Table 1. These ceramics are denoted as NBT\_111, NBT\_112, NBT\_211, NBT\_121, and NBT\_222, where 1 and 2 represent the row number. For example, NBT\_111 represents the ceramic prepared by Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> from the first row, and NBT\_121 by Na<sub>2</sub>CO<sub>3</sub> from the first row, Bi<sub>2</sub>O<sub>3</sub> from the second row, and TiO<sub>2</sub> from the first row, etc. By comparing the electrical conductivity of NBT\_111 and NBT\_112, the effect of TiO<sub>2</sub> can be evaluated. Similarly, effects of Na<sub>2</sub>CO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> can be analyzed by comparing  $\sigma_b$  of NBT\_111 and NBT\_211, and that of NBT\_111 and NBT\_121, respectively. After that, two more NBT ceramics were prepared using Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> reagents from the third and the fourth row of Table 1, denoted as NBT\_333 and NBT\_334. All NBT ceramics were dense (> 95%) and phase pure by laboratory XRD (Fig.S2).

The electrical properties of NB<sub>0.50</sub>T ceramics prepared using different combinations of Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> reagents from Table 1 are shown in Fig.2. The  $Z^*$  plots at 600 °C (Fig.2a) of these ceramics show two types of impedance responses. NBT\_222, NBT\_112, and NBT\_334 show a single arc in  $Z^*$  plots with an associated resistivity of > 10<sup>5</sup> Ω cm. The associated capacitance of the single arc is ~ 10<sup>-10</sup> F cm<sup>-1</sup>, corresponding to a relative permittivity ( $\epsilon_r$ ) of ~1000, which agrees well with the value for paraelectric NBT materials at this temperature<sup>22</sup>. Therefore, the single arc in the  $Z^*$  plots for NBT\_222, NBT\_112 and NBT\_334 represent the bulk response. NBT\_111, NBT\_211, NBT\_121, and NBT\_333 show

significantly smaller associated resistivity as indicated by the dashed rectangle in Fig.2a. An expanded view of the  $Z^*$  plots for these three ceramics show three arcs, Fig.2b. From high to low frequency and based on the magnitude of associated capacitances, these correspond to responses associated with bulk, grain boundary, and electrode effects, respectively. This is consistent with previous reports on the impedance response of ionically conductive NBT<sup>4, 23, 24</sup>.

Bulk resistance ( $R_b$ ) of these ceramics was obtained by equivalent circuit fitting of the impedance spectra using one  $R$ - $CPE$  element for NBT\_222, NBT\_112, and NBT\_334 (inset figure in Fig.2a), and three series-connected  $R$ - $CPE$  elements for NBT\_111, NBT\_121, NBT\_211, and NBT\_333 (inset figure in Fig.2b).  $R_b$  was subsequently converted to  $\sigma_b$  ( $= 1/R_b$ ), and presented in Arrhenius plots (Fig.2c). NBT\_222, NBT\_112, and NBT\_334,  $\sigma_b - 1000/T$  show a linear relationship with  $E_a \sim 1.7$  eV, which is ~ half of the optical bandgap of NBT [25], suggesting predominant intrinsic electronic conduction behaviour. The  $\sigma_b - 1000/T$  relationships for NBT\_111, NBT\_121, NBT\_211 and NBT\_333, show a change in  $E_a$  from ~ 0.85 eV below 300 °C to ~ 0.40 eV above 300 °C. A change of  $E_a$  at ~ 300 °C is a characteristic of ionically conductive NBT.

The two distinct types of electrical behaviour associated with these NBT ceramics can also be demonstrated by the dielectric loss-temperature profiles ( $\tan \delta - T$ , 1 MHz). As shown in Fig.2d, NBT\_222, NBT\_112, and NBT\_334 exhibit low  $\tan \delta$  over a wide temperature range (< 0.05 between 300 and 650 °C). On the contrary,  $\tan \delta$  for NBT\_111, NBT\_121, NBT\_211, and NBT\_333 shows a rapid increase in the intermediate temperature range (i.e., 300-400 °C) and exceeds 0.2 at ~ 400 °C. The above results suggest, although prepared under an identical solid-state processing route, NB<sub>0.50</sub>T can still present significantly different  $\sigma_b$  and conduction mechanisms.

