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**Supplementary information** 

# Optimisation of oxide-ion conductivity in acceptor-doped Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> perovskite: approaching the limit?

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### Methods

The powders were prepared by a solid state reaction method using oxides and carbonates: Bi<sub>2</sub>O<sub>3</sub> (99.9%, Acros Organics, USA), TiO<sub>2</sub> (99.9%, Sigma Aldrich, UK), Na<sub>2</sub>CO<sub>3</sub> (99.5%, Fisher Chemical, UK), K<sub>2</sub>CO<sub>3</sub> (99.0%, Fisher, UK), CaCO<sub>3</sub> (99.0%, Sigma Aldrich, UK), SrCO<sub>3</sub> (99.9%, Sigma Aldrich, UK), BaCO<sub>3</sub> (99.0%, Sigma Aldrich, UK), MgO (99.9%, Alfa Aesar, UK), Sc<sub>2</sub>O<sub>3</sub> (99.99%, Stanford Materials, USA), Al<sub>2</sub>O<sub>3</sub> (99.95%, Alfa Aesar, UK), Ga<sub>2</sub>O<sub>3</sub> (99.9%, Sigma Aldrich, UK), ZnO (99.9%, Fluka, UK). Prior to weighing, the raw powders were dried overnight at 180 °C (K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>), 300 °C (Na<sub>2</sub>CO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>), 600 °C (ZnO and Ga<sub>2</sub>O<sub>3</sub>) and 900 °C (MgO, Sc<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>), respectively. Appropriate amounts of each precursor were weighed and mixed thoroughly in iso-propanol using yttria-stabilised zirconia grinding media for 6 hours. The mixture was dried overnight at 85 °C, sieved and then calcined at 800 °C for 2 hours. The resultant powders were subjected to a second round of ball milling, drying, sieving and calcination and subsequently to a final, third round of ball milling and sieving. The products were compacted into pellets by uni-axial cold pressing followed by isostatic pressing at 200 MPa. Pellets were embedded in sacrificial powder of the same composition and sintered at 950-1150 °C for 2 hours.

Ceramic density was measured by the Archimedes' method. Phase purity was examined by X-ray diffraction on crushed pellets using a high resolution STOE STADI-P diffractometer (STOE & Cie GmbH, Darmstadt, Germany) operating with CuK $\alpha_1$  radiation with a linear position-sensitive detector. Ceramic microstructures were observed by scanning electron microscopy (JEOL JSM-6010LA, JEOL Ltd., Tokyo, Japan; Philips XL30) on thermally etched surfaces. Compositions were obtained by energy dispersive X-ray spectroscopy (EDX) on polished samples (without thermal etching). High temperature neutron diffraction on crushed pellets was carried out on GEM at the Rutherford Appleton Laboratory, UK.

Electrical properties were measured by high temperature impedance spectroscopy using an Agilent E4980A impedance analyser (Agilent Technologies Inc., Palo-Alto, CA) or a Solartron 1260 system (Solartron Analytical, UK) using Au paste (fired at 800 °C for 2 h) or Pt paste (fired at 900 °C for 2 h) as electrodes. For selected samples, impedance measurements were carried out in flowing air, nitrogen and oxygen. To probe possible proton conduction, wet atmosphere was generated across ceramics with electrodes in a sealed impedance rig by flowing compressed air through a water bubbler which was kept in a 70 °C water bath. Equivalent circuit fitting was performed using Zview software (Scribner Associates, Inc., Southern Pines, NC). Oxygen-ion transport number measurements were performed using a Probostat system (NorECs Norwegian Electro Ceramics AS, Oslo, Norway) from 600 to 800 °C. During measurements, a pellet was sealed onto a YSZ tube using a commercial glass frit. An oxygen partial pressure ( $pO_2$ ) difference was created across the ceramic by flowing N<sub>2</sub> into the YSZ tube and leaving the outside of the ceramic in air. The  $pO_2$  difference was monitored by measuring the voltage across the inner and outer electrodes on the YSZ tube. The voltage was measured using a Keithley 182 sensitive digital voltmeter.

