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We review the diversity of electrical behaviour of NBT induced by various defect mechanisms, including A-site Na or Bi non-stoichiometry, isovalent-, acceptor- and donor-doping.
Review: Defect chemistry and electrical properties of sodium bismuth titanate perovskite

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The ferroelectric perovskite Na0.5Bi0.5TiO3 (NBT), can exhibit three types of electrical behaviour, i.e. oxide-ion conduction (Type I), mixed ionic-electronic conduction (Type II) and insulating/dielectric (Type III) based on various defect mechanisms. Here we review how to tune the electrical properties of NBT via several mechanisms, including A-site Na or Bi nonstoichiometry, isovalent substitution, acceptor- and donor-doping. The diversity of electrical behaviour in the NBT lattice is attributed to the high level of oxide-ion conductivity originating from highly mobile oxygen ions which can be fine-tuned to optimise or suppress the ionic conduction. High oxide-ion conductivity can be obtained by manipulating the starting Na/Bi ≥ 1 and by acceptor-doping to make NBT a potential electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs). In contrast, the oxide-ion conduction can be partially or fully suppressed by having a starting (nominal) composition with Na/Bi < 1, donor-doping, or utilising the trapping between oxygen vacancies and some B-site acceptor dopants. This significantly reduces the dielectric loss and makes NBT-based materials excellent candidates as high-temperature dielectrics for capacitor applications.

Introduction

Sodium bismuth titanate, Na0.5Bi0.5TiO3 (NBT), is considered as one of the most promising lead-free piezoelectric materials to replace lead zirconate titanate (PZT) because of its high Curie temperature (~ 325 °C), relatively high remnant polarization (38 μC cm−2) and piezoelectric constant (73 pC N−1).1–2 NBT was first reported in the 1960s and has received increasing attention in recent years driven by the surge in developing lead-free materials.3 There has been extensive research on the crystal structure and phase transformation of NBT4–10, and numerous efforts have been devoted to improving its piezoelectric properties.4, 11–20

One major drawback of NBT as a piezoelectric/dielectric material is its high electrical conductivity which leads to high and unacceptable dielectric loss and leakage currents at elevated temperatures.1 To solve this problem improved understanding of the electrical conductivity and the conduction mechanism(s) of NBT is essential. Hiruma et al.21 and Sung et al.22, 23 have shown the electrical properties of NBT are highly sensitive to A-site cation nonstoichiometry and that small deviations in nominal A-site cation nonstoichiometry being related to a switch between oxide-ion and electronic conduction.25, 26 The nominally stoichiometric NBT (nominal Na0.5Bi0.5TiO3; NB0.50T), presents high conductivity with an oxide-ion transport number t0.5 ≈ 0.3 at 600 - 800 °C, suggesting the electrical conduction is dominated by oxide-ions. The predominance of oxide-ion conduction (as opposed to sodium ion or electronic conduction) in NB0.50T has been further confirmed by 23O tracer diffusion measurements. The high oxide-ion conductivity in NB0.50T is attributed to oxygen vacancies generated through low levels of Bi2O3 loss during ceramic processing and the Kroger-Vink equation,

\[ 2\text{Bi}_6^+ + 3\text{O}_3^- \rightarrow 2\text{V}_{\text{O}}^- + 3\text{V}_{\text{Bi}}^+ + \text{Bi}_2\text{O}_3 \]  

(1)

as well as the high oxygen ion mobility associated with highly polarized Bi3+ ions and weak Bi-O bonds.27 Higher oxide-ion conductivity is achieved in Bi-deficient NBT (nominal Na0.5Bi0.49TiO3: NB0.49T) due to generation of additional oxygen vacancies. In contrast, the oxide-ion conductivity is suppressed in Bi-excess NBT (nominal Na0.5B0.5,5TiO3: NB0.51T) as the excess Bi2O3 in NB0.51T can compensate for the loss during processing, thus NB0.51T exhibits electronic conduction with an activation energy of ~ 1.6 eV which is close to half of the band gap of NBT.28 The predominant electronic conduction in NB0.51T is confirmed by a t<sub>ion</sub> < 0.1 at 600 - 800 °C. Interestingly, recent work shows a further increase in the starting Bi-excess content (for example, Na0.5B0.5,5TiO3: NB0.53T) can reintroduce significant levels of oxide-ion conductivity into NBT. NB0.53T shows mixed conduction behaviour with comparable contributions from oxide-ion and electronic conduction showing a
t_{ion} close to 0.5, which is possibly linked to a change in the Bi-content in the NBT main phase or a space charge effect because of the presence of Bi-rich secondary phase.29

Based on the magnitude of bulk conductivity, $\sigma_b$ and $t_{ion}$ values, we have concluded that NBT can exhibit three types of electrical behaviour by tailoring the A-site Na/Bi non-stoichiometry (Fig. 1a): Type I, predominant oxide-ion conduction, high $\sigma_b$, $t_{ion}$ ~ 0.9; Type II, mixed ionic-electronic conduction, intermediate $\sigma_b$, $t_{ion}$ ~ 0.5; Type III, predominant electronic conduction, low $\sigma_b$, $t_{ion}$ < 0.1. These three types of electrical behaviour can also be clearly distinguished from the $\tan \delta$ - $T$ relationship, Fig. 1b. Type I NBT shows a sharp rise of $\tan \delta$ with increasing temperature and $\tan \delta$ exceeds 0.2 at ~ 350 °C. In contrast, Type III NBT presents low $\tan \delta$ in a wide temperature range (< 0.02 from 300 to 600 °C), making it an excellent high temperature dielectric material. In between Type I and III, Type II shows low $\tan \delta$ in a narrow temperature range and a steep rise above ~ 500 °C to exceed 0.1 at 600 °C.

