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Article:

Yang, F. orcid.org/0000-0002-6428-7755, Dean, J.S. orcid.org/0000-0001-7234-1822, Hu, Q. orcid.org/0000-0001-7639-9239 et al. (4 more authors) (2020) From insulator to oxide-ion conductor by a synergistic effect from defect chemistry and microstructure: acceptor-doped Bi-excess sodium bismuth titanate Na_{0.5}Bi_{0.51}TiO_{3.015}. *Journal of Materials Chemistry A*, 8 (47). pp. 25120-25130. ISSN 2050-7488

<https://doi.org/10.1039/d0ta10071d>

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Supplementary information

From insulator to oxide-ion conductor by a synergistic effect from defect chemistry and microstructure: acceptor-doped Bi-excess sodium bismuth titanate $\text{Na}_{0.5}\text{Bi}_{0.51}\text{TiO}_{3.015}$

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1. XRD patterns of other acceptor-doped $\text{NB}_{0.51}\text{T}$ ceramics

XRD patterns of $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{N}_y\text{O}_{3.015-0.5y}$ ($\text{N} = \text{Sc}, \text{Al}$ and Ga) ceramics are shown in Figs. S1-S3. Sc-doped $\text{NB}_{0.51}\text{T}$ ceramics are phase pure within the composition range investigated ($y \leq 0.05$). For Al- and Ga-doped $\text{NB}_{0.51}\text{T}$, peaks from secondary phases can be observed for $y = 0.05$ and 0.07 , respectively.

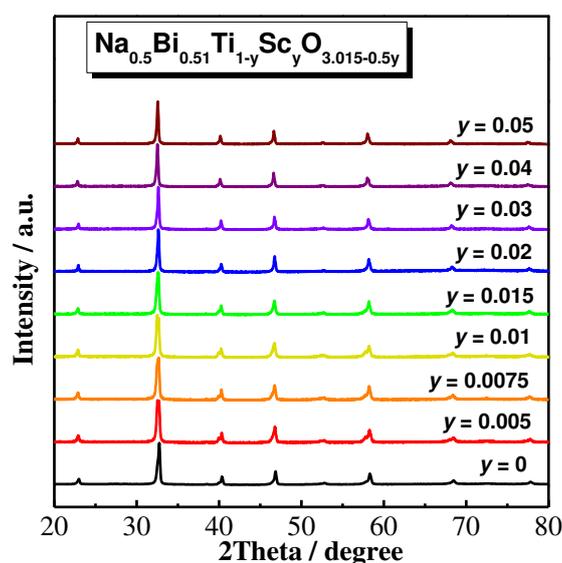


Fig.S1 XRD patterns of $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Sc}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.0075, 0.01, 0.015, 0.02, 0.03, 0.04$ and 0.05) ceramics.

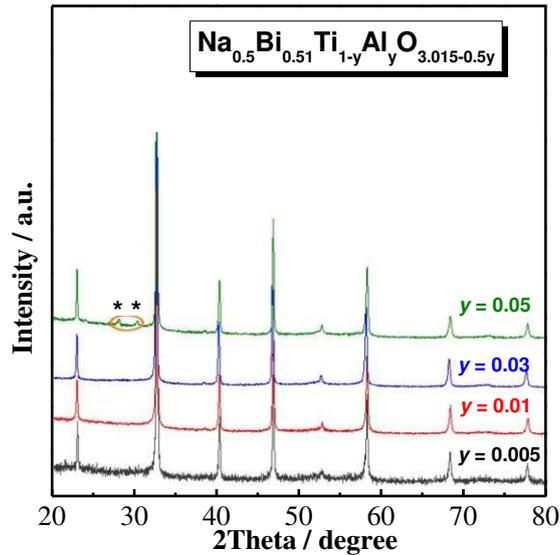


Fig.S2 XRD patterns of $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Al}_y\text{O}_{3.015-0.5y}$ ($y = 0.005, 0.01, 0.03$ and 0.05) ceramics. The star symbol indicates the presence of a secondary phase(s) for $y = 0.05$.

