

SPECIAL ISSUE ARTICLE

A-site acceptor-doping strategy to enhance oxygen transport in sodium–bismuth–titanate perovskite

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Abstract

Sodium–bismuth–titanate (NBT) has recently been shown to contain high levels of oxide ion conductivity. Here we report the effect of A-site monovalent ions, $M^+ = K^+$ and Li^+ , on the electrical conductivity of NBT. The partial replacement of Bi^{3+} with monovalent ions improved the ionic conductivity by over one order of magnitude without an apparent change of the conduction mechanism, which is attributed to an increase in the oxygen vacancy concentration based on an acceptor-doping approach. The ^{18}O tracer-diffusion coefficient (D^*) determined by the isotope exchange depth profile method in combination with secondary ion mass spectrometry confirmed that oxygen ions are the main charge carriers in the system. Among these acceptor-doped samples, 4% Li doping provides the highest total conductivity, leading to a further discussion of doping strategies for NBT-based materials to enhance the electrical behavior, is discussed. Comparisons with other oxide-ion conductors and an oxygen-vacancy diffusivity limit model in perovskite lattice suggested that the doped NBT-based materials might already have achieved the optimization of the ionic conductivity.

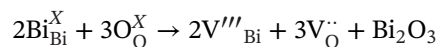
KEYWORDS

doping, non-stoichiometry, oxide-ion conductors, oxygen diffusion, sodium–bismuth–titanate

1 | INTRODUCTION

Oxide-ion conductors have been extensively researched because of their potential applications in various technological devices such as solid oxide fuel cells, oxygen sensors, and oxygen separation membranes.^{1–5} Recently, a new family of oxide-ion conductors, sodium–bismuth–titanate ($Na_{0.5}Bi_{0.5}TiO_3$, NBT), adopting the ABO_3 perovskite type structure, has received considerable attention due to their excellent ionic conductivity.^{6–12} The oxide-ion conduction originates from Bi deficiency and oxygen

vacancies created during the material processing and has been explained according to the following Kröger–Vink equation:



Furthermore, the highly polarizable Bi^{3+} ions have been proposed to provide pathways with low diffusion barriers, facilitating the migration of oxygen ions.^{6,13–15} It has also been suggested by Aidhy et al.¹⁶ that in order to achieve high oxygen-ion diffusivity, the cation polarizability is key,

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whilst Wachsman et al.¹⁷ have highlighted that the polarizability of Bi^{3+} leads to extensive long-range disorder in the anion sublattice, and that lower polarizability leads to the development of short-range vacancy ordering, explaining the oxide-ion mobility in the parent bismuth oxides. For the NBT materials, ^{18}O diffusion profile and electromotive force measurements have confirmed an ionic transport number $t_i > 0.9$ at 600–700°C.⁶ A computational study also highlighted that a migration path for oxygen vacancies with minimum energy barrier occurred at saddle points between two A-sites and a Ti-site when both A-sites were occupied by Bi ions,⁸ but there is no experimental evidence to support such a conclusion. Thus, the rate-limiting step in oxygen-ion migration in un-doped NBT is suggested to be the Na–Bi–Ti saddle points. On the other hand, the ordering of the $\text{Na}^+/\text{Bi}^{3+}$ cations on the A-site plays a significant role in oxygen diffusion. The (1 1 1)-ordered NBT yielded a higher oxide-ion conductivity because (1 0 0)- and (1 1 0)-layer ordering impedes the diffusion of oxide ions to the Bi-containing columns and the Bi-containing layers.¹⁸ Further insight from simulations was provided by Dawson et al.¹⁴ who explored the oxygen migration mechanisms using density-functional theory calculations finding strong correlation with the Bi–O bonding environments, concluding that weak Bi–O bonds promote the formation of oxygen vacancies and hence oxygen-ion mobility.

He et al.¹³ proposed a doping strategy for NBT materials using first-principle calculations and molecular dynamics. According to this model, introducing suitable dopants on the A-site is more effective in improving the ionic conductivity of NBT-based materials. The numerical results showed that acceptor-type B-site dopants, such as Mg^{2+} or Fe^{3+} for Ti^{4+} , increase the oxygen migration barriers by binding with oxygen vacancies, leading to a suppression of oxygen mobility. However, the calculations suggest that A-site doping 4% Na or K on the Bi-site can induce higher ionic conductivity than Mg-doped NBT at the same oxygen vacancy concentration. The enhancement of conductivity might be attributed to the disordered A-site sublattice. The disordered A-site sublattice can adopt different local atomistic configurations to accommodate the electrostatic and strain field of dopants, improves the phase stability of the doped structures, and reduces the undesired binding with B-site dopants.¹³