The above findings not only reveal the electrical conduction behaviour of NBT but also show the flexibility in tailoring the electrical conductivity and conduction mechanisms in NBT and expand the potential application of NBT-based materials from piezoelectric/dielectric devices to oxide-ion and mixed ionic-electronic conductors. They also highlight the importance of defect chemistry on the electrical properties of NBT. Here we review how to tune the electrical properties of NBT by various defect mechanisms including; A-site Na or Bi non-stoichiometry; isovalent substitution; acceptor- and donor-doping. In particular, we focus on controlling the oxide-ion conduction in NBT to switch the conduction mechanism and conductivity among Types I, II and III according to the requirements for different applications.

The structure of this review is as follows. First, we review the defect chemistry and electrical properties of undoped NBT, which consists only of Na, Bi, Ti and O without any other dopant and therefore rules out any possible influence from foreign ions. Second, results from isovalent doping which does not introduce any oxygen vacancies into NBT are discussed to unveil the important parameters that may affect oxide-ion conduction in NBT. Third, possible compensation mechanism(s) from acceptor-doping in NBT are discussed with an attempt to enhance the bulk conductivity and to explore the potential of NBT-based materials as electrolytes in IT-SOFCs. We also demonstrate the possibility of suppressing the oxide-ion conduction in NBT using the trapping effect between B-site acceptor-dopants and oxygen vacancies. Finally, the influence of donor-doping on the electrical properties are reviewed to demonstrate dielectric/insulating behaviour thus rendering NBT-based materials as potential candidates for high temperature dielectric/piezoelectric applications. The article concludes with a summary to highlight the important findings, to date.

**Defect chemistry and electrical properties of NBT**

**Undoped NBT**

Our earlier studies25, 26 showed the electrical conductivity and conduction mechanisms are highly sensitive to the A-site Na or Bi non-stoichiometry. For nominal Na/Bi ratios ≥ 1, NBT exhibits high oxide-ion conductivity; nominal Na/Bi ratios < 1 dramatically suppress the oxide-ion conduction and ‘switch’ NBT to a predominant n-type electronic semiconductor/insulator. In recent follow-on studies, three different mechanisms were employed to manipulate the A-site Na or Bi non-stoichiometry in attempts to fully establish the mechanism(s) and levels of nonstoichiometry in NBT.
and to improve our understanding of the oxide-ion conducting to semiconducting/insulating switch over.

First, we investigated finer increments of A-site non-stoichiometry with two series of materials, Bi non-stoichiometry based on the general formula Na$_{0.5+3w}$Bi$_{2-3w}$Ti$_{2+3w}$O$_{3+3w}$ (x = 0.02, 0.01, 0.005, 0.001, 0.0001 and 0.00005) and Na non-stoichiometry based on Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ (y = -0.01, 0 and 0.01). The phase purity and the electrical properties in these ceramics were examined using various techniques. Second, a Na:Bi 1:1 substitution mechanism (Na$^+$→Bi$^{3+}$) based on Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ (z = -0.02, -0.01, 0, 0.01, 0.02) was studied. This substitution mechanism aimed to alter the Na/Bi ratio while maintaining the A-site of the perovskite to be fully occupied. Third, a Na: Bi 3:1 substitution mechanism (3Na$^+$→Bi$^{3+}$) based on Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ (w = -0.05, -0.02, -0.01, 0, 0.05) was investigated. This mechanism maintains A-site charge neutrality without introducing any oxygen deficiency. Results of the above three non-stoichiometry mechanisms are summarised in this section.

**Bi or Na non-stoichiometry**

1) Bi non-stoichiometry Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ series is summarised in Table 1. Consistent with previous studies, nominally stoichiometric (x = 0) and Bi-deficient (x < 0) NBTs show oxide-ion conduction behaviour (Type I), slightly Bi-excess (0 < x ≤ 0.01) NBTs show predominant electronic conduction (Type III) and more Bi-excess (x ≥ 0.02) NBTs present mixed ionic-electronic conduction (Type II). The defect mechanisms for such electrical behaviour induced by Bi non-stoichiometry are described by Equation (1) and makes NBT oxide-ion conducting (Type I).

\[ \text{Bi}^{3+}_\text{a} + \text{O}_{\text{a}}^2- \rightarrow \text{Bi}^{4+}_\text{a} + 2\text{O}_{\text{a}}^2- \]

With this defect mechanism, single phase NBT (based on SEM) was detected for z = -0.02 and Na or Bi non-stoichiometry, NBT also exhibits Type I behaviour with starting Na/Bi ratios ≥ 1 and Type III with Na/Bi ratios < 1.

2) Na non-stoichiometry Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$

NBTs with Na non-stoichiometry behave in the opposite way compared to those with Bi non-stoichiometry. As also shown in Table 1, Na-deficient NBT is insulating (similar to Bi-excess in Bi non-stoichiometric NBT) and Na-rich NBT is conducting (similar to Bi-deficient in Bi non-stoichiometric NBT). For Na-deficient NBT (y < 0), if the defect mechanism is via generating oxygen vacancies according to

\[ 2\text{Na}^+_\text{a} \rightarrow 2\text{Na}^0 \]

it should be more ioni-cally conductive than stoichiometric NBT (y = 0) because of the creation of oxygen vacancies. In contrast, Na-rich NBT (y > 0) should exhibit lower conductivity than stoichiometric NBT as the excess Na should fill the Bi vacancies and lead to partial elimination of oxygen vacancies according to

\[ 2\text{Na}_\text{a}^0 + 3\text{V}^+_\text{a} \rightarrow 2\text{Na}_\text{a}^+ + 2\text{V}^0_\text{a} \]

However, the observed electrical properties of the NBT series with Na non-stoichiometry are not consistent with equations (2) and (3), therefore suggesting these mechanisms are inappropriate for this series.