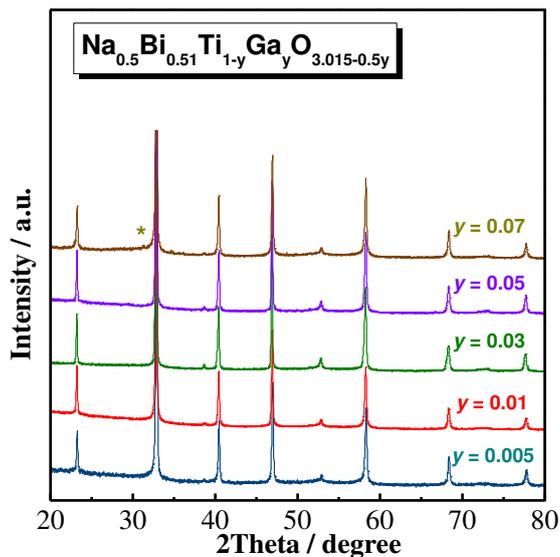


Fig.S3 XRD patterns of $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Ga}_y\text{O}_{3.015-0.5y}$ ($y = 0.005, 0.01, 0.03, 0.05$ and 0.07) ceramics. The star symbol indicates the presence of a secondary phase for $y = 0.07$.

2. Microstructure of $\text{NB}_{0.51}\text{T}$ and grain size distribution in Mg-doped $\text{NB}_{0.51}\text{T}$ ceramics

Undoped $\text{NB}_{0.51}\text{T}$ ceramics have uniform, small grains with an average grain size of $\sim 1\text{-}2\ \mu\text{m}$ (Fig. S4(a)). To make sure the thermal-etched surface morphology can represent the bulk, the grain structure is also observed from the cross-sectional, fracture surface (Fig.S4(b)). It also shows uniform, small grains and therefore confirms the surface grain structure is representative. In this work, statistics of grain size is based on the thermal-etched surface for easy comparison

with those reported in literature. For Mg-doped $\text{NB}_{0.51}\text{T}$ ceramics the grain size shows an increasingly broad distribution with increasing doping level (x), as well as an increase in the average value (Fig. S5).

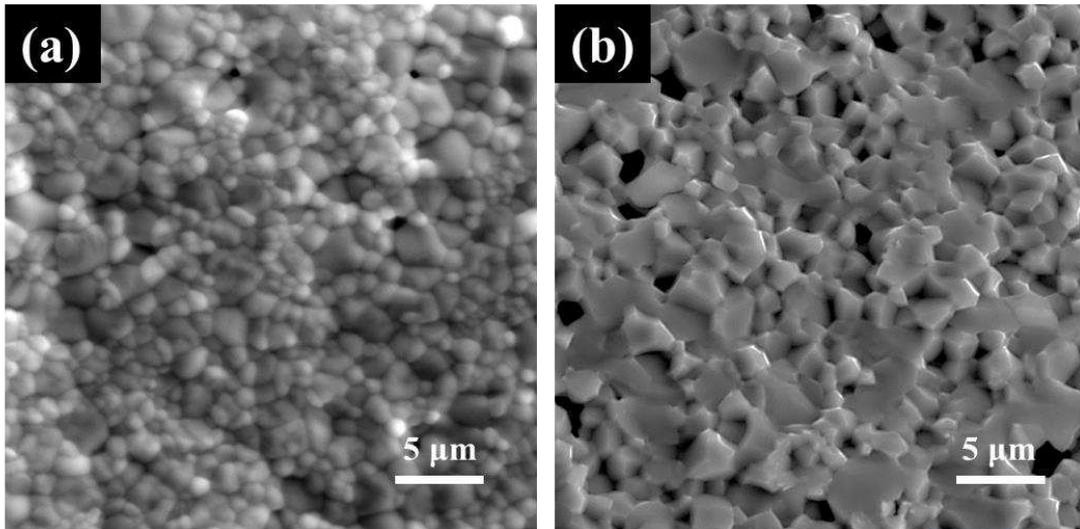


Fig.S4 SEM images of an $\text{NB}_{0.51}\text{T}$ ceramic: (a) thermal-etched surface and (b) fracture surface.