#### **Doping mechanism**

There are two possible compensation mechanisms for acceptor doping in NBT: electronic compensation to create holes or ionic compensation to create oxygen vacancies. Table S1 shows that with acceptor doping, the bulk conductivity,  $\sigma_b$  is enhanced and the oxide-ion transport number,  $t_{ion}$ , also increases to be close to unity. Furthermore, the <sup>18</sup>O tracer diffusion coefficient, D\*, increases by ~2 orders of magnitude, from 2.64 × 10<sup>-10</sup> cm<sup>2</sup> s<sup>-1</sup> for undoped NB<sub>0.49</sub>T to  $1.17 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> for Mg-doped NB<sub>0.49</sub>T. These results prove that acceptor doping in NBT is by an ionic compensation mechanism to create additional oxygen vacancies. Acceptor doping can enhance the oxide-ion conductivity.

Table S1. Bulk conductivity ( $\sigma_b$ ), oxide-ion transport number ( $t_{ion}$ ) and tracer diffusion coefficient (D\*) of undoped, 2%Mg-doped and 2%Sr-doped NB<sub>0.49</sub>T.

	$\sigma_b / \mathrm{S} \mathrm{cm}^{-1}$			t <sub>ion</sub>		D*/ cm <sup>2</sup> s <sup>-1</sup>
	150 °C	300 °C	500 °C	600 °C	700 °C	632 °C
NB <sub>0.49</sub> T [1]	$2.08 \times 10^{-7}$	$1.19 \times 10^{-4}$	$1.42 \times 10^{-3}$	0.93	0.92	$2.64 \times 10^{-10}$
2%Mg-doped NB <sub>0.49</sub> T [1]	$7.62 \times 10^{-7}$	$2.57 \times 10^{-4}$	$4.06 \times 10^{-3}$	0.98	0.95	$1.17 \times 10^{-8}$
2%Sr-doped NB <sub>0.49</sub> T	$1.44 \times 10^{-6}$	$4.81  imes 10^{-4}$	$5.13  imes 10^{-3}$	0.96	0.94	-