**XRD, SEM and TEM analysis on Na non-stoichiometric NBT** reveals the observed electrical behaviour originates from changes in the composition of the main phase in these ceramics. For example, for Na-deficient NBT, i.e., y = -0.01, STEM HAADF Z-contrast images revealed the presence of TiO$_2$ secondary phase. Thus the bulk composition is deficient in both Na and Ti, and therefore the chemical formula Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ can be rewritten as Na$_{0.5-3w}$Bi$_{2+3w}$Ti$_{2+3w}$O$_{5+3w}$ where TiO$_2$ is the secondary phase observed by TEM. Therefore, the bulk composition of y = -0.01 was essentially Bi-rich to make NBT insulating (Type III). For Na-rich NBT, a Na-rich secondary phase was detected under SEM, indicating the excess Na in the starting material does not enter into the lattice. The bulk composition is Bi-deficient due to the Bi-loss during ceramic processing. Consequently, oxygen vacancies are generated according to Equation (1) and make NBT oxide-ion conducting (Type I).

Na$^+$→Bi$^{3+}$

As Na or Bi deficiency will introduce vacancies on the A-site, a Na:Bi 1:1 substitution mechanism (Na$^+$→Bi$^{3+}$) with nominal composition of Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$O$_{6+3w}$ (z = -0.02, -0.01, 0, 0.01, 0.02), which maintains the A-site of the perovskite lattice being fully occupied, was investigated. The phase purity and electrical behaviour of this series are summarised in Table 2.

With this defect mechanism, single phase NBT (based on SEM) can be obtained for -0.01 ≤ z ≤ 0.01. Na$_2$TiO$_3$ secondary phase was detected for z = -0.02 and Na$_{0.5+3w}$Bi$_{2+3w}$Ti$_{3+3w}$ secondary phase was detected for z = 0.02. Similar to Na or Bi non-stoichiometry, NBT also exhibits Type I behaviour with starting Na/Bi ratios ≥ 1 and Type III with Na/Bi ratios < 1.

**XRD**

Based on XRD, large amounts of Bi$_4$Ti$_3$O$_{12}$ can be detected for w = -0.05 and a small amount of Na$_2$TiO$_3$ for w = 0.05. Phase pure NBT is only obtained for w = 0.01 based on XRD. However, according to the nominal composition of w = 0.01, A-site occupancy is > 1, which is unlikely to happen. Normalising the A-site occupancy to 1 gives the formula Na$_{0.5+3w}$Bi$_{4.52}$Ti$_{3.48}$O$_{2.94}$ and would therefore generate a Na$_{1}$/Ti-rich secondary phase that has not been detected by XRD.
These results suggest this substitution mechanism does not yield an extensive single phase NBT solid solution. NBT with \( w > 0 \) exhibits Type I behaviour which is a result of Bi-deficient bulk NBT with the presence of a Na,Ti-rich secondary phase.

**Summary**

In this section, three different A-site defect mechanisms have been applied to NBT and their effects on the electrical properties are summarised in Fig. 2. In general, NBTs with Na/Bi ratios \( \geq 1 \) exhibit high oxide-ion conductivity (Type I) and those with Na/Bi ratios < 1 show low conductivity which is dominated by low levels of electronic conduction (Type III). NBTs with significant levels of Bi-rich secondary phases can present mixed-conduction with comparable contributions from electronic and oxide-ion conduction (Type II). It should be stressed that the level of allowed non-stoichiometry within NBT is extremely low, usually below the detection limit of most readily available analytical methods. But such low levels of non-stoichiometry can result in more than three orders of magnitude difference in the bulk conductivity, therefore electrical measurements are the most sensitive and reliable method to detect the predominant type of non-stoichiometry in NBT.

### Table 1. Electrical behaviour and phase purity of NBT with Bi and Na non-stoichiometry: \( \text{Na}_0.5\text{Bi}_{0.5-y}\text{TiO}_3 \)