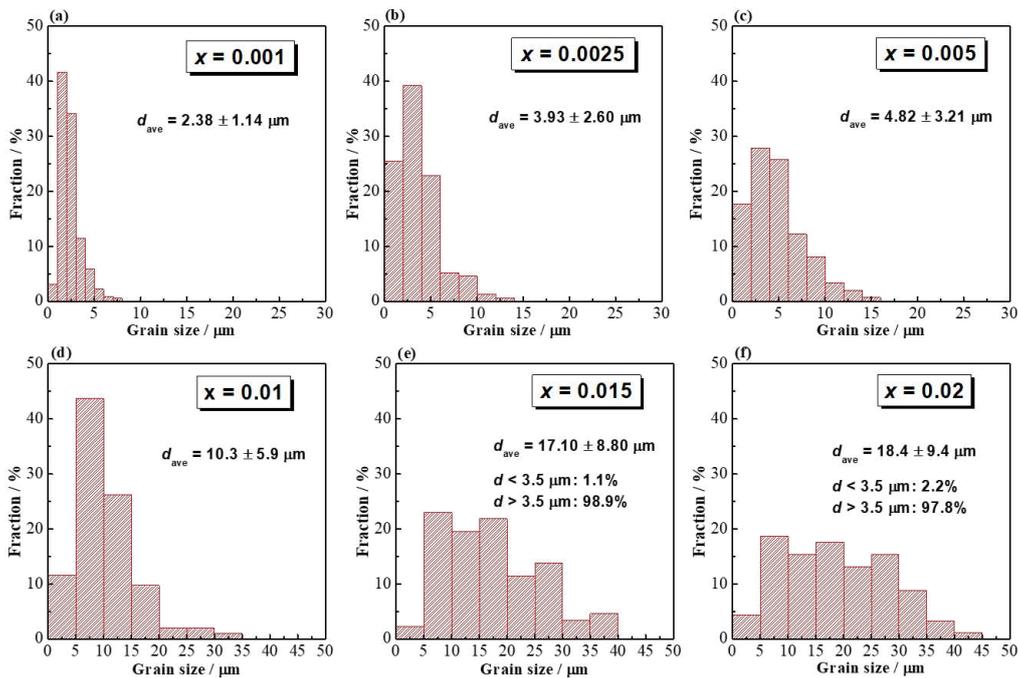


Fig. S5 Grain size distribution in $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-x}\text{Mg}_x\text{O}_{3.015-x}$ ceramics. (a) $x = 0.001$, (b) $x = 0.0025$, (c) $x = 0.005$, (d) $x = 0.01$, (e) $x = 0.015$ and (f) $x = 0.02$. Average grain size and its associated error is indicated in each figure.

3. Microstructure of other acceptor-doped $\text{NB}_{0.51}\text{T}$ ceramics

NB_{0.51}T ceramics doped with other B-site acceptor-dopants show similar inhomogeneous distributions of large grains embedding in small grains at low doping levels, as shown in Fig.S6 for Zn and Fig.S7 for Sc. With increasing doping level y , the grain size of Sc-doped NB_{0.51}T ceramics increases.

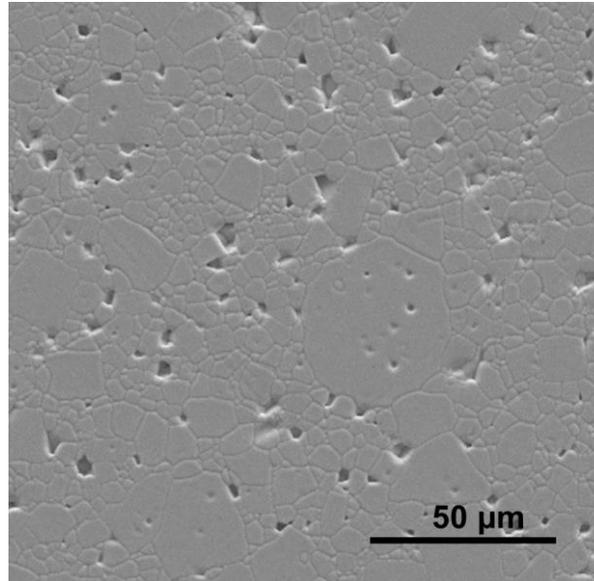


Fig. S6 SEM image of a thermally-etched surface of Na_{0.5}Bi_{0.51}Ti_{1-x}Zn_xO_{3.015-x} ($x = 0.005$).