Several acceptors have been experimentally tested to further improve the ionic conductivity of NBT materials.¹⁹ Doping 2 at% divalent ions (Ca^{2+} , Sr^{2+} , and Ba^{2+}) on the Bi-site of NBT improves the bulk conductivity (σ_{bulk}) by approximately one order of magnitude. At 500°C, Sr^{2+} doping provides the highest conductivity ($5 \times 10^{-3} \text{ S cm}^{-1}$) among the three dopants due to its minimum ionic size mismatch with the host Bi^{3+} ions, its relatively high polarizability, and reasonable bonding strength with oxygen

ions.¹⁹ Ag^+ has also been confirmed as an alternative on the Bi-site, which enhances the bulk conductivity to $1.36 \times 10^{-3} \text{ S cm}^{-1}$ at 500°C.²⁰ Fe^{3+} doping on the Ti-site is also very effective in improving ionic conductivity. At the 4% doping level, the bulk conductivity of Fe-doped NBT can reach up to 0.1 S cm^{-1} at 500°C.²¹ Experimentally, the highest total conductivity (σ_{total}) is observed by doping Mg^{2+} on the Ti-site, improving the total conductivity to $3.98 \times 10^{-3} \text{ S cm}^{-1}$ at 500°C or further to $7.28 \times 10^{-3} \text{ S cm}^{-1}$ at 600°C.⁶ Mg not only improves the ionic conductivity by generating additional oxygen vacancies but also stabilizes the ceramics in reducing atmospheres and lowers the sintering temperature.⁶ However, Mg-doped NBT delivers relatively low power density in a single-cell fuel cell test, which may prevent the application of this material.²²

In previous work,²³ the excellent ionic conductivity of Li-doped NBT in the intermediate temperature range, in which Li^+ replaces Bi^{3+} on the A-site of NBT with the creation of oxygen vacancies, was reported. Here, the influence of K^+ doping on the Bi-site and its effect on the electrical conductivity and oxygen diffusion were investigated. More importantly, the enhancements of electrical conductivity by monovalent ions (K^+ and Li^+) are compared with that of divalent ions. The comparisons are from the perspectives of the ionic size, polarizability, and bonding strength with oxygen of the dopant and doping site. The purpose of this study is not only to demonstrate the effect of the K dopant but also to establish dopant selection criteria and doping strategies to achieve higher ionic conductivity in NBT-based materials.

2 | EXPERIMENTAL PROCEDURE

Powders with nominal starting compositions of $\text{Na}_{0.5}\text{Bi}_{0.5-x}\text{K}_x\text{TiO}_{3-\delta}$ (K-NBT, for $x = 0.02, 0.04$, and 0.06) were synthesized with a modified Pechini citrate–nitrate synthesis route²⁴ using NaNO_3 (Alfa Aesar, 99.999%), Bi_2O_3 (Alfa Aesar, 99.9%), KNO_3 (Alfa Aesar, 99.994%), and $\text{C}_{10}\text{H}_{14}\text{O}_5\text{Ti}$ (Alfa Aesar) as starting materials. The reagents were mixed and dissolved in 200 ml of citric acid (Sigma Aldrich) and 10 ml of nitric acid (68%, VWR Chemicals). The solution was dehydrated by stirring on a hotplate until the solution turned into a yellow gel. This gel was cooled down naturally to ambient temperature and then combusted in a decomposition furnace at 650°C for 12 h. The resultant powder was ground into a fine powder with a mortar and pestle, compacted into pellets in a uniaxial steel die and then isostatically pressed for 30 s at 300 MPa. The green-bodies were embedded in calcined powders of the same composition to minimize the loss of Na and Bi during the firing process, and sintered in

air at 1050 for 2 h. The density of the sintered pellets was measured using the Archimedes method.

A combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) spectroscopy was employed to examine the phase purity and ceramic microstructure. AC impedance spectroscopy (IS) was performed using a Solartron 1260 frequency response analyzer (Solartron Analytical, UK) with an AC amplitude of 100 mV, over a frequency range from 10 mHz to 10 MHz. Prior to measurements, Au or Pt paste electrodes were coated on the polished surfaces of the samples and fired at 900°C for 2 h in air. Impedance data were collected from 300 to 750°C with an interval of 25°C during heating and cooling. The data were normalized to sample geometry (thickness/area of pellet). High-frequency instrumental-related (impedance analyzer, lead, and sample rig) inductance effects were corrected by performing a short-circuit measurement. Equivalent circuit fitting was performed using the ZView software (Scribner Associates, Inc., Southern Pines, NC).

For ^{18}O tracer diffusion measurements, a combination of oxygen isotope labeling and secondary ion mass spectrometry (TOF-SIMSV, IONTOF GmbH, Münster, Germany) was employed to determine the oxygen tracer diffusion coefficient, D^* . Oxygen isotope exchanges were performed in the temperature range of 450–700°C, with ~ 200 -mbar oxygen pressure, and an exchange time of 2 h. The addition of a platinum coating, sintered at 1000°C for 2 h, facilitated the surface oxygen exchange process. Each of the samples was equilibrated in $^{16}\text{O}_2$ for a period of 10 times the exchange time prior to the exchange. More detailed experimental information can be found in Refs. [25–27].