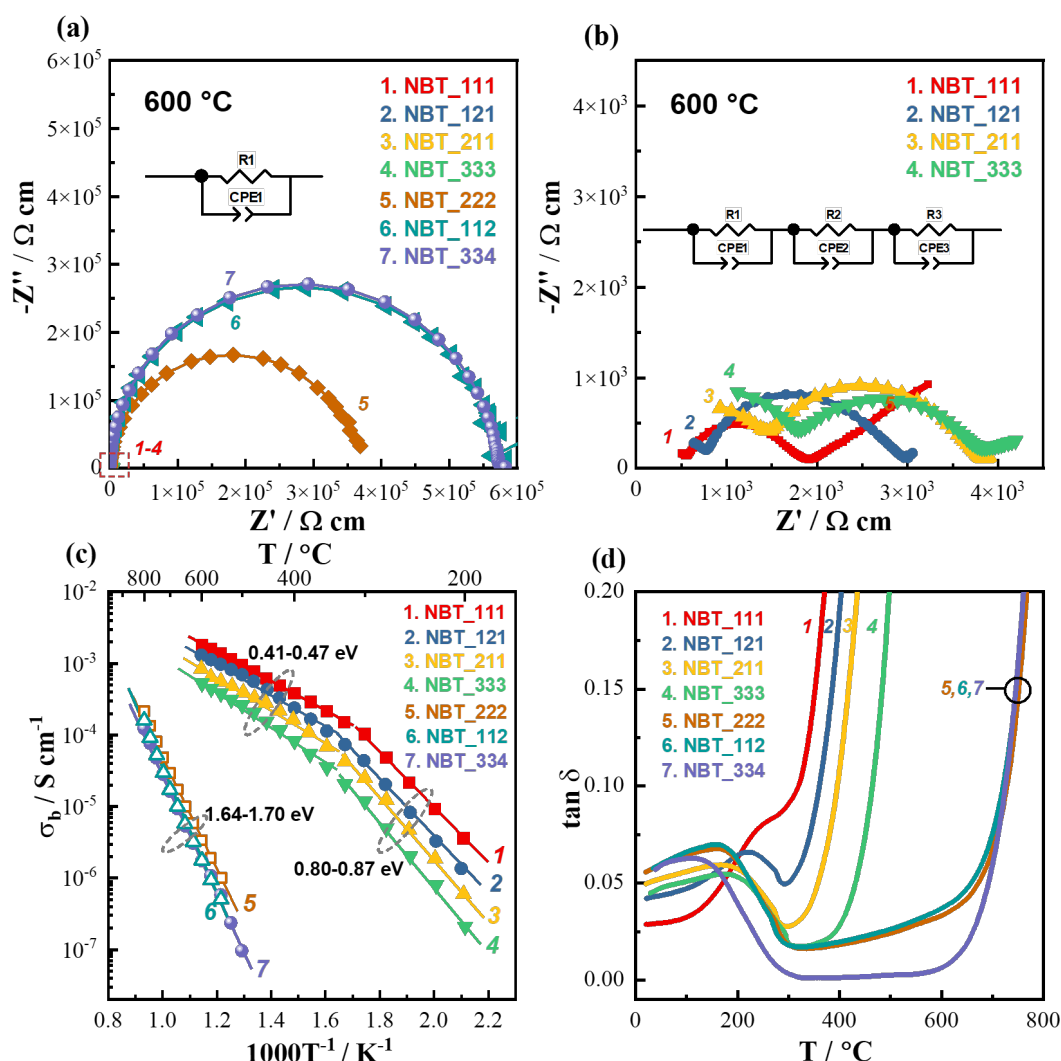


Fig.2 Electrical properties of  $\text{NB}_{0.50}\text{T}$  ceramics prepared using different combinations of  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  reagents. (a)  $Z^*$  plots and the equivalent circuit for the fitting of impedance data for NBT\_222, NBT\_112, and NBT\_334; (b) an expanded view of the dashed rectangular region in (a) showing  $Z^*$  plots for NBT\_111, NBT\_121, NBT\_211, and NBT\_333. The inset figure is the equivalent circuit used for fitting the data; (c) Arrhenius plots of  $\sigma_b$ . The numbers in eV are the activation energies ( $E_b$ ) for  $\sigma_b$ ; (d)  $\tan \delta - T$  plots at 1 MHz.

For a clearer illustration of the impact from different reagents,  $\sigma_b$ ,  $E_a$  and the conduction mechanisms of these NBT ceramics are summarized in Table 2. The different  $\text{Na}_2\text{CO}_3$  and  $\text{Bi}_2\text{O}_3$  reagents produce only small variations in  $\sigma_b$  and  $E_a$  without changing the conduction mechanism. In contrast, using different  $\text{TiO}_2$  reagents can induce a change in the conduction mechanism between predominantly oxide-ion and electronic conduction, and thus lead to 3 orders of magnitude variation in  $\sigma_b$ .



Table 2 Effect of reagents on the electrical properties of NB<sub>0.50</sub>T ceramics.

Effect	Sample	$\sigma_b$ (600 °C) / S cm <sup>-1</sup>	$E_a$ / eV	Conduction mechanism
Na <sub>2</sub> CO <sub>3</sub>	NBT_111	0.0018	0.41 (> 300 °C)	Oxide-ion conduction
			0.80 (< 300 °C)	
	NBT_211	8.34×10 <sup>-4</sup>	0.44 (> 300 °C)	Oxide-ion conduction
			0.85 (< 300 °C)	
Bi <sub>2</sub> O <sub>3</sub>	NBT_111	0.0018	0.41 (> 300 °C)	Oxide-ion conduction
			0.80 (< 300 °C)	
	NBT_121	0.0013	0.44 (> 300 °C)	Oxide-ion conduction
			0.82 (< 300 °C)	
TiO <sub>2</sub>	NBT_111	0.0018	0.41 (> 300 °C)	Oxide-ion conduction
			0.80 (< 300 °C)	
	NBT_112	1.76×10 <sup>-6</sup>	1.75 (> 550 °C)	Electronic conduction
	NBT_333	5.25×10 <sup>-4</sup>	0.47 (> 300 °C)	Oxide-ion conduction
			0.87 (< 300 °C)	
	NBT_334	1.75×10 <sup>-6</sup>	1.68 (> 550 °C)	Electronic conduction