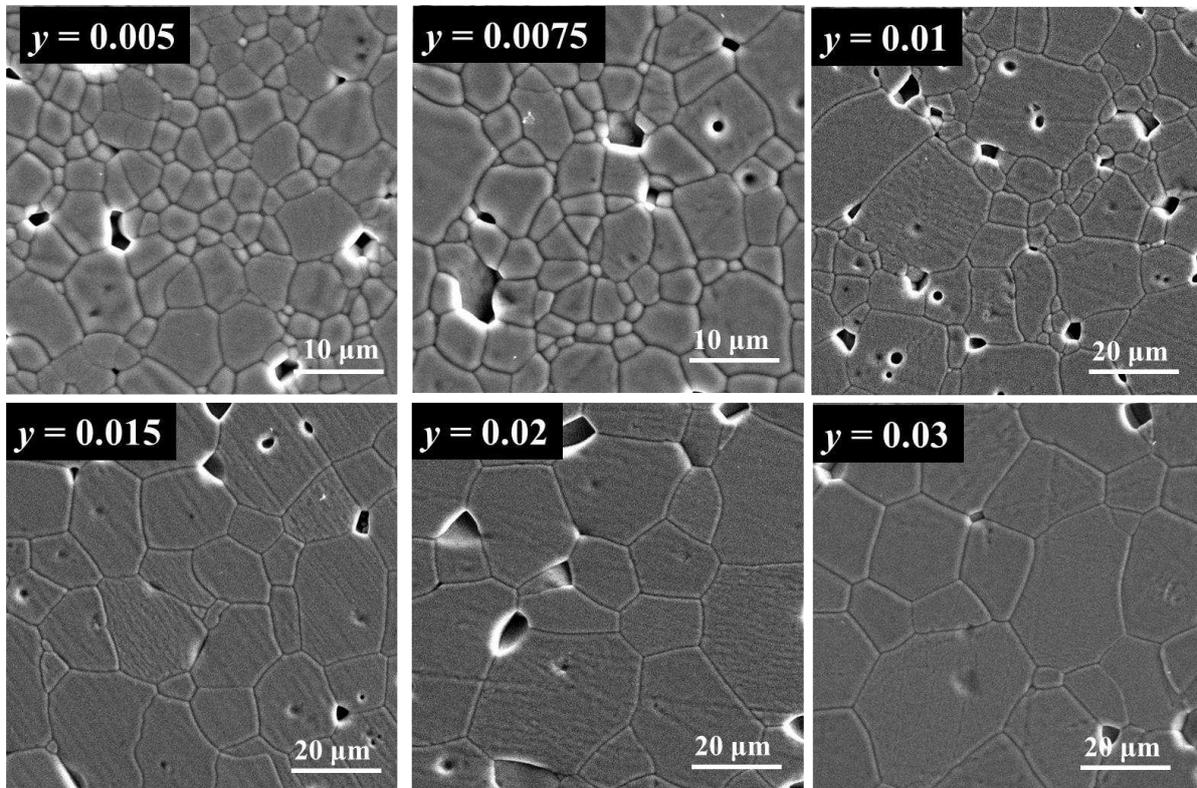


Fig.S7 SEM micrographs of thermally-etched surfaces of Na_{0.5}Bi_{0.51}Ti_{1-y}Sc_yO_{3.015-0.05y} ($y = 0.005, 0.0075, 0.01, 0.015, 0.02$ and 0.03).

4. Compositional analysis of a thermally-etched Zn-doped $\text{NB}_{0.51}\text{T}$ ($x = 0.005$) ceramic

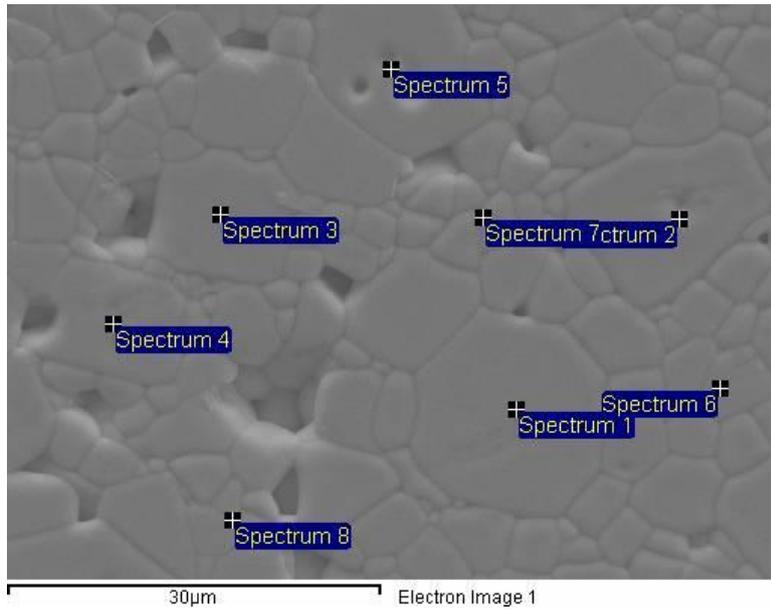


Table S1 Relative atomic percentage of cations in $x = 0.005 \text{ Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-x}\text{Zn}_x\text{O}_{3.015-x}$ ceramics measured by EDS.