3 | RESULTS AND DISCUSSION

3.1 | Electrochemical impedance spectroscopy

The phase purity of the sintered pellets was confirmed by XRD, Figure S1. The K-doped NBT materials were dense ($>95\%$ of the theoretical X-ray density) and exhibited a homogeneous grain size of 5–10 μm as illustrated by SEM on thermally etched surfaces, Figure S2. EDX analysis on the polished surface (without thermal etch) indicated that the cation concentration was close to the nominal stoichiometry and thus confirmed the proposed doping mechanism. The electrical conductivity of the K-doped NBT was measured by electrochemical IS (EIS). A typical complex impedance plane (Z^*) plot of K-doped NBT ceramics measured at 600°C is shown in Figure 1. Three arcs were observed for the 2% K-doped ceramic, whereas only two

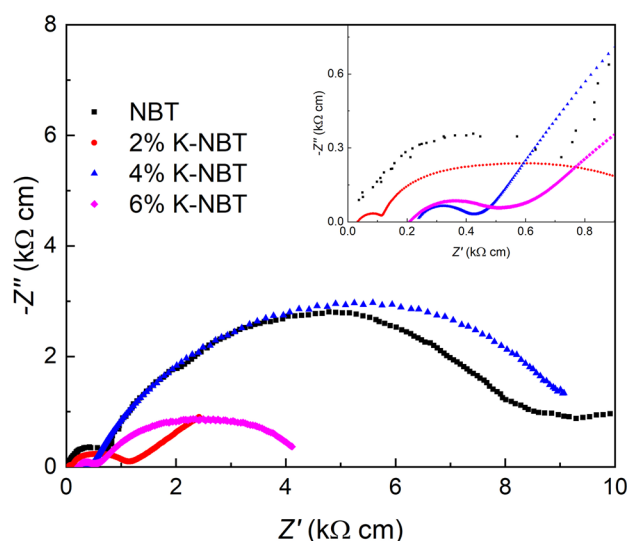


FIGURE 1 Complex impedance (Z^*) plot for K-doped NBT ceramics measured at 600°C in air. The inset figure shows high-frequency data on an expanded scale. Fitting of the 2% K-doped sample is provided as Figure S3. NBT, sodium–bismuth–titanate

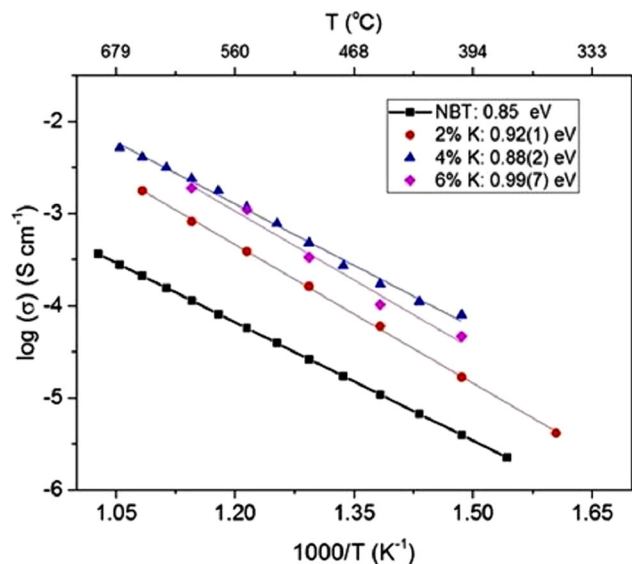
arcs were observed for the 4 and 6% K-doped materials. The capacitance of the intermediate frequency arc was found to be $\sim 10^{-9}$ F, indicating that this arc was associated with the grain boundary. The arc in the low-frequency region had a capacitance of 10^{-6} F, representing the response from the electrode. The arc associated with the bulk component was outside of the frequency range measured. The bulk response can be determined by the high-frequency intercept with the known ohmic contribution from the EIS setup. An equivalent circuit of three resistor-constant phase elements connected in series was used to analyze the data.

The grain-boundary response is dominant in the electrical conduction for un-doped NBT, about 10 times higher than the bulk contribution.⁶ At 600°C, the K dopant significantly improved the grain-boundary conductivity (σ_{gb}) by an order of magnitude as summarized in Table 1. With increasing K-doping level, the σ_{bulk} continues to increase, whereas the σ_{gb} reaches the lowest level at the 4% doping concentration. The σ_{bulk} is enhanced threefold with 4% K doping and further increased by sevenfold at the 6% doping level. The σ_{bulk} is generally higher than the grain-boundary contribution for the K-doped NBT. The total conductivity (σ_{total}) of the K-doped NBT plotted using the Arrhenius relation is shown in Figure 2. The optimal 4% K-doping level improves the total electrical conductivity by more than one order of magnitude compared to the un-doped phase. The 4% and 6% K-doped NBTs have σ_{total} of 2.27×10^{-3} and 1.84×10^{-3} S cm^{-1} , respectively. With a higher expected oxygen vacancy concentration, the 6% K-doped NBT surprisingly shows a lower conductivity that is