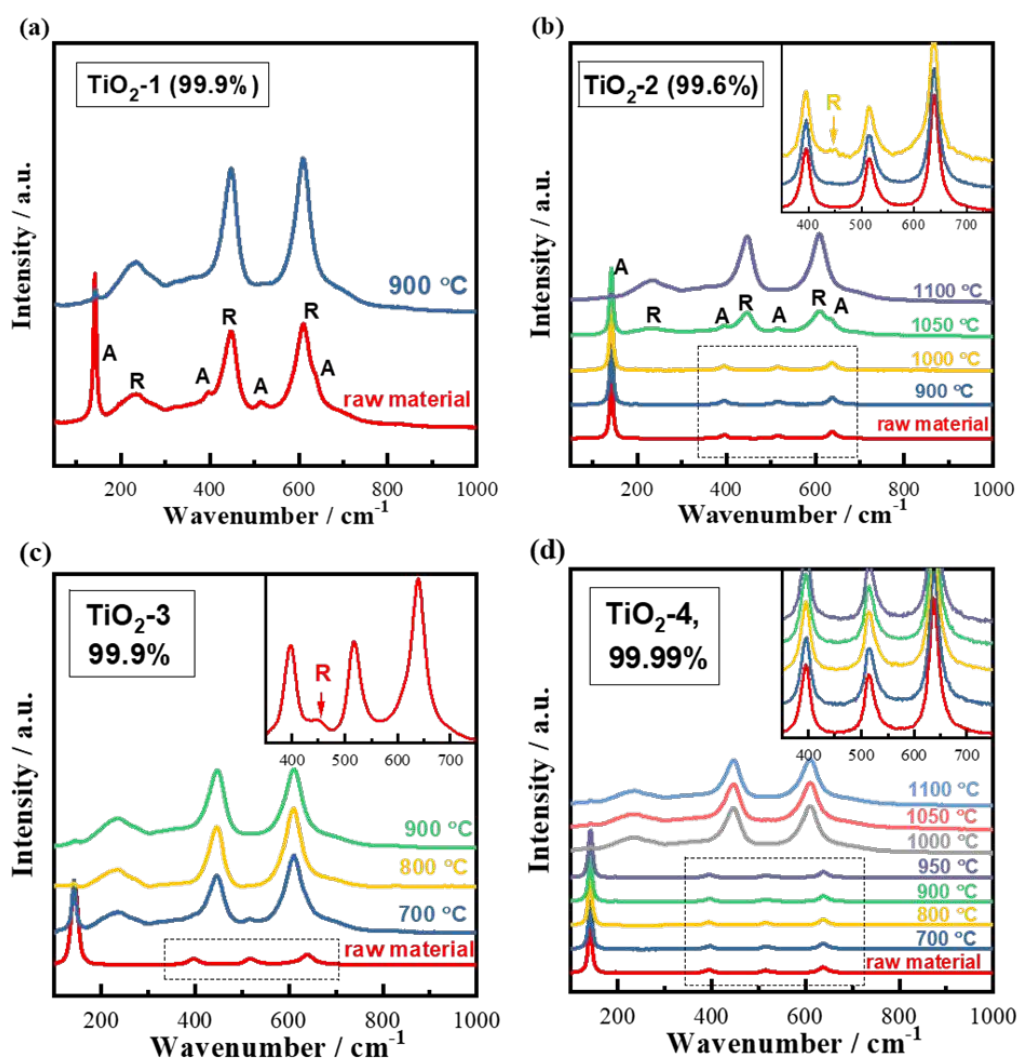


Fig.3 Raman spectra of the TiO<sub>2</sub> reagents before and after pre-drying at different temperatures. (a) TiO<sub>2</sub>-1 (99.9%, Sigma Aldrich, UK); (b) TiO<sub>2</sub>-2 (99.6%, Alfa Aesar, Germany); (c) TiO<sub>2</sub>-3 (99.9%, Alfa Aesar, China) and (d) TiO<sub>2</sub>-4 (99.99%, Aladdin, China). The inset figures in (b)-(d) are expanded views of the dashed rectangular regions. A and R denote anatase and rutile, respectively.

In our solid-state processing route, raw  $\text{TiO}_2$  reagents are subjected to pre-drying at 900 °C for 8 h prior to weighing. For our NBT preparation, the starting phase is therefore rutile for  $\text{TiO}_2$ -1 and  $\text{TiO}_2$ -3 and anatase for  $\text{TiO}_2$ -2 and  $\text{TiO}_2$ -4. The significantly different electrical properties of  $\text{Nb}_{0.50}\text{T}$  ceramics prepared from different  $\text{TiO}_2$  reagents may originate from 1) different purity levels of the  $\text{TiO}_2$  and/or 2) different phases (rutile versus anatase). To identify the critical factors that influence the electrical conduction behaviour,  $\sigma_b$  and  $E_a$  of NBT prepared by different  $\text{TiO}_2$  reagents (after pre-drying at 900 °C) are plotted as a function of purity of the  $\text{TiO}_2$  reagents, Fig.4. NBT ceramics prepared using anatase  $\text{TiO}_2$ , with low purity (99.6%) and high purity (99.99%), show low  $\sigma_b$  ( $\sim 10^{-6} \text{ S cm}^{-1}$  at 600 °C) and high  $E_a$  ( $> 1.6 \text{ eV}$ ); in contrast, those prepared using rutile  $\text{TiO}_2$  with medium purity (99.9%) have high  $\sigma_b$  ( $\sim 10^{-3} \text{ S cm}^{-1}$  at 600 °C) and low  $E_a$  ( $\sim 0.40 \text{ eV}$  at  $> 300 \text{ °C}$  and  $\sim 0.85 \text{ eV}$  at  $< 300 \text{ °C}$ ). Compared to grade purity, the polymorphic form of  $\text{TiO}_2$  has a determinant effect on the electrical conductivity and conduction mechanism of  $\text{Nb}_{0.50}\text{T}$  ceramics.

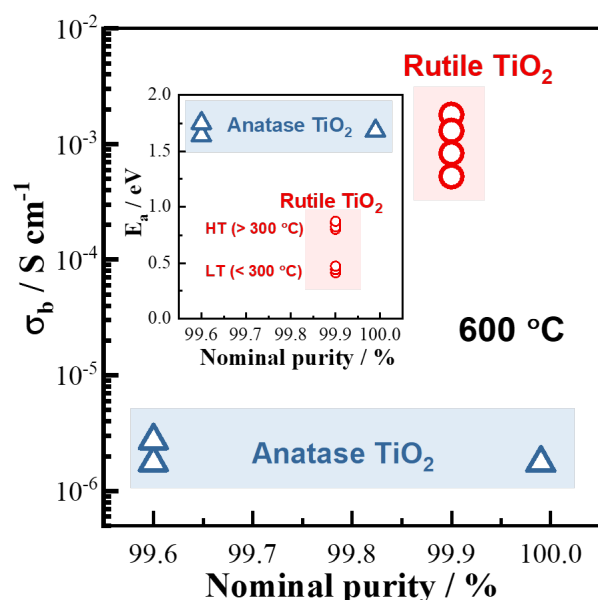


Fig.4 Variation of  $\sigma_b$  (at 600 °C) as a function of  $\text{TiO}_2$  reagent purity. The inset figure is a plot of  $E_a$  versus  $\text{TiO}_2$  reagent purity.

## Discussion

The major discovery of this work is that the polymorphism of  $\text{TiO}_2$  plays a critical role in the electrical conductivity and conduction mechanism of nominally stoichiometric NBT ( $\text{Nb}_{0.50}\text{T}$ ) ceramics prepared by solid-state reaction.  $\text{Nb}_{0.50}\text{T}$  prepared by anatase  $\text{TiO}_2$  is insulating, whereas that prepared by rutile  $\text{TiO}_2$  is ionically conductive. Possible reasons for the dramatic impact of  $\text{TiO}_2$  polymorph on the electrical properties of  $\text{Nb}_{0.50}\text{T}$  are discussed below.