# Nominal composition, $\sigma_b$ and activation energy $(E_a)$

	Site Dopant		Doping level	Nominal composition	g₀ /S cm <sup>-1</sup>		Ea / eV	
			%		200 °C	400 °C	≤	≥ 350 °C
Bi occupancy							300	
							°C	100 - 100 dee
		undoped		Na <sub>0.5</sub> Bi <sub>0.5</sub> TiO <sub>3</sub>	$7.69 \times 10^{-7}$	$1.54 \times 10^{-4}$	0.86	0.45
				Na0.5Bi0.49TiO2.985	2.94 × 10-°	$5.80 \times 10^{-4}$	0.89	0.42
				Na0.5Bi0.48TiO2.97	1.04 × 10-5	$1.66 \times 10^{-3}$	0.93	0.37
	A site	Na⁺	1	Na0.5(B10.49Na0.01)T1O2.99	7.40 × 10-0		0.83	
			2	Na0.5(B10.48Na0.02)T1O2.98	8.55 × 10-°		0.86	
		_K+	2	Na0.5(Bi0.48K0.02)TiO2.98	8.69 × 10-6		0.92	
		Ca <sup>2+</sup>	2	Na0.5(Bi0.48Ca0.02)TiO2.99	1.21 × 10-5	$1.61 \times 10^{-3}$	0.84	0.36
		Sr <sup>2+</sup>	2	Na0.5(Bi0.48Sr0.02)TiO2.99	1.27 × 10-5	$1.63 \times 10^{-3}$	0.84	0.37
		Ba <sup>2+</sup>	2	Na0.5(Bi0.48Ba0.02)TiO2.99	$2.26  imes 10^{-5}$	$2.46  imes 10^{-3}$	0.85	0.42
Stoichiometric		Mg <sup>2+</sup>	1	Na0.5Bi0.5(Ti0.99Mg0.01)O2.99	3.61 × 10 <sup>-6</sup>	9.97 × 10-4	0.89	0.45
		Sc <sup>3+</sup>	2	Na0.5Bi0.5(Ti0.98Sc0.02)O2.985	2.03 × 10 <sup>-6</sup>	3.16 × 10 <sup>-4</sup>	0.80	0.45
	B-site		3	Na0.5Bi0.5(Ti0.97Sc0.03)O2.985	2.76 × 10-6	7.26 × 10 <sup>-4</sup>	0.89	0.32
		Ga <sup>3+</sup>	1	Na0.5Bi0.5(Ti0.99Ga0.01)O2.995	4.03 × 10 <sup>-6</sup>	7.98 × 10 <sup>-4</sup>	0.86	0.46
			3	Na0.5Bi0.5(Ti0.97Ga0.03)O2.985	$2.18 \times 10^{-6}$	5.94 × 10-4	0.90	0.53
		Ca <sup>2+</sup>	2	Na0.5(Bi0.47Ca0.02)TiO2.975	$1.41 \times 10^{-5}$	$2.31 \times 10^{-3}$	0.88	0.48
			4	Na0.5(Bi0.45Ca0.04)TiO2.965	$1.89 \times 10^{-5}$	$2.92 \times 10^{-3}$	0.82	0.50
			6	Na0.5(Bi0.43Ca0.06)TiO2.955	$1.67 \times 10^{-5}$	$2.11 \times 10^{-3}$	0.73	0.63
			8	Na0.5(Bi0.41Ca0.08)TiO2.945	8.67 × 10 <sup>-6</sup>	$1.67 \times 10^{-3}$	0.82	0.68
		Sr <sup>2+</sup>	2	Na0.5(Bi0.47Sr0.02)TiO2.975	$1.71 \times 10^{-5}$	$2.25 \times 10^{-3}$	0.83	0.46
			4	Na0.5(Bi0.45Sr0.04)TiO2.965	$1.69 \times 10^{-5}$	$2.81 \times 10^{-3}$	0.84	0.52
	A-site		6	Na0.5(Bi0.43Sr0.06)TiO2.955	$1.67 \times 10^{-5}$	$2.83 \times 10^{-3}$	0.81	0.56
			8	Na0.5(Bi0.41Sr0.08)TiO2.945	$1.10 \times 10^{-5}$	$2.01 \times 10^{-3}$	0.83	0.62
		Ba <sup>2+</sup>	1	Na0.5(Bi0.48Ba0.01)TiO2.98	8.12 × 10 <sup>-6</sup>	1.37 × 10-3	0.94	0.35
			2	Na0.5(Bi0.47Ba0.02)TiO2.975	$1.66 \times 10^{-5}$	$1.47 \times 10^{-3}$	0.89	0.41
			3	Na0.5(Bi0.46Ba0.03)TiO2.97	$2.05 \times 10^{-5}$	$2.25 \times 10^{-3}$	0.82	0.39
			4	Na0.5(Bi0.45Ba0.04)TiO2.965	$2.33 \times 10^{-5}$	$1.94 \times 10^{-3}$	0.81	0.43
			5	Na0.5(Bi0.44Ba0.05)TiO2.96	1.91 × 10 <sup>-5</sup>	$1.88 \times 10^{-3}$	0.74	0.37
			6	Na0.5(Bi0.43Ba0.06)TiO2.955	1.71 × 10 <sup>-5</sup>	$1.90 \times 10^{-3}$	0.79	0.43
Bi-deficient		Mg <sup>2+</sup>	1	Na0.5Bi0.49(Ti0.99Mg0.01)O2.975	1.44 × 10 <sup>-5</sup>	$1.84 \times 10^{-3}$	0.78	0.48
		2000. <del>-</del> 70	2	Na0.5Bi0.49(Ti0.98Mg0.02)O2.97	7.70 × 10 <sup>-6</sup>	$1.38 \times 10^{-3}$	0.84	0.54
			4	Na0.5Bi0.49(Ti0.96Mg0.04)O2.96	4.97 × 10 <sup>-6</sup>	$1.15 \times 10^{-3}$	0.88	0.46
			5	Na0.5Bi0.49(Ti0.95Mg0.05)O2.955	4.72 × 10 <sup>-6</sup>	$1.10 \times 10^{-3}$	0.89	0.45
		Zn <sup>2+</sup>	1	Na0.5Bi0.49(Ti0.99Zn0.01)O2.975	2.51 × 10-6	5.13 × 10 <sup>-4</sup>	0.88	0.44
		Sc <sup>3+</sup>	3	Na0.5Bi0.49(Ti0.97Sc0.03)O2.97	3.54 × 10-6	7.81 × 10 <sup>-4</sup>	0.89	0.42
			4	Na0.5Bi0.49(Ti0.96Sc0.04)O2.965	$4.04 \times 10^{-6}$	7.59 × 10-4	0.85	0.54
			5	Na0.5Bi0.49(Ti0.95Sc0.05)O2.96	3.54 × 10-6	$8.15 \times 10^{-4}$	0.88	0.48
	<b>B</b> -site	A13+	1	Na0.5Bi0.49(Ti0.99Al0.01)O2.975	3.76 × 10-6	9.29 × 10 <sup>-4</sup>	0.89	0.43
			3	Na0.5Bi0.49(Ti0.97Al0.03)O2.97	1.75 × 10-6	$6.08 \times 10^{-4}$	0.95	0.47
			5	Na0.5Bi0.49(Ti0.95Al0.05)O2.965	$1.48 \times 10^{-6}$	$4.38 \times 10^{-4}$	0.93	0.45
		Ga <sup>3+</sup>	1	Na0.5Bi0.49(Ti0.99Ga0.01)O2.075	4.03 × 10-6	9.72 × 10 <sup>-4</sup>	0.89	0.42
			3	Na0.5Bi0.49(Ti0.97Ga0.03)O2.07	1.64 × 10 <sup>-6</sup>	5.83 × 10-4	0.90	0.49
			5	Nan Bin to Tin of Gan of ) On off	9.52 × 10-7	$4.35 \times 10^{-4}$	0.94	0.48