<table>
<thead>
<tr>
<th>Nonstoichiometry</th>
<th>( x ) or ( y )</th>
<th>Na/Bi</th>
<th>Electrical behaviour</th>
<th>XRD</th>
<th>SEM</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>-0.02</td>
<td>1.04</td>
<td>I</td>
<td>Na(_2)\text{Ti}<em>6\text{O}</em>{13}</td>
<td>Na(_2)\text{Ti}<em>6\text{O}</em>{13}</td>
<td>--</td>
</tr>
<tr>
<td>( \text{Na}<em>0.5\text{Bi}</em>{0.5-y}\text{TiO}_3 )</td>
<td>-0.01</td>
<td>1.02</td>
<td>I</td>
<td>clean</td>
<td>Na(_2)\text{Ti}<em>6\text{O}</em>{13}</td>
<td>Ti(_2)</td>
</tr>
<tr>
<td>-0.005</td>
<td>1.01</td>
<td>I</td>
<td>clean</td>
<td>Na(_2)\text{Ti}<em>6\text{O}</em>{13}</td>
<td>Ti(_2)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.00</td>
<td>I</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
<td>Ti(_2)</td>
</tr>
<tr>
<td>0.005</td>
<td>0.99</td>
<td>III</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
</tr>
<tr>
<td>0.01</td>
<td>0.98</td>
<td>III</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
<td>Bi(_2)</td>
</tr>
<tr>
<td>0.02</td>
<td>0.96</td>
<td>II</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
<td>Bi(_2)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.91</td>
<td>II</td>
<td>Bi(_2)\text{O}_3, Na(<em>2)\text{Bi}</em>{4.5}\text{Ti}<em>2\text{O}</em>{15}</td>
<td>B(_2)O(_3)</td>
<td>Na(<em>2)\text{Bi}</em>{4.5}\text{Ti}<em>2\text{O}</em>{15}</td>
<td>B(_2)O(_3)</td>
</tr>
<tr>
<td>Na</td>
<td>-0.01</td>
<td>0.98</td>
<td>III</td>
<td>clean</td>
<td>clean</td>
<td>Ti(_2)</td>
</tr>
<tr>
<td>0</td>
<td>1.00</td>
<td>I</td>
<td>clean</td>
<td>clean</td>
<td>clean</td>
<td>Ti(_2)</td>
</tr>
<tr>
<td>( \text{Na}<em>0.5\text{Bi}</em>{0.5+y}\text{TiO}_3 )</td>
<td>0.01</td>
<td>1.02</td>
<td>I</td>
<td>clean</td>
<td>Na-rich phase</td>
<td>--</td>
</tr>
</tbody>
</table>

### Table 2. Phase purity and electrical behaviour of NBT with Na:Bi 1:1 substitution: \( \text{Na}_0.5\text{Bi}_{0.5-y}\text{TiO}_3 \) \( z = 0.02, -0.01, 0, 0.01, 0.02 \)

<table>
<thead>
<tr>
<th>( z )</th>
<th>Nominal composition</th>
<th>Na/Bi</th>
<th>Electrical behaviour</th>
<th>Phase purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.02</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.48}\text{TiO}<em>2\text{O}</em>{2.98}</td>
<td>1.08</td>
<td>I</td>
<td>clean</td>
</tr>
<tr>
<td>-0.01</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.49}\text{TiO}<em>2\text{O}</em>{2.99}</td>
<td>1.04</td>
<td>I</td>
<td>clean</td>
</tr>
<tr>
<td>0</td>
<td>Na(_0.5)\text{BiO}_3</td>
<td>1.00</td>
<td>I</td>
<td>clean</td>
</tr>
<tr>
<td>0.01</td>
<td>Na(<em>0.49)\text{Bi}</em>{0.51}\text{TiO}<em>3\text{O}</em>{3.01}</td>
<td>0.96</td>
<td>III</td>
<td>clean</td>
</tr>
<tr>
<td>0.02</td>
<td>Na(<em>0.48)\text{Bi}</em>{0.52}\text{TiO}<em>3\text{O}</em>{3.02}</td>
<td>0.92</td>
<td>III</td>
<td>Na(<em>2)\text{Bi}</em>{4.5}\text{Ti}<em>2\text{O}</em>{15}</td>
</tr>
</tbody>
</table>

### Table 3. Phase purity and electrical behaviour of NBT with Na:Bi 3:1 substitution: \( \text{Na}_0.5\text{Bi}_{0.5-w}\text{TiO}_3 \) \( w = 0.05, -0.02, -0.01, 0, 0.05 \)

<table>
<thead>
<tr>
<th>( w )</th>
<th>Nominal composition</th>
<th>Na/Bi</th>
<th>Electrical behaviour</th>
<th>Phase purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.05</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.55}\text{TiO}_3</td>
<td>0.63</td>
<td>-</td>
<td>NBT + Bi(_2)\text{Ti}<em>2\text{O}</em>{12}</td>
</tr>
<tr>
<td>0</td>
<td>Na(_0.5)\text{BiO}_3</td>
<td>1.00</td>
<td>I</td>
<td>clean</td>
</tr>
<tr>
<td>0.01</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.48}\text{TiO}_3</td>
<td>1.08</td>
<td>I</td>
<td>clean</td>
</tr>
<tr>
<td>0.02</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.48}\text{TiO}_3</td>
<td>1.17</td>
<td>I</td>
<td>Na-rich phase</td>
</tr>
<tr>
<td>0.05</td>
<td>Na(<em>0.5)\text{Bi}</em>{0.45}\text{TiO}_3</td>
<td>1.44</td>
<td>I</td>
<td>Na-rich phase</td>
</tr>
</tbody>
</table>
K-doped, Y-doped, La-doped and Zr-doped NBT obtained from impedance spectroscopy is shown in Fig. 4. The ionic radius, $K^{+}$ cations on the oxide-ion conduction in NBT, isovalent doping, such as weaker bonding strength with oxygen compared to Na $^{+}$, have been carried out. The Arrhenius plot of bulk conductivity, $\sigma_b$, of K-doped, Y-doped, La-doped and Zr-doped NBT obtained from impedance spectroscopy is shown in Fig. 4. The ionic radius, polarisability and bonding strength with oxygen of these elements are listed in Table 4.

Partial replacement of Na $^{+}$ by K $^{+}$, La $^{3+}$ or Y $^{3+}$ on the A-site decreases the bulk conductivity of NBT, which can be attributed to the lower polarisability of Y and La compared to Bi, as well as the much stronger Y-O or La-O bond compared to the Bi-O bond. Although the polarisability of Zr is higher than Ti, partial replacement of Ti $^{4+}$ by Zr $^{4+}$ also decreases the bulk conductivity of NBT, which suggests the bonding strength with oxygen plays a key role in the oxide-ion migration. The high cation-oxygen bond strength limits the mobility of oxygen ions in NBT and therefore suppresses the oxide-ion conduction. It can be predicted that these isovalent doped NBTs have much lower dielectric loss and can be excellent high-temperature dielectric materials with appropriate doping levels.