### “Accidental” doping from impurities in the raw materials

Previous studies<sup>9, 14, 15, 26, 27</sup> show low levels of acceptor-doping, such as  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  to replace  $\text{Bi}^{3+}$  on A-site, and  $\text{Mg}^{2+}$ ,

$\text{Zn}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ga}^{3+}$  to replace  $\text{Ti}^{4+}$  on B-site, can create oxygen vacancies in NBT by an ionic compensation mechanism, and consequently introduce high-levels of oxide-ion conductivity into NBT. On the contrary, low levels of donor-type dopants such as  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$  can fill oxygen vacancies to suppress oxide-ion conduction. For example, 0.5%Nb-doping on the Ti-site can change the electrical conduction mechanism of NBT from high oxide-ion to low electronic conduction<sup>28</sup>. In this work, two groups of NBT samples, i.e., NBT\_111 and NBT\_112, NBT\_333 and NBT\_334, were prepared using the same  $\text{Na}_2\text{CO}_3$  and  $\text{Bi}_2\text{O}_3$  but different  $\text{TiO}_2$  reagents. They present dramatically different electrical properties: NBT ceramics prepared using the rutile phase  $\text{TiO}_2$ -1 (99.9%) and  $\text{TiO}_2$ -3 (99.9%) are conductive; those prepared using the anatase phase  $\text{TiO}_2$ -2 (99.6%) and  $\text{TiO}_2$ -4 (99.99%) are insulating. Although Fig.4 shows  $\sigma_b$  is independent of the grade purity, it is still necessary to clarify the impurity elements in the  $\text{TiO}_2$  reagents, in particular, whether donor-type elements are presented in anatase  $\text{TiO}_2$ -2 and  $\text{TiO}_2$ -4.

The dominant impurity elements of these four types of  $\text{TiO}_2$  from their Certificate of Analysis (CoA) provided by the suppliers are listed in Table 3. Many impurities in  $\text{TiO}_2$ -1,  $\text{TiO}_2$ -2, and  $\text{TiO}_2$ -3 are acceptor-type elements. Donor-type impurities such as Nb, Ta, and V are absent or below 10 ppm. Compared to  $\text{TiO}_2$ -1,  $\text{TiO}_2$ -2 has a significantly higher level of K impurity. The effect of K on  $\sigma_b$  of NBT has been previously investigated by intentional doping of K to replace either  $\text{Bi}^{3+}$  or  $\text{Na}^+$  on the A-site of NBT<sup>15,16</sup>. Acceptor-doping of  $\text{K}^+$  to replace  $\text{Bi}^{3+}$  creates oxygen vacancies to enhance oxide-ion conductivity. In contrast, partial replacement of  $\text{Na}^+$  by  $\text{K}^+$  decreases  $\sigma_b$ , which is attributed to the more significant K-loss than Bi-loss during sintering, and therefore makes K-doped NBT Bi-rich on the A-site. For NBT\_112, if all the K impurities in  $\text{TiO}_2$ -2 replace Na, the nominal composition of NBT can be written as  $\text{Na}_{0.498844}\text{K}_{0.001156}\text{Bi}_{0.5}\text{Ti}_{0.998844}\text{O}_{3-6}$ . Under our processing route, the Bi-loss was previously estimated to be in the range of 0.0017-0.0033, corresponding to a formula of  $\text{Na}_{0.5}\text{Bi}_{0.4967-0.4983}\text{Ti}_{0.995-2.9975}\text{O}_{29}$ . Assuming a complete loss of K during sample preparation, the nominal composition of the prepared NBT is  $\text{Na}_{0.498844}\text{Bi}_{0.4967-0.4983}\text{Ti}_{0.998844}\text{O}_{3-6}$ , which can be considered as Bi-deficient NBT and should present oxide-ion conduction behaviour. Consequently, the relatively high level of K impurities in  $\text{TiO}_2$ -2 is not sufficient to explain the insulating behavior of NBT\_112.

The COA of the high-purity  $\text{TiO}_2$ -4 (99.99%) suggests a total metallic impurity level of 97 ppm without specifying the impurity elements. If we assume all the impurities in  $\text{TiO}_2$ -4 are donor-type dopants (i.e.,  $\text{Nb}^{5+}$ ), the prepared ceramics corresponds to 0.01% Nb-doped NBT. Our previous study<sup>27</sup> showed 0.2% Nb-doping can only partially fill the oxygen vacancies in NBT ceramics prepared by our “standard” route. 0.2% Nb-doped NBT presents mixed ionic-electronic conduction behavior with  $E_a \sim 0.9 \text{ eV}$  and  $t_{\text{ion}} \sim 0.5$ . Therefore, 0.01% Nb-doping is insufficient to fully eliminate oxygen vacancies to result in predominant electronic conduction behavior of NBT\_334.

To conclude the above, “accidental” donor-doping from anatase  $\text{TiO}_2$  ( $\text{TiO}_2$ -2 and  $\text{TiO}_2$ -4) is not the dominant reason for the electrically insulating behavior of NBT\_112 and NBT\_334. Alternative reason(s) need to be considered.

Table 3 Major metallic impurities (>10 ppm) in TiO<sub>2</sub> reagents.

TiO <sub>2</sub>	Na	K	Ca	Mg	Zn	Al	Cr	Pb	Pd	Pt
TiO <sub>2</sub> -1		45.5					23.9	13.4	25.8	18.5
TiO <sub>2</sub> -2	36	1156	< 20			50				
TiO <sub>2</sub> -3	<100	<100	<100	<100	<100	<100				
TiO <sub>2</sub> -4	Unspecified, total metallic impurities 97 ppm									

### Formation process of NBT

Our previous studies<sup>4, 5</sup> show the oxide-ion conductivity of undoped NB<sub>0.50</sub>T originates from the oxygen vacancies generated by Bi-loss during ceramic processing. The insulating NB<sub>0.50</sub>T prepared using anatase TiO<sub>2</sub> suggests a lower amount of Bi-loss than the conductive NB<sub>0.50</sub>T prepared using rutile TiO<sub>2</sub>. During solid state processing, there are several possible sources for Bi-loss, including the following. (1) Bi<sub>2</sub>O<sub>3</sub> loss caused by materials transfer from the milling bottle to beaker. Although carefully rinsed using isopropanol several times after the first round of ball milling, small amounts of Bi<sub>2</sub>O<sub>3</sub> powder may still stick on the inner side of the milling bottle or on the surfaces of the milling balls. (2) Volatility of Bi<sub>2</sub>O<sub>3</sub> during calcination. To form NBT, the ball-milled and sieved Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> mixture is heated from room temperature to 800 °C, where solid-state reaction of the reagents takes place to form NBT perovskite. The polymorphism of TiO<sub>2</sub> (rutile or anatase) may influence the reaction pathway or reaction rate for NBT formation and consequently may result in different levels of Bi<sub>2</sub>O<sub>3</sub> loss. (3) Volatility of Bi<sub>2</sub>O<sub>3</sub> during sintering. After calcination, single-phase NBT with a perovskite structure has formed. To prepare dense ceramics, green bodies of pressed NBT pellets are subjected to sintering at 1150 °C. Although fully embedded in sacrificial powder, exposure to such high temperature may induce Bi-loss of NBT considering its volatility.