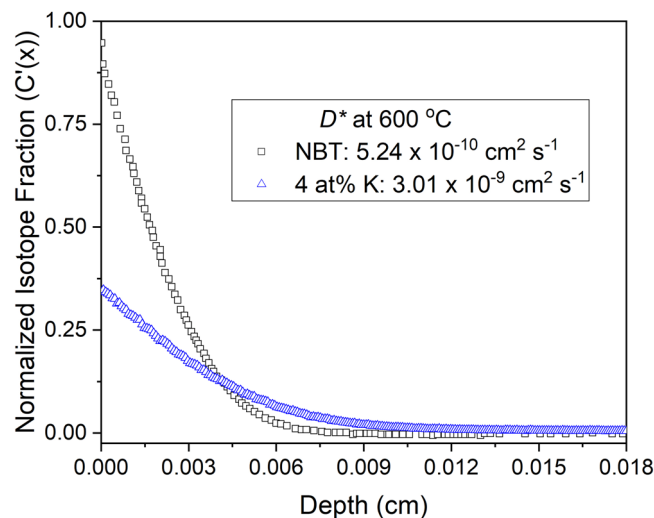
TABLE 1 Bulk, grain boundary and total conductivity of K-doped and un-doped NBT at 600°C

	Bulk		Grain boundary		Total
	σ_{bulk} (S cm ⁻¹)	E_a (eV)	σ_{gb} (S cm ⁻¹)	E_a (eV)	
NBT ⁶	1.25×10^{-3}	~0.8–0.9	1.15×10^{-4}		1.14×10^{-4}
2% K-NBT	2.59×10^{-3}	0.48	1.03×10^{-3}	0.97	7.4×10^{-4}
4% K-NBT	4.74×10^{-3}	0.43	4.32×10^{-3}	1.07	2.27×10^{-3}
6% K-NBT	9.17×10^{-3}	0.42	2.30×10^{-3}	1.04	1.84×10^{-3}

Abbreviations: NBT, sodium–bismuth–titanate.

**FIGURE 2** The Arrhenius plot of electrical conductivities of K-doped NBT samples in a comparison with the un-doped NBT. NBT, sodium–bismuth–titanate

most likely because of the immobilization of oxygen vacancies. For dilute solutions, the association of the dopant cation and oxygen vacancies is known to hinder migration of oxygen ions, whereas in non-dilute systems, as is the case in this work, there are a range of energy barriers that could impact the oxygen migration. Of these, it has been proposed that metal oxygen bond strength is a key descriptor of oxygen migration,²⁸ whereas the local cation coordination has also been proposed as impacting the migration barrier.²⁹ It is acknowledged that oxygen mobility in non-dilute systems cannot be simply attributed to one factor; however, there is good correlation experimentally of ion conductors reaching conductivity maxima on substitution, as highlighted here, and that beyond this limit, conductivity decreases. In the present system, one should consider that the substitution of K on the A-site can affect oxygen vacancy formation, cation ordering, and oxygen mobility. The activation energies (E_a) for conduction were found to be higher for the K-doped NBT in comparison to the un-doped phase, suggesting that although low levels of K substitution can be beneficial for the creation of oxygen vacancies, initially facilitating oxygen transport, the substitution

**FIGURE 3** Diffusion profiles of the un-doped and 4% K-doped NBT samples isotopically exchanged at 600°C. NBT, sodium–bismuth–titanate

with K at higher molar fractions can be in turn be detrimental for the oxygen mobility within the lattice, which supports the link with Bi polarizability.

3.2 | ¹⁸O diffusion measurements

¹⁸O tracer diffusion measurements of dense ceramics (Table S3) confirmed the oxide-ion conductivity in K-doped NBT. Samples of the 4% K-doped NBT composition, which exhibited the highest total conductivity among the K-doping levels, were exchanged in ¹⁸O₂ at a number of temperatures between 450 and 650°C. A typical diffusion profile, measured at 600°C, is shown in Figure 3 compared with the profile for an un-doped sample, with all other diffusion data provided in Figure S4. The difference in the diffusion length between the un-doped and K-doped ceramics is conspicuous, which is due to the difference in the diffusion coefficients (D^*) of the two samples. No grain-boundary diffusion tail was observed, consistent with fast bulk transport. The surface exchange coefficient (k^*) is not reported as a thin layer of Pt was applied as a coating to activate the oxygen exchange process. At 600°C,

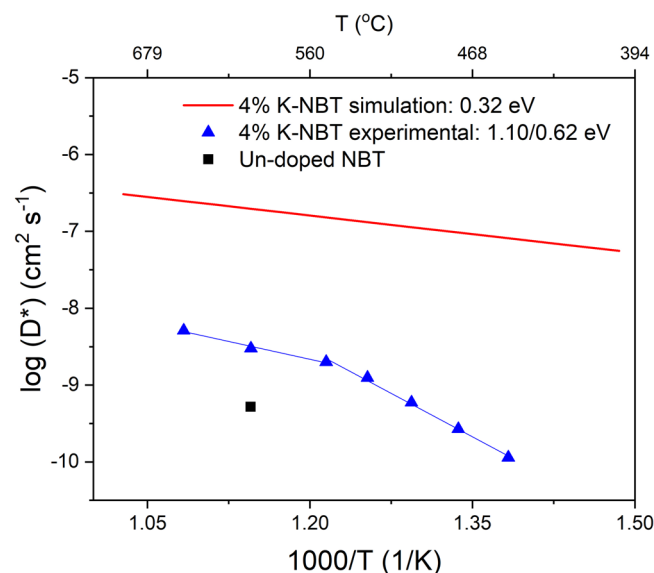


FIGURE 4 Comparison of D^* between the experimental and simulation results. The simulation data are adapted from Ref. [13]