Position	Na	Bi	Ti	Zn
1	23.29	26.76	49.80	0.15
2	26.18	26.35	47.77	-0.30
3	25.12	26.46	47.97	0.45
4	23.45	26.91	49.08	0.55
5	24.74	26.26	48.90	0.10
6	25.37	26.17	47.86	0.60
7	22.04	27.21	50.75	0
8	24.12	26.80	49.34	-0.25
Average	24.29 ± 1.30	26.62 ± 0.36	48.93 ± 1.04	0.16 ± 0.35
Nominal	24.88	25.37	49.50	0.25

5. Bulk conductivity of Zn, Sc, Al and Ga-doped NB_{0.51}T ceramics

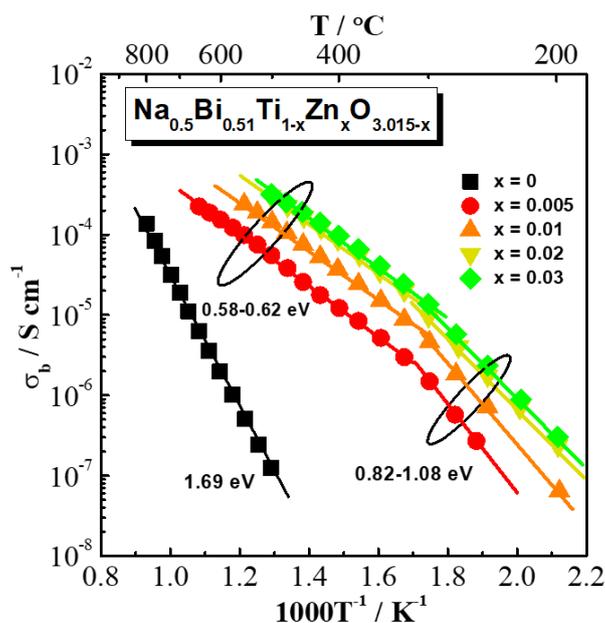


Fig.S8 Arrhenius plot of bulk conductivity, σ_b , for Na_{0.5}Bi_{0.51}Ti_{1-x}Zn_xO_{3.015-x} ($x = 0, 0.005, 0.01, 0.02$ and 0.03) ceramics measured in air. Numbers in eV are the activation energies associated with σ_b .

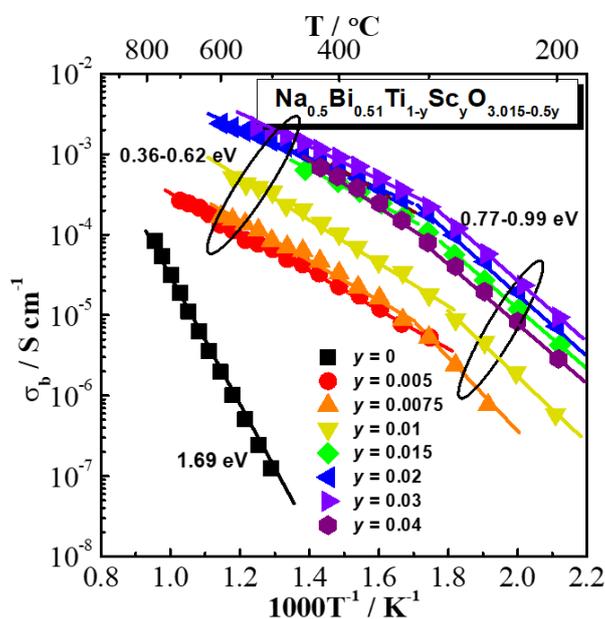


Fig.S9 Arrhenius plot of bulk conductivity, σ_b , for Na_{0.5}Bi_{0.51}Ti_{1-y}Sc_yO_{3.015-0.5y} ($y = 0, 0.005, 0.0075, 0.01, 0.015, 0.02, 0.03$ and 0.04) ceramics measured in air. Numbers in eV are the activation energies associated with σ_b .