In the three above-mentioned possible sources, if there is any Bi-loss in (1) and (3), it should be similar for both rutile and anatase TiO<sub>2</sub> as we have followed a strict processing route for the NBT preparation. It is, therefore, necessary to investigate the NBT formation process during heating to identify the possible impact of rutile and anatase TiO<sub>2</sub> on the reaction pathway or reaction rate. For this purpose, the ball-milled and sieved mixtures of pre-dried Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> (TiO<sub>2</sub>-3 and TiO<sub>2</sub>-4) were calcined between 400-800 °C (at 50 °C increments) for 2 h and the reaction products identified by both laboratory and synchrotron XRD. The formation process of NBT during solid-state reaction was previously investigated by Aksel and Jones using *in situ* high-temperature diffraction<sup>30</sup>. In their study, anatase TiO<sub>2</sub> powder (without pre-drying) was mixed with Na<sub>2</sub>CO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> and heated continuously from room temperature to 700 °C with a ramp rate of 4 °C min<sup>-1</sup>. Two transient phases (Bi<sub>12</sub>TiO<sub>20</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) were observed at 500-650 °C. In our work, the mixed powder was held at each temperature for 2 h to allow a longer reaction time than *in situ* heating for easier identification of the reaction products.

Full synchrotron XRD patterns of the calcined powder in the 2θ range of 15-80° are shown in Fig.S3 and the patterns in a narrower 2θ range between 20-50° displayed in Figure 5. Evolution of the XRD pattern with increasing calcination temperature in the case of rutile

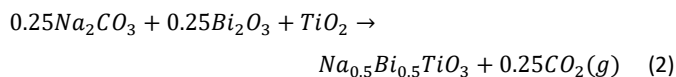
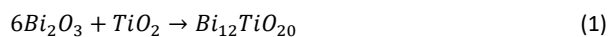
TiO<sub>2</sub> is presented in Fig.5a. At 500 °C, the XRD pattern is dominated by peaks corresponding to α-Bi<sub>2</sub>O<sub>3</sub>. Peaks for rutile TiO<sub>2</sub> at 2θ~27.5 (partially overlapping with one from Bi<sub>2</sub>O<sub>3</sub>), 36, 39.2, 41.2, and 44° can also be identified. A weak peak at 2θ~30.1° corresponds to the (002) reflections of the monoclinic phase of Na<sub>2</sub>CO<sub>3</sub>. At 550 °C, apart from the reagent peaks, a weak peak at 2θ~32.8° from the (321) reflections of Sillénite Bi<sub>12</sub>TiO<sub>20</sub> can be detected. At 600 °C, the (310) peak for Bi<sub>12</sub>TiO<sub>20</sub> at 2θ~27.7° appears and NBT perovskite peaks (2θ~23, 32.5, 40 and 47°) start to appear. At 650 °C, the XRD pattern is dominated by peaks from NBT perovskite with two weak peaks from Bi<sub>12</sub>TiO<sub>20</sub>. At 700 and 800 °C, only NBT peaks can be detected, suggesting the reaction is complete. In the case of anatase TiO<sub>2</sub>, as shown in Fig.5b, the reaction starts at 550 °C, as indicated by the peak at 2θ~27.7°, corresponding to diffraction from the (310) planes of Bi<sub>12</sub>TiO<sub>20</sub>. At 600 °C, the NBT perovskite starts to form with the presence of a significant amount of sillénite Bi<sub>12</sub>TiO<sub>20</sub>. At 650 °C, the diffraction pattern is dominated by Bi<sub>12</sub>TiO<sub>20</sub> and NBT, with one small peak from unreacted TiO<sub>2</sub> at 2θ~25.4°. The sillénite phase is still present at 700 °C. Single phase NBT is obtained after calcination at 800 °C.

As summarized in Table 4, the most significant difference in the formation process of NBT prepared by rutile and anatase TiO<sub>2</sub> is the Bi<sub>12</sub>TiO<sub>20</sub> phase formed at intermediate temperatures. When using rutile TiO<sub>2</sub>, only a small amount of Bi<sub>12</sub>TiO<sub>20</sub> is detected at 550-650 °C. In contrast, when using anatase TiO<sub>2</sub>, a large amount of Bi<sub>12</sub>TiO<sub>20</sub> is formed during heating and is present over a wider temperature range up to 700 °C.

Recent studies by Thong *et al.*<sup>31, 32</sup> have suggested the chemical reaction among Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub> during formation of (K,Na)NbO<sub>3</sub> perovskite is strongly dependent on the size of Nb<sub>2</sub>O<sub>5</sub> precursor. To elucidate the impact of rutile and anatase TiO<sub>2</sub> on NBT formation, particle size analysis was conducted on TiO<sub>2</sub> reagents and the ball-milled mixture prior to calcination. As shown in Fig.S4a and 4b, the particle size of raw TiO<sub>2</sub>, both rutile and anatase, shows a wide distribution between 0.1 to 1000 μm due to different levels of particle agglomeration. After ball milling (Fig.S4c and 4d), mixtures with rutile TiO<sub>2</sub> and anatase TiO<sub>2</sub> both show a single, normal distribution of particle size with an average value of 4.51 and 4.61 μm, respectively. The different formation process of NBT using rutile and anatase TiO<sub>2</sub> is, therefore, a polymorphic effect and not a particle size effect.