the K content improved the D^* of the NBT material by nearly one order of magnitude to $3.01 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. According to He et al.'s simulation,¹³ doping 4% K^+ ion can enhance the ionic conductivity and D^* to $9.6 \times 10^{-2} \text{ S cm}^{-1}$ and $2.21 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively, which are considerably higher than the experimental results. As plotted in Figure 4, the E_a for diffusion is split into two different regimes by an inflection temperature of 525°C. In the low-temperature region, the activation energy required for oxide-ion conduction is $\sim 1.10 \text{ eV}$ and drops to 0.62 eV at high temperatures. This change in activation energy could be due to a crystallographic phase transition that governs oxygen vacancy migration barriers. NBT undergoes a sequence of phase transitions from rhombohedral ($R3c$) at room temperature to a tetragonal phase ($P4bm$) at 250°C and then to a cubic phase ($Pm3m$) at 540°C.³⁰ As demonstrated in Figure S5, the lowest migration barrier of 0.36 eV³⁰ exists in the tetragonal phase, whereas the activation energy extracted from the experimental results in the high-temperature range is very close to the rhombohedral phase. Furthermore, Meyer et al.³¹ discovered that trapping of oxygen vacancies in locally 0 0 1-ordered regions leads to a high oxygen migration barrier up to 1.11 eV, whereas the migration barriers show values in the range of 0.33–0.55 eV for the 1 1 1-order. It still remains uncertain if the K-doped NBT materials undergo a sequence of phase transitions associated with distinct oxygen vacancy migration barriers as in un-doped NBT. On the other hand, the possibility of the change in activation energy due to the change in charge carrier from oxygen ions to protons can be excluded. The EIS measurements performed in wet and dry atmosphere show

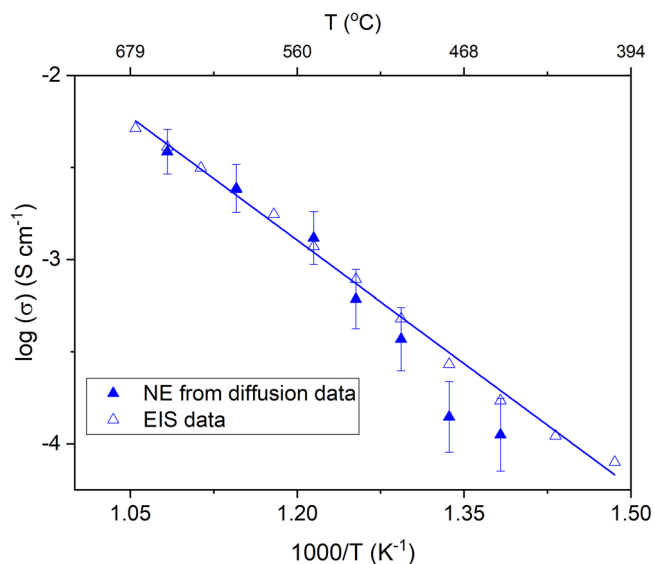


FIGURE 5 Comparison of the total conductivity of 4% K-doped NBT ceramics obtained from the oxygen diffusion data using the NE relation and EIS data. EIS, electrochemical impedance spectroscopy; NBT, sodium–bismuth–titanate; NE, Nernst–Einstein

no change in conductivity, meaning there is no significant level of protonic conduction (Figure S6). In addition, Na^+ ions are not considered potential charge carriers as there is no open framework as observed in NASICON,³² or Na-layers as in P2-type Na_xCoO_2 ³³ in the NBT structure that would provide pathways for Na^+ mobility, and the measurements are specific to the oxygen species. Indeed, this view is further supported by the extensive studies of Li et al.⁷ and Yang et al.¹¹ in which they have investigated nominally A-site-deficient NBT, finding that in these phases a secondary titania phase is formed, producing an A-site stoichiometric phase plus TiO_2 , and that those with Bi deficiency exhibit fast oxide ion transport.

The conduction mechanism in the 4% K-doped NBT materials was studied using the Nernst–Einstein (NE) relation and compared with the EIS data as displayed in Figure 5. The calculated oxide-ion conductivity for 4% K-doped NBT at 600°C is $1.4 \times 10^{-3} \text{ S cm}^{-1}$, which is close to the total conductivity $\sim 2.4 \times 10^{-3} \text{ S cm}^{-1}$ obtained from the EIS data. Overall, the calculated oxide-ion conductivities are in reasonable agreement with the EIS data, indicating that oxygen ions are the dominant conducting species.