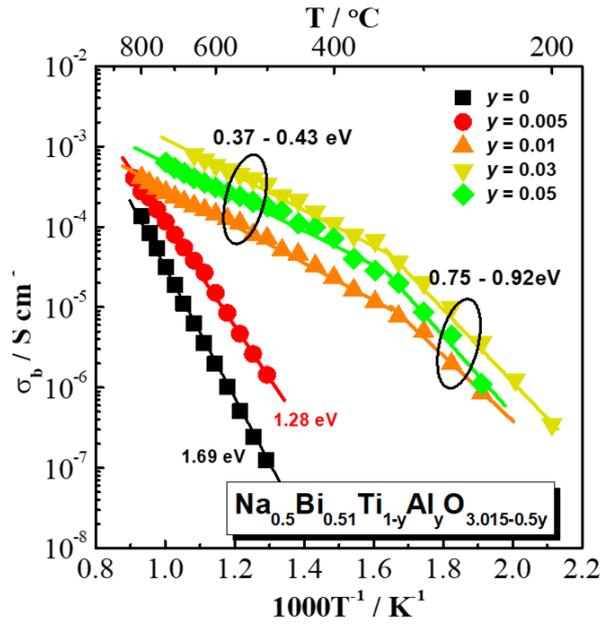


Fig.S10 Arrhenius plot of bulk conductivity, σ_b , for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Al}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.01, 0.03$ and 0.05) ceramics measured in air. Numbers in eV are the activation energies associated with σ_b .

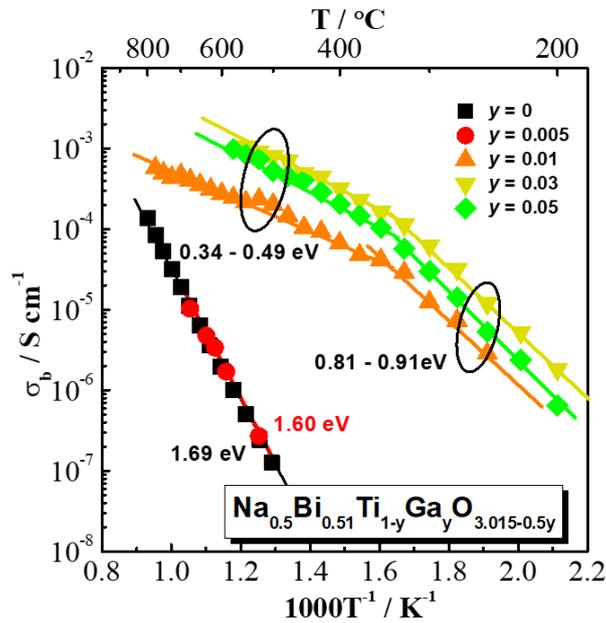


Fig.S11 Arrhenius plot of bulk conductivity, σ_b , for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Ga}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.01, 0.03$ and 0.05) ceramics measured in air. Numbers in eV are the activation energies associated with σ_b .