Table S2. Nominal composition,  $\sigma_b$  at selected temperatures and  $E_a$  of acceptor-doped NBT. Values for undoped NBT are listed for comparison.

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# Low solution limit of acceptor dopants in NBT

The solid solution limit of acceptor dopants in NBT is low. Figure S1 shows examples of the presence of secondary phases in 2% Sr-doped and 2% Mg-doped  $NB_{0.49}T$  under SEM. EDX analysis indicates the secondary phase for Sr-doped  $NB_{0.49}T$  is a Na,Ti-rich compound, and in Mg-doped  $NB_{0.49}T$  it is MgTiO<sub>3</sub>.



(c)

		Na (at.%)	Bi (at.%)	M (at.%)	Ti (at.%)
2%Sr-doped NB <sub>0.49</sub> T	Main phase	25.6 (± 0.3)	24.3 (± 0.3)	1.1 (± 0.3)	49.0 (± 0.3)
	Secondary phase	30.6 (± 4.1)	11.5 (± 3.9)	0.5 (± 0.3)	57.4 (± 0.7)
2%Mg-doped NB <sub>0.49</sub> T	Main phase	25.3 (± 0.3)	25 (± 0.1)	0.6 (± 0.2)	49.1 (± 0.2)
	Secondary phase	2 (± 1)	1 (± 1)	48 (± 1)	49 (± 1)

Figure S1. SEM images of polished surfaces (without thermal-etching) of (a) 2%Sr-doped  $NB_{0.49}T$  and (b) 2%Mg-doped  $NB_{0.49}T$ . Both show the presence of secondary phases. (c) EDX analysis showing the composition of the main and secondary phases of the above two samples.