The reason(s) why anatase TiO<sub>2</sub> is more beneficial to the formation of the Bi<sub>12</sub>TiO<sub>20</sub> phase during solid-state reaction is beyond the scope of this paper but is worthy of further in-depth investigation based on variations in crystal structure, thermodynamics, and reaction kinetics. The key information extracted from Fig.5 is formation of NBT by solid-state reaction among Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> is a competition between the following two reactions:





In Equation (1), 1 mole of  $\text{TiO}_2$  reacts with 6 moles of  $\text{Bi}_2\text{O}_3$  to form  $\text{Bi}_{12}\text{TiO}_{20}$ ; in Equation (2), 1 mole of  $\text{TiO}_2$  reacts with 0.25 moles of  $\text{Bi}_2\text{O}_3$  to form NBT. Here we calculated a parameter ( $f$ ) from the intensity of the strongest peak from the XRD patterns of  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_{12}\text{TiO}_{20}$ , and NBT according to

$$f_{\text{Bi}_2\text{O}_3} = \frac{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ}}{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ} + I_{\text{Bi}_{12}\text{TiO}_{20}, 2\theta \sim 27.7^\circ} + I_{\text{NBT}, 2\theta \sim 32.6^\circ}} \times 100\% \quad (3a)$$

$$f_{\text{Bi}_{12}\text{TiO}_{20}} = \frac{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ}}{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ} + I_{\text{Bi}_{12}\text{TiO}_{20}, 2\theta \sim 27.7^\circ} + I_{\text{NBT}, 2\theta \sim 32.6^\circ}} \times 100\% \quad (3b)$$

$$f_{\text{NBT}} = \frac{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ}}{I_{\text{Bi}_2\text{O}_3, 2\theta \sim 27.5^\circ} + I_{\text{Bi}_{12}\text{TiO}_{20}, 2\theta \sim 27.7^\circ} + I_{\text{NBT}, 2\theta \sim 32.6^\circ}} \times 100\% \quad (3c)$$

as an indicator of relative change of  $\text{Bi}_2\text{O}_3$  content in these three Bi-containing phases. (Please note, for accurate calculation of the mass fraction, a mass absorption coefficient for each phase should be considered. Here a simplified fraction is used to show the trends). Variation of  $f_{\text{Bi}_2\text{O}_3}$  with temperature is presented in Fig.S5a, where a

faster drop of  $f_{\text{Bi}_2\text{O}_3}$  can be observed when anatase  $\text{TiO}_2$  is used. At 600 °C,  $f_{\text{Bi}_2\text{O}_3}$  values are ~35% in the mixture with anatase  $\text{TiO}_2$  and this is significantly lower than ~65% in the mixture with rutile  $\text{TiO}_2$ . Sublimation of  $\text{Bi}_2\text{O}_3$  below its melting temperature has been previously investigated by Cheng *et al.*<sup>33</sup>. They tested the mass loss of  $\text{Bi}_2\text{O}_3$  at 650 °C in an air box furnace for different holding times up to 100 h, and reported ~ a 0.125% mass loss of  $\text{Bi}_2\text{O}_3$  after 5 h. The mass loss of  $\text{Bi}_2\text{O}_3$  was effectively reduced by  $\text{SnO}_2$ -doping. 1% and 10% Sn-doping reduced the mass loss to 0.05 and < 0.01%, respectively. Therefore, when NBT is prepared using anatase  $\text{TiO}_2$ , formation of a large amount of  $\text{Bi}_{12}\text{TiO}_{20}$  phase can effectively immobilise  $\text{Bi}_2\text{O}_3$  to reduce its sublimation and consequently prohibits creation of oxygen vacancies to result in insulating behavior of NBT.

The atomic fractions of Na, Bi, and Ti of NBT prepared from rutile and anatase  $\text{TiO}_2$ , in the form of calcined powder and dense ceramics, were determined by ICP-AES analysis and are listed in Table 5. Calcined powder and sintered pellets of NBT prepared by rutile  $\text{TiO}_2$  show a Na/Bi ratio > 1, and those prepared by anatase  $\text{TiO}_2$  show a Na/Bi ratio < 1. This gives evidence for the reduced Bi-loss during calcination of NBT when anatase  $\text{TiO}_2$  is used.

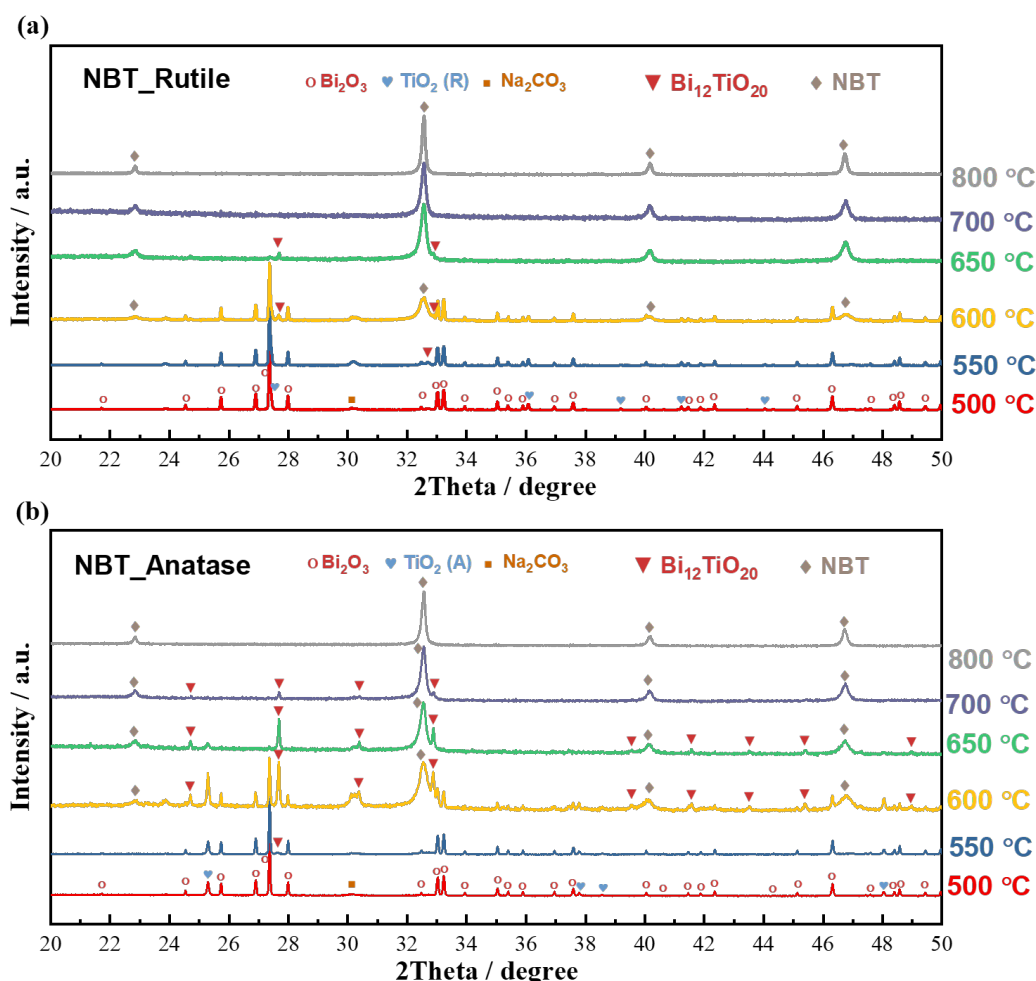


Fig.5 Synchrotron XRD patterns of the  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  mixtures after heat treatment at 500-800 °C (at increments of 50 °C) for 2 h: (a) Rutile  $\text{TiO}_2$  and (b) anatase  $\text{TiO}_2$ .