4. Dielectric properties of Zn, Sc, Al and Ga-doped $\text{NB}_{0.51}\text{T}$ ceramics

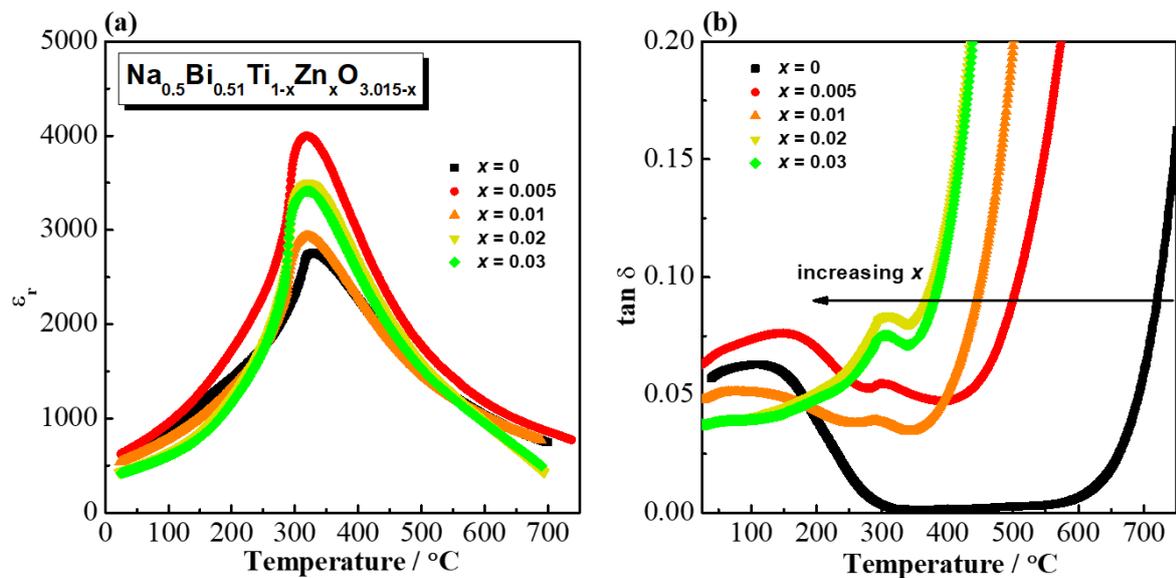


Fig.S12 Dielectric spectroscopy for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-x}\text{Zn}_x\text{O}_{3.015-x}$ ($x = 0, 0.005, 0.01, 0.02$ and 0.03) ceramics: (a) permittivity at 1 MHz versus temperature and (b) dielectric loss, $\tan \delta$, (1 MHz) versus temperature.

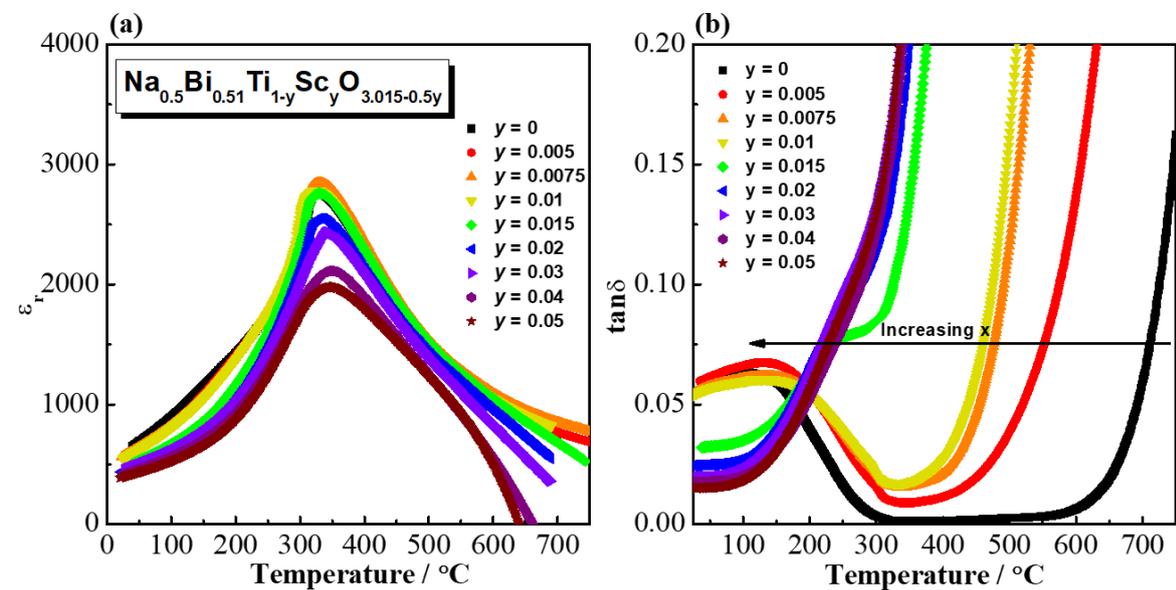


Fig.S13 Dielectric spectroscopy for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Sc}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.0075, 0.01, 0.015, 0.02, 0.03, 0.04$ and 0.05) ceramics: (a) permittivity at 1 MHz versus temperature and (b) dielectric loss, $\tan \delta$, (1 MHz) versus temperature.