#### Change of Ea ~ 300 °C

Impedance spectra for a Sr-doped NB<sub>0.49</sub>T pellet measured in flowing oxygen, air and nitrogen at 200 and 400 °C are shown in Figure S2. There is no change in the bulk conductivity with pO<sub>2</sub>, indicating the absence of any significant electronic (or hole) conduction. Measurements carried out in wet and dry atmospheres show there is no significant change to the bulk conductivity (Figure S3a), indicating the absence of significant protonic conduction in doped NBT samples at temperatures above~ 150 °C. Measurements were also carried out during heating and cooling.  $\sigma_b$  values are similar on both heating and cooling (Figure S3b). The absence of any hysteresis for  $\sigma_b$  on heating and cooling gives further evidence that there is no significant protonic conduction as protons (water) would be driven off at higher temperatures and not reabsorbed on cooling to the same extent. The possibility of a change in the charge carrier species from oxygen ions to electrons, holes or protons can therefore be excluded.



Figure S2. Complex impedance (Z\*) plots of a 2%Sr-doped NB<sub>0.49</sub>T ceramic measured in flowing N<sub>2</sub>, Air and O<sub>2</sub> using Pt as electrodes at (a) 200 °C and (b) 400 °C. The inset in each figure is an expanded view of the bulk response.



Figure S3. (a) Z\* plots for a 2%Sr-doped  $NB_{0.49}T$  ceramic measured in dry and wet air. (b) Bulk conductivity of a 2%Sr-doped  $NB_{0.49}T$  ceramic measured during heating and cooling cycles.

### Evidence for two-phase coexistence in NBT

Coexistence of rhombohedral (R) and tetragonal (T) phases in NBT between 250 to 400 °C has been reported previously [2, 3], and is confirmed by variable temperature neutron diffraction data (Figure S4). At 200 °C, diffraction peaks can be indexed on the rhombohedral polymorph (space group R3c). With increasing temperature, the (210) and (211) peaks associated with the tetragonal polymorph (space group P4bm) emerge and increase in intensity. The (113) peak associated with the rhombohedral polymorph gradually decreases but is still detectable at 400 °C. R and T phase coexistence has also been confirmed by our previous high temperature electron diffraction studies using TEM [4].



Figure S4. Portion of the neutron diffraction patterns of  $NB_{0.49}T$  from 200 to 400 °C showing the co-existence of rhombohedral and tetragonal phases.

## Conductivity decay at 500 °C: comparison with δ-Bi<sub>2</sub>O<sub>3</sub> phases

The two best-known  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phases, 20ESB and 8D4WSB, suffer from conductivity degradation at 500 °C due to anion ordering. NBT materials show almost no degradation of  $\sigma_b$  at this temperature. For example,  $\sigma_b$  for 2%Sr-doped NB<sub>0.49</sub>T is initially lower than 20ESB and 8D4WSB and it is stable over time. After 50 h, it is higher by a factor of 3 than that of 20ESB and 8D4WSB. Although the conductivity degradation of  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> can be alleviated by increasing dopant concentration, considering the price and availability of rare-earth oxides such as Dy<sub>2</sub>O<sub>3</sub>, doped NBT is competitive as a more sustainable material.

Table S3. Time-dependence of  $\sigma_b$  of 2%Sr-doped NB<sub>0.49</sub>T at 500 °C in comparison with 20ESB and 8D4WSB. (Unit for  $\sigma_b$ : S cm<sup>-1</sup>)

	0h	10h	50h
2%Sr-doped NB <sub>0.49</sub> T	$5.13 \times 10^{-3}$	$5.13 \times 10^{-3}$	$5.13 \times 10^{-3}$
20ESB [5]	$1.48 \times 10^{-2}$	$2.51 \times 10^{-3}$	$1.20 \times 10^{-3}$
8D4WSB [6]	$2.11 \times 10^{-2}$	$2.04 \times 10^{-3}$	$1.26 \times 10^{-3}$

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