Table 4 Reaction products at each temperature identified by synchrotron XRD. “weak” and “strong” are defined according to the peak intensity relative to the strongest peak on each pattern. Very weak: < 5%; weak: 10-20%; strong: 50-90%; very strong: > 90%.

TiO <sub>2</sub> polymorph	Product	Temperature / °C					
		500	550	600	650	700	800
Rutile	Na <sub>2</sub> CO <sub>3</sub>	✓	✓	✓			
	Bi <sub>2</sub> O <sub>3</sub>	✓	✓	✓	✓		
	TiO <sub>2</sub>	✓	✓	✓			
	Bi <sub>12</sub> TiO <sub>20</sub>		✓, very weak	✓, weak	✓, weak		
	NBT			✓	✓	✓	✓
Anatase	Na <sub>2</sub> CO <sub>3</sub>	✓	✓	✓			
	Bi <sub>2</sub> O <sub>3</sub>	✓	✓	✓			
	TiO <sub>2</sub>	✓	✓	✓	✓		
	Bi <sub>12</sub> TiO <sub>20</sub>		✓, very weak	✓, very strong	✓, strong	✓, weak	
	NBT			✓	✓	✓	✓

Table 5 Atomic fractions of Na, Bi, and Ti in the calcined powder and sintered ceramics of NBT prepared by rutile and anatase TiO<sub>2</sub>. The numbers are the average value from 3 ICP-AES tests.

	TiO <sub>2</sub> Polymorph	Na / %	Bi / %	Ti / %	Na/Bi
Calcined powder	Rutile	25.75	25.28	48.97	> 1
	Anatase	24.23	25.82	49.95	< 1
Sintered ceramics	Rutile	25.43	24.76	49.80	> 1
	Anatase	24.47	25.08	50.46	< 1

The above analysis suggests rutile and anatase TiO<sub>2</sub> have different abilities to pre-react and “trap” Bi<sub>2</sub>O<sub>3</sub> in the solid-state reaction with Na<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub>. To further support the above statement, an additional NBT ceramic sample was prepared using a mixture of rutile and anatase TiO<sub>2</sub> with a weight ratio of 1:1 following the same processing route (denoted as NBT\_ R<sub>0.5</sub>A<sub>0.5</sub>). Fig. 6 compares the microstructure of NBT\_R, NBT\_A, and NBT\_ R<sub>0.5</sub>A<sub>0.5</sub>. The ionic conductive NBT\_R has large grains (~ 15-20 μm, Fig.6a), the insulating NBT\_A shows small grains (~ 1-2 μm, Fig.6b). This is consistent with the empirical conductivity-grain size relationship summarized in Ref.13. NBT\_ R<sub>0.5</sub>A<sub>0.5</sub>, as shown in Fig.6c, displays a random mixture of large (~ 5 μm) and small (~ 1 μm) grains. Although the large grains in NBT\_ R<sub>0.5</sub>A<sub>0.5</sub> are much smaller than those in NBT\_R possibly because the grain growth is inhibited by the neighbouring small grains, the distinguishable presence of two types

of grains gives additional evidence that rutile and anatase TiO<sub>2</sub> react independently with Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> during NBT formation.

$\sigma_b$  of NBT\_ R<sub>0.5</sub>A<sub>0.5</sub> was estimated from  $Z^*$  and  $M''$ -logf plots (Fig.S5) and plotted as a function of 1000/T, as shown in Fig.6d.  $\sigma_b$  of NBT\_ R<sub>0.5</sub>A<sub>0.5</sub> is intermediate to that of NBT\_R and NBT\_A, with a change of  $E_a$  from 0.51 eV (300-550 °C) to 0.76 eV (550-750 °C). In the lower temperature range, the small grains are too insulative to contribute to electrical conduction. Therefore,  $\sigma_b$  is dominated by the large, conductive grains and thus presents an  $E_a$  similar to that of NBT\_R. With increasing temperature, the small grains also contribute to electrical conduction to result in an increase in  $E_a$ . The ceramic microstructure and electrical conductivity of NBT\_ R<sub>0.5</sub>A<sub>0.5</sub> further support our conclusion that the dramatically different electrical behavior of NBT\_R and NBT\_A originate from the use of different TiO<sub>2</sub> polymorphs in the solid-state preparation of NBT.