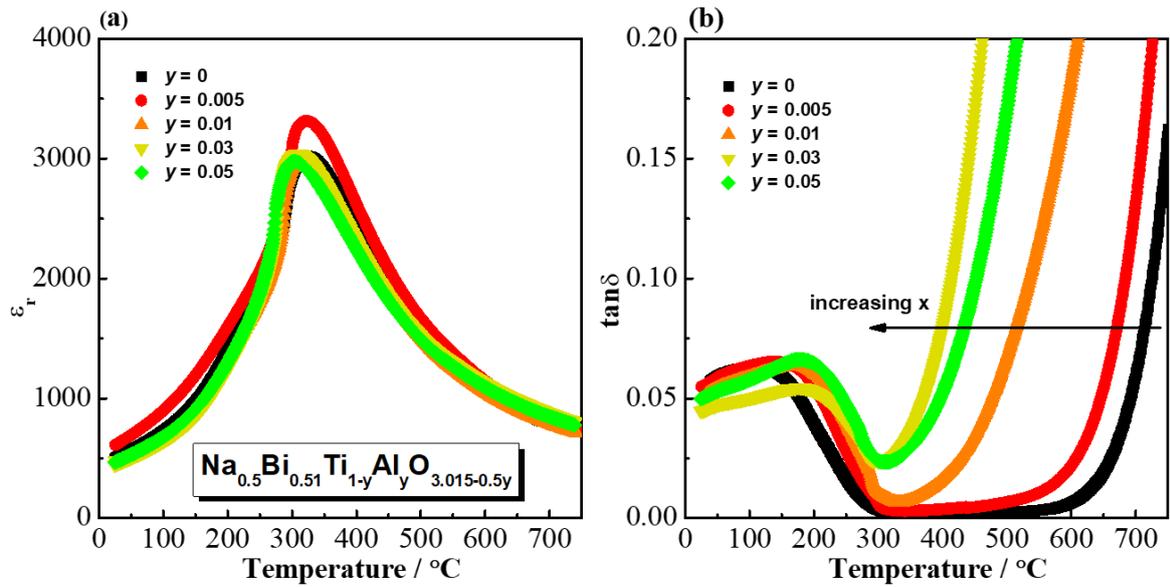


Fig.S14 Dielectric spectroscopy for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Al}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.01, 0.03$ and 0.05) ceramics: (a) permittivity at 1 MHz versus temperature and (b) dielectric loss, $\tan \delta$, (1 MHz) versus temperature.

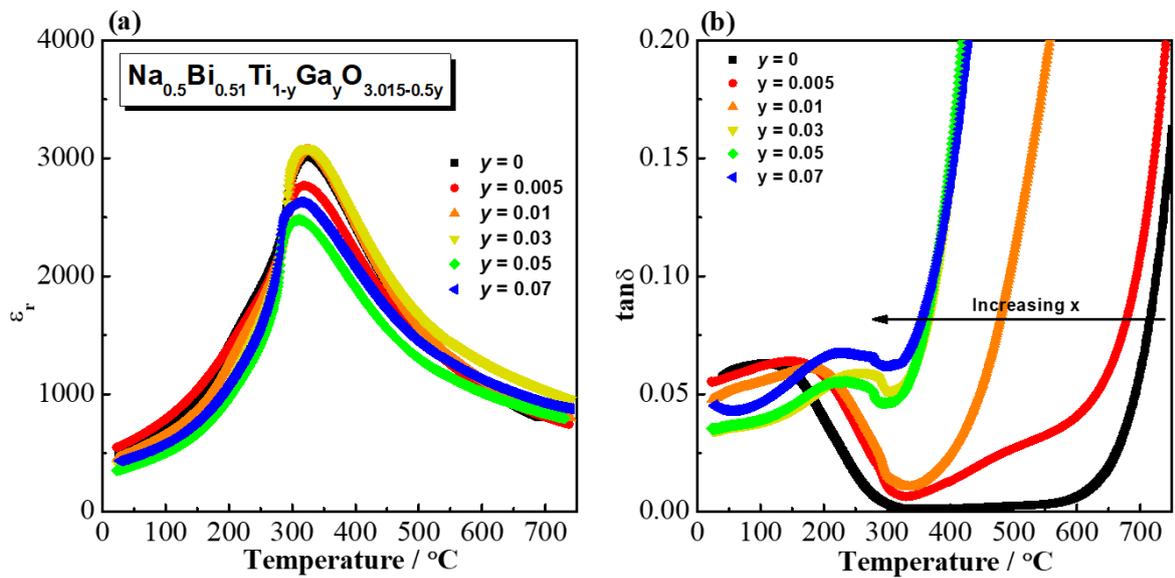


Fig.S15 Dielectric spectroscopy for $\text{Na}_{0.5}\text{Bi}_{0.51}\text{Ti}_{1-y}\text{Ga}_y\text{O}_{3.015-0.5y}$ ($y = 0, 0.005, 0.01, 0.03, 0.05$ and 0.07) ceramics: (a) permittivity at 1 MHz versus temperature and (b) dielectric loss, $\tan \delta$, (1 MHz) versus temperature.