**Isovalent doping**

Nominally stoichiometric NBT exhibits high oxide-ion conductivity, which originates from the oxygen vacancies generated through a small amount of $\text{Bi}_2\text{O}_3$ loss during ceramic processing. A previous study showed that $0.5 \times 1$ at.% Nb doping on the B-site can fill up the oxygen vacancies and significantly decrease the electrical conductivity. Therefore, the bismuth and oxygen nonstoichiometry in NBT can be estimated to be in the range of 0.0017-0.0033 for Bi and 0.0025-0.005 for oxygen, corresponding to a formula of $\text{Na}_{0.4967-0.4983}\text{Bi}_{2.995-2.9975}\text{O}_3$.

The fact that such a low level of oxygen vacancy concentration can result in such high oxide-ion conductivity implies the mobility of oxygen ions in NBT is very high. In perovskites, the oxygen ion migration is through a saddle point which is a triangle formed by two A-site cations and one B-site cation. In NBT, first-principles calculations showed the lowest energy barriers for oxygen ion migration occur in saddle points between Bi-Bi-Ti ions (0.22 eV), whereas higher barriers are observed for Na-Bi-Ti (0.6 – 0.85 eV) and Na-Na-Ti (1.0 – 1.3 eV) saddle points, as shown in Fig. 3. Experimentally, there is no evidence for long-range ordering of the A-site cations in NBT, therefore the Na-Bi-Ti saddle points are considered as the rate-limiting step in the overall oxide-ion migration in NBT. It is generally accepted that the high polarisability of Bi $^{3+}$ and weak Bi-O bonds on the A-site are critical to the high mobility of oxygen ions.

To further understand the local configuration and properties of cations on the oxide-ion conduction in NBT, isovalent doping, such as $K^{+}$ to replace Na $^{+}$, Y $^{3+}$ or La $^{3+}$ to replace Bi $^{3+}$ and Zr $^{4+}$ to replace Ti $^{4+}$, have been carried out. The Arrhenius plot of bulk conductivity, $\sigma_b$, of K-doped, Y-doped, La-doped and Zr-doped NBT obtained from impedance spectroscopy is shown in Fig. 4. The ionic radius, polarisability and bonding strength with oxygen of these elements are listed in Table 4.

Partial replacement of Na $^{+}$ by $K^{+}$ significantly decreases the bulk conductivity, which is surprising as $K^{+}$ has higher polarisability and weaker bonding strength with oxygen compared to Na $^{+}$, which should be beneficial for oxide-ion conduction. Here the suppressed conductivity is attributed to compositional variations associated with the higher volatility of K compared to Na. The K loss is more significant than Bi-loss during sintering, and therefore makes KNBT Bi-rich on the A-site. Partial replacement of Bi $^{3+}$ by Y $^{3+}$ or La $^{3+}$ on the A-site decreases the bulk conductivity of NBT, which can be attributed to the lower polarisability of Y and La compared to Bi, as well as the much stronger Y-O or La-O bond compared to the Bi-O bond. Although the polarisability of Zr is higher than Ti, partial replacement of Ti $^{4+}$ by Zr $^{4+}$ also decreases the bulk conductivity of NBT, which suggests the bonding strength with oxygen plays a key role in the oxide-ion migration. The high cation-oxygen bond strength limits the mobility of oxygen ions in NBT and therefore suppresses the oxide-ion conduction. It can be predicted that these isovalent doped NBTs have much lower dielectric loss and can be excellent high-temperature dielectric materials with appropriate doping levels.

**Fig. 2** Bulk conductivity of NBT at 600 °C with various Na/Bi ratios.

**Fig. 3** Saddle-point configuration and associated activation energies for oxygen ion migration in NBT. Values taken from ref. 37.

**Fig. 4** Arrhenius plot of bulk conductivity, $\sigma_b$, of K-, Y-, La- and Zr-doped NBT.
mechanism based on the uptake of oxygen (on cooling) as given by the following

\[ V_0^{**} + \frac{1}{2} O_2 \rightarrow O_0^* + 2h^* \]

Therefore, acceptor-doping in NBT can either enhance oxide-ion conductivity by creating oxygen vacancies as described by Equation 4 or enhance \( p \)-type hole conduction as described by Equation 5. Electrical property measurements on 2\% Mg-doped and 2\% Sr-doped \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \) show enhanced bulk conductivity, enhanced oxide-ion transport number and higher oxygen diffusion coefficient compared to undoped \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \), as listed in Table 5. These electrical properties prove that acceptor-doping of \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \) on both sites is predominantly by an ionic compensation mechanism to create oxygen vacancies. Acceptor-doping is therefore effective to enhance oxide-ion conduction of \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \) without introducing any significant electronic contribution.

Based on the above understanding, various acceptor-type dopants have been selected to dope NBT and \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \) in an attempt to optimise the oxide-ion conductivity in this perovskite. Among all the dopants and doping levels, a maximum enhancement of \( \sigma_b \) by less than 1 order of magnitude compared to \( \text{NB}_{0.4}\text{O}_{0.6} \text{T} \) is achieved by 2\%Sr-doping on the A-site or 1\%Mg-doping on the B-site, as shown in Fig. 5. With other dopants and doping levels the bulk conductivity values are all within the shaded region.