3.3 | Comparisons with A-site divalent acceptor-doped NBT and other oxide-ion conductors

A comparison of σ_{bulk} for the 4% K-doped NBT with A-site divalent acceptor-doped NBT is shown in Figure 6. A-site

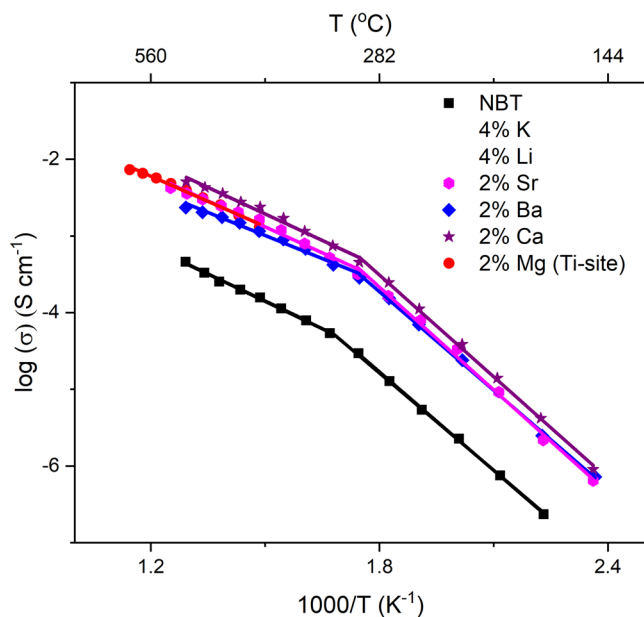


FIGURE 6 The Arrhenius plot for the bulk conductivity of pure NBT and acceptor-doped NBT materials. Experimental data of the Ba, Sr, Ca-doped sample is taken from Ref. [19]. The experimental data of 2% Mg-doped are adapted from Ref. [6] and for the Li data adapted from Ref. [23]. NBT, sodium–bismuth–titanate

K- and Li-dopings enhance σ_{bulk} by more than one order of magnitude compared to un-doped NBT. At 500°C, monovalent acceptor-doped NBT exhibits comparable σ_{bulk} to the divalent acceptor-doped counterpart. Among all the dopants, Li^+ is the most effective in increasing the σ_{bulk} ($8.35 \times 10^{-3} \text{ S cm}^{-1}$), which is twice that of the 2% Sr-doped NBT.¹⁹ These enhancements in the conductivity agree well with the proposed upper limits for enhancement by acceptor doping as proposed by Yang et al.¹⁰ based on the work of de Souza.³⁴ However, de Souza also states that although the oxygen vacancy diffusivities for a range of oxides are all very close regardless of oxygen vacancy site fraction, it is impossible to reach a firm conclusion regarding the limit for vacancy diffusivity. The key to enhancing vacancy diffusivity is proposed to lie in the identification of materials with a high entropy of vacancy migration that have high concentrations of randomly distributed vacancies with high stability. Whether this is possible is a point of conjecture, and it is clear that the limit in NBTs suggested by Yang et al.¹⁰ appears to apply in the current work. Further discussion of ionic transport factors is provided in Section 3.4.

The Arrhenius plot of divalent acceptor-doped NBT shows a change in activation energy at $\sim 300^\circ\text{C}$. The reason for this change in activation energy remains unclear. The possible explanation is a polymorphic phase transition of NBT between 250 and 400°C . As temperature increases, the phase transitions do not develop completely.²² There-

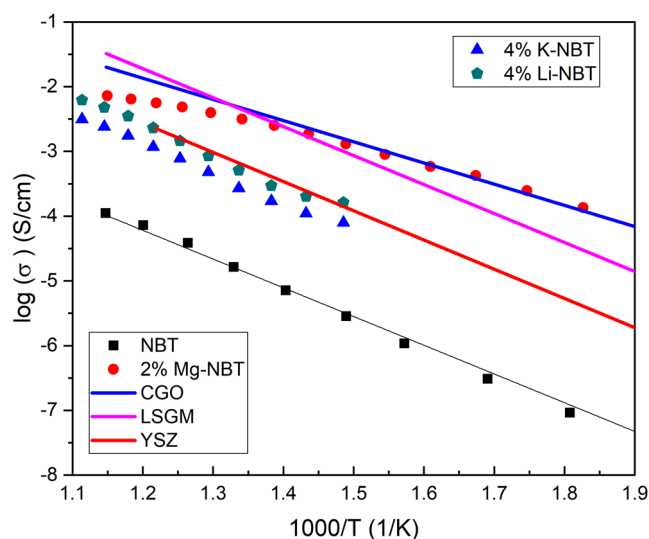


FIGURE 7 Total conductivity of 4% K-, 4% Li-,²² 2% Mg-doped,⁶ and un-doped NBT⁶ in comparison with conventional oxide-ion conductors: CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$),³⁶ YSZ ($\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$),³⁷ and LSGM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$).³⁸ NBT, sodium–bismuth–titanate

fore, divalent-doped NBT exhibits a mixture of rhombohedral and tetragonal phases below 500°C .

The σ_{total} of 4% K- and that of 4% Li-doped NBT are compared with several of best known oxide-ion conductors in Figure 7. Compared to YSZ, the Li-doped NBT shows equivalent or higher conductivities, whereas the σ_{total} of K-doped NBT is lower than YSZ at low temperatures ($<400^\circ\text{C}$). In the high-temperature region, Li-doped NBT has a comparable electrical conductivity to the Mg-doped sample and those of the best oxide-ion conducting electrolytes. At 600°C , the acceptor-doped NBT samples have D^* values of $3.01\text{--}7.04 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which is higher than the D^* value for YSZ ($2.26 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$)³⁵ and slightly lower than the D^* value of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$ (LSGM, $2.29 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) at 636°C .