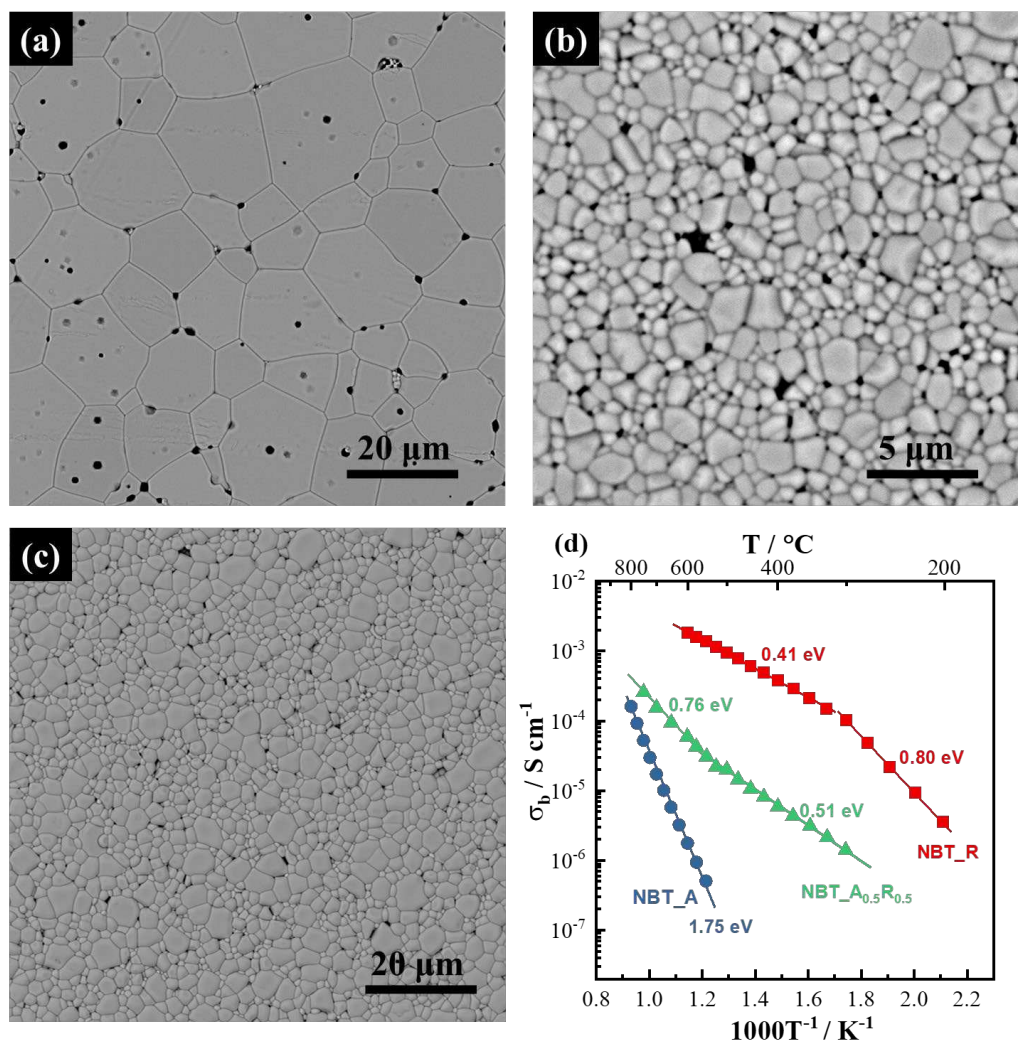


Figure 6. (a)–(c) SEM micrographs of thermally etched surfaces of NBT\_R, NBT\_A and NBT\_R<sub>0.5</sub>A<sub>0.5</sub>, respectively. (d) Arrhenius plots for  $\sigma_b$  of NBT\_R, NBT\_A and NBT\_R<sub>0.5</sub>A<sub>0.5</sub>. The numbers in eV are the  $E_a$  values.

### Perspectives on the reproducible synthesis of NBT by solid-state processing

Solid-state reaction is the most readily available and economical method for large-scale production of NBT-based materials. As  $\sigma_b$  of NBT is highly sensitive to small compositional variations, it is essential to follow a strict processing procedure and to be aware of the influence of reagent grade purity and polymorphism on the reaction mechanism and final electrical properties. Particular attention should be given to the following: 1) pre-drying of the raw reagents. This is not only important to guarantee precise weighing of the reagents to control the starting NBT stoichiometry but also to know the polymorphism of the dried TiO<sub>2</sub> reagent. 2) The grade purity of the raw reagents. The reagents used in this work all have reasonably high purity (>99.5%). If low purity reagents are used to prepare NBT, it is necessary to consider the possible impact from “accidental” doping from any high-level impurity elements. 3) The polymorphism of any dried TiO<sub>2</sub> reagents used prior to milling and mixing. Given the sensitivity of the anatase to rutile polymorphic transition on low levels of impurities, it is conceivable that batches of TiO<sub>2</sub> from the same supplier may show variations in their anatase to rutile content after drying at 900 °C.

Finally, it is worth mentioning that although  $\sigma_b$  of NBT can be tuned by manipulating the Na/Bi ratio or by chemical doping, the ability of accommodating A-site Na (or Bi) nonstoichiometry or dopants can be very low in NBT. Our previous studies<sup>4, 24, 27</sup> have shown the presence of Na,Ti-rich secondary phase(s) in Bi-deficient NBT (NB<sub>0.49</sub>T) or acceptor-doped NBT (Mg-doped NBT) and Bi-rich secondary phase(s) in Bi-excess NBT (NB<sub>0.51</sub>T) and Nb-doped NBT. Nominally stoichiometric NBT is usually cleaner than the above mentioned non-stoichiometric or doped NBTs<sup>4</sup>. To avoid possible impact from secondary phases on the materials properties, in many circumstances a nominally stoichiometric NBT is preferred. Therefore, to make sure the conductivity meets the requirement for different applications, it is suggested rutile TiO<sub>2</sub> should be used to prepare ionically conducting NBT, and anatase TiO<sub>2</sub> for preparing insulating NBT.

### Conclusion

The dramatic impact of the TiO<sub>2</sub> polymorph on the electrical conductivity and conduction mechanisms of nominally stoichiometric NBT ceramics (NB<sub>0.50</sub>T) prepared by solid-state

reaction method is reported. Based on our processing route, NBT ceramics prepared using rutile  $\text{TiO}_2$  are ionically conductive, and those prepared using anatase  $\text{TiO}_2$  are electrically insulating. The dramatic difference in electrical properties of NBT prepared using rutile and anatase  $\text{TiO}_2$  is strongly linked to the NBT formation process: the intermediate, Bi-rich Sillenite phase  $\text{Bi}_{12}\text{TiO}_{20}$  is more stable and forms in larger amounts during formation of NBT when anatase  $\text{TiO}_2$  is used. The intermediate  $\text{Bi}_{12}\text{TiO}_{20}$  immobilises significant amounts of  $\text{Bi}_2\text{O}_3$  and therefore reduces  $\text{Bi}_2\text{O}_3$ -loss during heating, and consequently lowers the oxygen vacancy concentration to suppress oxide-ion conduction in NBT prepared by anatase  $\text{TiO}_2$ . This work provides a plausible explanation for the large variation of  $\sigma_b$  for NBT reported in the literature and highlights the importance of selecting appropriate  $\text{TiO}_2$  reagents to obtain controllable  $\sigma_b$  in NBT-based ceramics. For ion-conducting applications, rutile  $\text{TiO}_2$  should be used, and for dielectric applications anatase  $\text{TiO}_2$  should be used. Furthermore, any study of the effect of additional doping with foreign elements on NBT or solid solutions with NBT should start with anatase  $\text{TiO}_2$ . This work also demonstrates the importance of understanding the solid-state reaction mechanisms in the formation and compositional control of NBT.

## Conflicts of interest

There are no conflicts to declare.

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