Possible reasons for the limited enhancement of bulk conductivity by acceptor-doping in NBT are 1) a low solubility limit of these acceptor dopants (typically < 2 at.\%) and 2) trapping of oxygen vacancies especially by B-site acceptor dopants, which decreases the mobility of charge carriers.37 More fundamentally, R. A. De Souza45 recently reviewed oxygen vacancy diffusion in a wide variety of \( \text{ABO}_3 \)-type perovskites ranging from ferroelectric dielectrics such as \( \text{BaTiO}_3 \) and mixed ionic-electronic conductors such as \((\text{Ba}_{0.5}\text{Sr}_{0.5})_0.8\text{CoO}_0.2\text{Fe}_0.2\text{O}_3\) to electrolytes such as \((\text{La}_{0.5}\text{Sr}_{0.5})_1\text{Ga}_0.5\text{Mg}_{0.5}\text{O}_3\). He reported a surprising result that regardless of the level of oxygen vacancies in these materials, the oxygen vacancy diffusivity is very similar and considered the possibility of a fundamental limit to oxygen-vacancy diffusivity in the \( \text{ABO}_3 \) perovskite lattice. Using this oxygen vacancy diffusivity limit for cubic perovskites proposed by De Souza, at an upper limit for \( \sigma_b \) of NBT with an oxygen deficiency of 0.025, calculated from Nernst-Einstein equation, is predicted, as shown by the dashed line in Fig. 5. Above 300 °C, the highest bulk conductivity obtained by either Sr- or Mg-doping is consistent with the value calculated from this upper limit, therefore suggesting optimisation of oxide-ion conductivity in the NBT lattice may have been achieved.

Nevertheless, these acceptor-doped NBTs show attractive bulk conductivity. Comparing with the two best known 8–8–0.5 oxide conductors used in intermediate-temperature solid oxide fuel cells (IT-SOFCs), \((\text{Ba}_{0.5}\text{Sr}_{0.5})_{0.8}\text{CoO}_0.2\text{Fe}_0.2\text{O}_3\) and \((\text{Bi}_{0.5}\text{La}_{0.5})_{0.8}\text{DyO}_0.2(\text{WO}_3)_{0.8}\text{O}_2\), 20ESB and \((\text{Bi}_{0.5}\text{La}_{0.5})_{0.8}\text{DyO}_0.2(\text{WO}_3)_{0.8}\text{O}_2\) (all doped to 8–8–0.5), although \( \sigma_b \) of doped \( \text{NB}_{0.4}\text{O}_{0.6} \) T is initially lower than 20ESB and 84DSWB, it shows no appreciable degradation with time contrary to the rapid conductivity degradation of 20ESB and 84DSWB.46 They also have the advantage over these 8–8–0.5 phases as a more sustainable (rare-earth free) material. With excellent ionic conductivity, extremely low levels of degradation and reasonable stability in reducing atmospheres,42,43 acceptor-doped NBTs can be promising electrolyte materials for IT-SOFCs.
It is worth mentioning that the log_{10} \( \sigma_0 \sim 1/T \) relationship of undoped and acceptor-doped NBT shows a change in activation energy, \( E_a \) from \( \sim 0.4 \) eV above 300 °C to \( \sim 0.9 \) eV below 300 °C (Fig. 5). The reason(s) for a change of \( E_a \) around this temperature has not been fully established but the possibility of a change in charge carrier from oxygen ions to electrons, holes or protons has been excluded by previous studies.\(^\text{41} \) A plausible explanation for the change of \( E_a \) is the coexistence of rhombohedral (R) and tetragonal (T) phases in the temperature range from 250 to 400 °C, which was revealed by variable temperature neutron diffraction and TEM studies.\(^\text{41} \) An estimation of \( \sigma_0 \) from the Maxwell model for a two-phase composite showed good agreement with the experimental data of \( \sigma_0 \), suggesting coexistence of R and T phases may be a plausible explanation for the change in \( E_a \) at \( \sim 300 \) °C.\(^\text{42} \) Other possible reasons for the change of \( E_a \) are dissociation of defect clusters and/or changing of conduction paths associated with the various NBT polymorphs as recently proposed by Meyer and Albe.\(^\text{47} \)

<table>
<thead>
<tr>
<th>( \sigma_0 / \text{S cm}^{-1} )</th>
<th>( t_{\text{ion}} )</th>
<th>( D^* / \text{cm}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C</td>
<td>300 °C</td>
<td>500 °C</td>
</tr>
<tr>
<td>NB0.49T</td>
<td>2.08 \times 10^{-7}</td>
<td>1.19 \times 10^{-4}</td>
</tr>
<tr>
<td>2%Mg-doped NB0.49T</td>
<td>7.62 \times 10^{-7}</td>
<td>2.57 \times 10^{-4}</td>
</tr>
<tr>
<td>2%Sr-doped NB0.49T</td>
<td>1.44 \times 10^{-6}</td>
<td>4.81 \times 10^{-4}</td>
</tr>
</tbody>
</table>