3.4 | Factors that influence ionic conductivity

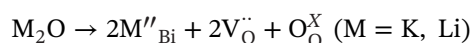
The oxygen non-stoichiometry in nominally cation stoichiometric NBT is in the range of 0.0025–0.0050, whereas the Bi non-stoichiometry is in the range of 0.0017–0.0033.⁶ This suggests that the level of intrinsic oxygen vacancies in NBT is relatively low compared to other well-known oxide-ion conductors, such as $\delta\text{-Bi}_2\text{O}_3$; therefore, the mobility of oxygen ions in NBT needs to be significantly high to promote such a comparable oxygen-ion conductivity. As K^+ and Li^+ ions are introduced to replace Bi^{3+} , the enhancement of oxide-ion conduction is due to the generation of

TABLE 2 Tolerance factor, t , specific free volume, V_{sf} , and critical radius, r_C , of the acceptor-doped and un-doped NBT ceramics

Composition	t	V_{sf}	r_C (Å)
NBT	0.984	0.201	0.907
4% K-NBT	0.988	0.209	0.901
4% Li-NBT	0.981	0.208	0.912
2% Sr-doped $\text{NB}_{0.49}\text{T}$	0.979	0.196	0.916
2% Mg-doped $\text{NB}_{0.49}\text{T}$ (Ti-site)	0.978	0.200	0.916

Abbreviations: NBT, sodium–bismuth–titanate.

extra oxygen vacancies. A plausible charge compensation mechanism is as follows:



Based on the experimental results, acceptor doping in NBT ceramics improves the total electrical conductivity of the materials that is correlated with an increase in the oxygen diffusion coefficient, suggesting that the enhancement in total conductivity is due to the improved oxygen transport properties of the phases. The ionic conductivities calculated from the diffusion data using the NE equation are in excellent agreement with the EIS data suggesting that the partial replacement of Bi^{3+} with acceptor dopants increases oxygen vacancy concentration without introducing electronic conduction and consequentially results in the enhancement of oxide-ion conductivity.

The Goldschmidt tolerance factor,³⁹ t , represents the degree of lattice distortion in the perovskite structure. A large t means small lattice distortion and is beneficial to oxide-ion conduction.⁴⁰ The specific free volume, V_{sf} , describes the free space inside a unit cell, and a large V_{sf} provides larger channels for oxygen ions to migrate, leading to a higher ionic conduction. In general, the t decreases with increasing the V_{sf} . Hayashi et al.⁴¹ found that the optimum t of ~ 0.96 exhibited maximum conductivity in perovskites with low oxygen deficiency, suggesting it is due to the balance between V_{sf} and t . The critical radius, r_C , describes the saddle points formed by two A-site and one B-site cations. A large r_C means that it is easier for the oxygen ions to pass through the saddle points and favorable for the oxygen migration. A further derivation of these parameters is provided in the Supplementary Information.

The values of the parameters of the acceptor-doped phase are summarized in **Table 2**. In most cases, the perovskite structure is stable when $0.8 < t < 1.05$.^{42,43} Compared to the un-doped NBT sample, the Li dopant increases V_{sf} and r_C , which are beneficial for oxygen-ion migration. These factors may explain why the Li-doped NBT samples with the reduced unit cell volume show a superior ionic conductivity with lower activation energy. On the other hand, the 4% K-NBT ceramics have larger t and V_{sf} but

exhibit a reduction in r_C . The decrease in r_C prevents the movement of oxygen ions, resulting in a decrease in oxygen mobility. The smaller r_C may cause a higher E_a for electrical conduction for the K-doped NBT phases.

Compared to 2% Sr-doped and Mg-doped NBT,¹⁹ the acceptor-doped NBT ceramics in this study have both larger t and V_{sf} but varying critical radius. These results may imply that large t and V_{sf} are desirable for oxygen-ion conduction for NBT-based materials. More importantly, the E_a for oxide-ion conduction is governed by r_C .

3.5 | Durability and stability in the oxidizing atmosphere

The durability and stability of 4% K- and 4% Li-NBT was tested in flowing air and oxygen atmospheres. The variation in electrical performance was monitored for 100 h at 600°C. The surface morphology and crystal structure of the samples were investigated after annealing. As shown in Figure 8, the 4% Li-NBT composition shows a minor decay in σ_{total} by less than 1%, whereas the electrical conductivity of 4% K-doped NBT decreases by about $\sim 10\%$. Overall, the 4% K- and Li-doped NBT materials show mild degradation over the limited T-pO₂ range at 600°C. After annealing, the surface of monovalent-doped NBT becomes porous, whereas the cross section remains dense with only a few pores (Figure S7). For 4% K-doped NBT, the XRD patterns, as illustrated in Figure 9, indicate the increase in peak intensity (32° and 40° at 2θ) due to Bi contribution and an additional peak for Bi_2O_3 (29.5° at 2θ) could be detected after annealing, implying that the decomposition of the material and formation of unfavorable impurity phase occurred. Combined with the authors' previous work,²² the volatilization of elements from the A-site, such as Bi and potentially other elements (Na, K, and Li), has an adverse impact on material stability and electrical performance over time.