It is interesting to note that many B-site acceptor-doped NBT materials exhibit significantly lower bulk conductivity when compared to A-site acceptor-doped materials with the same nominal oxygen vacancy concentration, Fig. 6. This suggests a strong tendency for the trapping of oxygen vacancies by B-site acceptor dopants, which is supported by first-principle calculations.\(^\text{37} \) Trapping of oxygen vacancies decreases their mobility and therefore is detrimental to the oxide-ion conduction. However, it provides an opportunity to control the oxide-ion conduction in NBT using this trapping effect. As the solid solution limit of B-site acceptor dopants in NBT is rather low, some Bi-based high-pressure phases such as BiAlO\(_3\), BiGaO\(_3\) and BiScO\(_3\) were used to form solid solutions with NBT to expand the B-site acceptor-dopant level. For example, with BiAlO\(_3\), 8% Al\(^{3+}\) can be incorporated into NBT to replace Ti\(^{4+}\)\(^\text{20,48} \) compared to < 3% by single B-site doping with Al\(^{3+}\). Impedance spectroscopy measurements show a systematic decrease of bulk conductivity with increasing x in (NBT)\(_{1-x}\)(BiAlO\(_3\))\(_x\) solid solutions, Fig. 7a and electromotive force measurements show a continuous decrease of oxide-ion transport number with increasing x, Fig. 7b. As incorporation of BiAlO\(_3\) into NBT does not induce any additional oxygen vacancies or create any additional oxygen ions it can therefore be considered as a ‘stoichiometric’ doping mechanism.

The suppressed oxide-ion conductivity by BiAlO\(_3\) incorporation can be attributed mainly to a decrease in oxide vacancy mobility associated with Al acceptor trapping. A simple calculation suggests 7% Al\(^{3+}\) can trap all the oxygen vacancies in the solid solution,\(^\text{49} \) which is consistent with the \( \sigma_0 \) - x and \( t_{\text{ion}} \) - x relationships in Fig. 7. Therefore, using the trapping effect between oxygen vacancies and B-site acceptor dopants, it is possible to fine tune the electrical conduction mechanism from predominant ionic, to mixed ionic-electronic to predominant (but low level) electronic conduction.

To summarise this section, low levels of acceptor-type dopants can be introduced to either the A-site to replace Bi\(^{3+}\) or to the B-site to replace Ti\(^{4+}\) to generate oxygen vacancies to enhance the bulk conductivity of NBT. However, the bulk conductivity of acceptor-doped NBT (above 300 °C) seems to approach an upper limit which is restrained by the oxygen vacancy diffusivity in the perovskite lattice. These acceptor-doped NBTs can be promising electrolyte materials for IT-SOFCs. Comparison between A- and B-site dopants suggests that some B-site dopants are more effective at trapping oxygen vacancies to decrease their mobility. This is detrimental for oxide-ion conduction but it provides an opportunity to fine tune the electrical conductivity and conduction mechanism of NBT using the trapping between B-site acceptor dopants and oxygen vacancies to create excellent dielectric materials.
Donor-doping \cite{29,34}

Donor-dopants such as Nb can be incorporated into NBT to replace Ti on the B-site. The doping limit of Nb in Na$_{0.5}$Bi$_{0.5}$Ti$_{1-x}$Nb$_x$O$_{3+0.5x}$ is low with the presence of small amounts of Bi$_2$Ti$_2$O$_7$- or Na$_{0.5}$Bi$_{4.5}$Ti$_{4}$O$_{15}$-related secondary phases for $x \geq 0.02$.\cite{34} However, extremely low levels of Nb doping can significantly change the electrical conductivity and conduction mechanism of NBT, as summarised below.

When Nb is introduced to replace Ti in NBT, there are at least two possible compensation mechanisms: a) electronic compensation, described by

$$\text{Nb}_2\text{O}_5 + 2\text{Ti}^{4+}_x \rightarrow 2\text{Nb}^{5+}_y + 2\text{TiO}_2 + 2c^+ + \frac{1}{2}\text{O}_2(g),$$

or b) ionic compensation, described by

$$\text{Nb}_2\text{O}_5 + 2\text{Ti}^{4+}_x + V^{2+}_y \rightarrow 2\text{Nb}^{5+}_y + 2\text{TiO}_2 + \text{O}_2^y.$$  

The electronic compensation mechanism is commonly adopted by BT or ST-based perovskites, which induces high levels of $n$-type semiconductivity to the materials. For example, Nb doping on the Ti-site can transform BT from a dielectric material to an $n$-type semiconductor with room temperature conductivity $> 0.01$ S cm$^{-1}$\cite{49}. 

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**Fig.6** Comparison of bulk conductivity, $\sigma_b$, with A-site and B-site acceptor-dopants at (a) 200 °C and (b) 400 °C.

**Fig.7** (a) Arrhenius plots for bulk conductivity and (b) oxide-ion transport number at 600 °C of the (NBT)$_{1-x}$(BiAlO$_3$)$_x$ ($0 \leq x \leq 0.08$) solid solutions. \cite{48}
Concluding remarks

The ferroelectric perovskite NBT can present three types of electrical behaviour based on oxide-ion conduction (Type I), mixed ionic-electronic conduction (Type II) and insulator/dielectric (Type III) by controlling the defects introduced by various mechanisms. The flexibility in fine tuning the electrical properties of NBT make it an attractive material to be applied in various technologically important conditions. The local configuration at the saddle point is critical to the oxide-ion conduction in NBT. Polarisability and bonding strength with oxygen of the cations, especially the latter, are the most important factors that influence the oxide-ion migration. Due to the high polarisability and weak Bi-O bond, it can be predicted that most isovalent dopants on starting Na/Bi ratio. Based on our current processing conditions Na/Bi ≥ 1 is required to obtain high oxide-ion conductivity. Na/Bi < 1 switches the electrical conduction mechanism from predominant oxide-ion conduction to predominant (but low level) electronic conduction. NBT ceramics with a considerable amount of Bi-rich secondary phase can exhibit mixed ionic-electronic conduction.

The continuous decrease in oxide-ion conduction in NBT by Nb doping originates from a decrease in the number of oxygen vacancies. It is expected that similar effects can be observed by Ta-, Mo- and W-doping. This mechanism is different from the NBT-BiAlO₃ solid solutions where the suppression of oxide-ion conduction is attributed to a decrease in the oxygen vacancy mobility via trapping by the acceptor-dopants.