4 | CONCLUSIONS

Alkali acceptor-doped NBT perovskite materials exhibit excellent ionic conductivity over the temperature range of 400–600°C. Among all the doping levels, 4% K- or Li-doped NBT exhibited the highest electrical conductivity, displaying a significant enhancement over the un-doped phase. The improvement in conductivity is mainly attributed to an increase in the oxygen vacancy concentration and this was confirmed through the observation of a commensurate increase in the oxygen self-diffusion coefficient. Furthermore, it was confirmed that A-site acceptor doping is as promising as B-site acceptor doping,

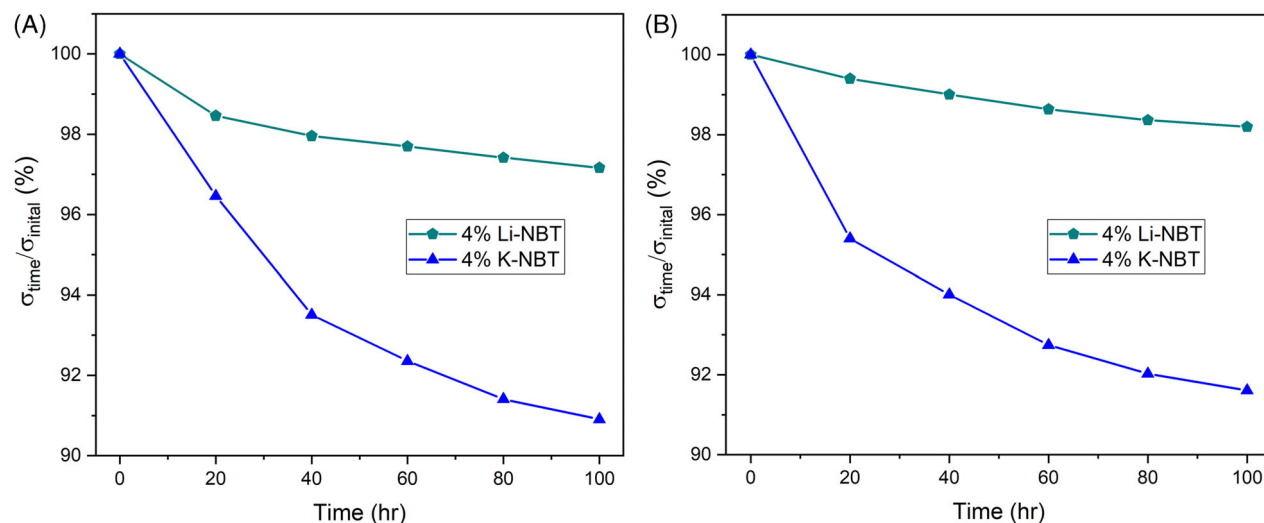


FIGURE 8 Variation in electrical conductivity of the 4% K- and 4% Li-doped⁴⁴ NBT aged at 600°C in flowing oxygen (A) and air (B). The electrical conductivity over the whole measurement time is normalized to the value measured in the first hour. NBT, sodium-bismuth-titanate

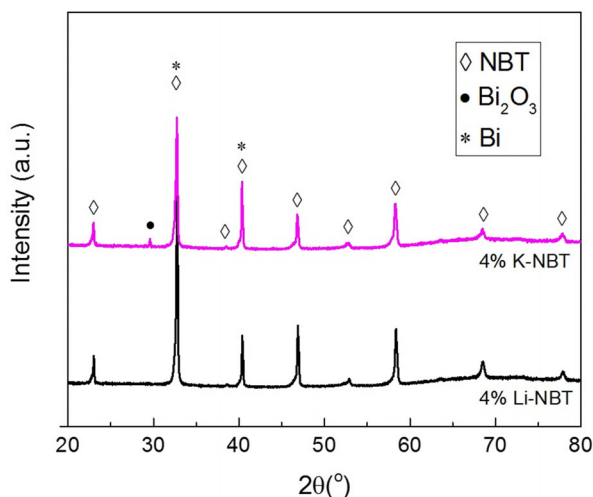


FIGURE 9 XRD patterns of 4% K- and 4% Li-doped NBT pellets after annealing in oxygen at 600°C for 100 h, highlighting the emergence of impurities in the K-doped sample. NBT, sodium-bismuth-titanate. XRD, X-ray diffraction

such as Mg-doped NBT, in promoting oxygen transport in this family of materials. Compared with conventional oxide-ion conductors such as YSZ, 4% Li-doped NBT shows competitive levels of oxide-ion conductivity at intermediate-temperature ranges, and good stability in terms of total conductivity as a function of time. It is also notable that the Li-substituted composition exhibited greater stability than the corresponding K composition. Consideration of the tolerance factor, critical radius and specific free volume of the doped NBT ceramics highlights that a careful balance is required to maximize the oxygen transport of these phases.

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