Table 6. Oxide-ion transport number at 600 – 800 °C, dielectric loss at 600 °C and electrical behaviour of Nb-doped NBT at various doping levels.

<table>
<thead>
<tr>
<th>Doping level (%)</th>
<th>Nominal composition</th>
<th>$t_{\text{ion}}$ at 600 °C</th>
<th>$t_{\text{ion}}$ at 700 °C</th>
<th>$t_{\text{ion}}$ at 800 °C</th>
<th>tan δ at 600 °C</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Na₅.₅Ti₀.₅TiO₃</td>
<td>0.69</td>
<td>0.93</td>
<td>0.85</td>
<td>&gt;&gt; 0.2</td>
<td>I</td>
</tr>
<tr>
<td>0.2</td>
<td>Na₃Bi₁₅Ti₀.₉₉Nb₀.₀₂O₁.₀₀₁</td>
<td>0.57</td>
<td>0.63</td>
<td>0.63</td>
<td>0.083</td>
<td>II</td>
</tr>
<tr>
<td>0.3</td>
<td>Na₃Bi₁₅Ti₀.₉₉Nb₀.₀₂O₁.₀₀₁</td>
<td>0.47</td>
<td>0.49</td>
<td>0.53</td>
<td>0.016</td>
<td>II</td>
</tr>
<tr>
<td>0.5</td>
<td>Na₃Bi₁₅Ti₀.₉₉Nb₀.₀₂O₁.₀₀₁</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>&lt; 0.01</td>
<td>III</td>
</tr>
<tr>
<td>1</td>
<td>Na₃Bi₁₅Ti₀.₉₉Nb₀.₀₂O₁.₀₀₁</td>
<td>Not available</td>
<td>Not available</td>
<td>Not available</td>
<td>&lt; 0.01</td>
<td>III</td>
</tr>
<tr>
<td>5</td>
<td>Na₃Bi₁₅Ti₀.₉₉Nb₀.₀₂O₁.₀₀₁</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>&lt; 0.01</td>
<td>III</td>
</tr>
</tbody>
</table>

10 % Nb-doped ST can achieve an electronic conductivity of ~ 500 S cm⁻¹,⁵⁰ which makes it a promising oxide-based thermoelectric material. However, the fact that Nb-doping reduces the bulk conductivity of NBT significantly (Fig. 8) indicates the electronic compensation mechanism is not applicable to NBT. This is attributed to the different band structure of NBT compared with BT or ST. NBT has a high conduction band minimum (ECB) and a high valence band maximum (EVB),⁴⁴ which makes it less favourable for electronic donor-doping. Therefore, Nb-doping in NBT occurs via an ionic compensation mechanism described by Equation (6). The excess positive charge from Nb⁵⁺ ions is compensated by filling oxygen vacancies with oxygen. As a result, the oxide-ion conductivity is suppressed due to a decrease in the charge carrier concentration. Consequently the ionic transport number, $t_{\text{ion}}$, decreases from 0.93 for NBT to 0.57 for 0.2 at.% Nb-doping, further down to 0.47 for 0.3 at.% Nb-doping and finally below 0.1 for ≥ 0.5 at.% Nb-doping (Table 6).

The continuous decrease in oxide-ion conduction in NBT by Nb doping originates from a decrease in the number of oxygen vacancies. It is expected that similar effects can be observed by Ta-, Mo- and W-doping. This mechanism is different from the NBT-BiAlO₃ solid solutions where the suppression of oxide-ion conduction is attributed to a decrease in the oxygen vacancy mobility via trapping by the acceptor-dopants.

Concluding remarks

The ferroelectric perovskite NBT can present three types of electrical behaviour based on oxide-ion conduction (Type I), mixed ionic-electronic conduction (Type II) and insulator/dielectric (Type III) by controlling the defects introduced by various mechanisms. The flexibility in fine tuning the electrical properties of NBT make it an attractive material to be applied in various technologically important devices such as SOFCs (Type I) and electronic components such as capacitors and piezoelectric sensors/actuators (Type III). To date, the major findings include:

1) The A-site Na or Bi non-stoichiometry level in NBT is very low. The electrical conductivity of NBT is dependent on the...
the A-site to replace Bi$^{4+}$ are detrimental to the oxide-ion conduction.

3) Low levels of acceptor dopants can be introduced to either the A-site to replace Bi$^{4+}$ or to the B-site to replace Ti$^{4+}$ to create oxygen vacancies and consequently enhance the oxide-ion conductivity. Acceptor-doped NBTs have high oxide-ion conductivity, extremely low levels of conductivity degradation and reasonable stability in reducing atmospheres (at least below 550 °C) and are therefore promising electrolyte materials for IT-SOFCs. Comparison between A- and B-site dopants suggests a stronger tendency for trapping of oxygen vacancies by B-site acceptor-dopants. Using this trapping effect, it is possible to control the level of oxide-ion conduction and therefore fine-tune the electrical conductivity and conduction mechanism of NBT according to the requirements of different applications.

4) Low levels of donor-dopants can be introduced at the B-site to replace Ti$^{4+}$. Donor doping fills the oxygen vacancies in NBT and therefore suppresses the oxide-ion conduction. Depending on the doping level, NBT can present mixed ionic-electronic conduction (Type II) and finally insulating/dielectric behaviour based on a low level of electronic conduction (Type III).

Conflicts of interest
There are no conflicts to declare.

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