-Supporting Information-

Enhanced ionic conductivity of Ag addition in acceptor-doped Bi$_{0.5}$Na$_{0.5}$TiO$_3$ ferroelectrics

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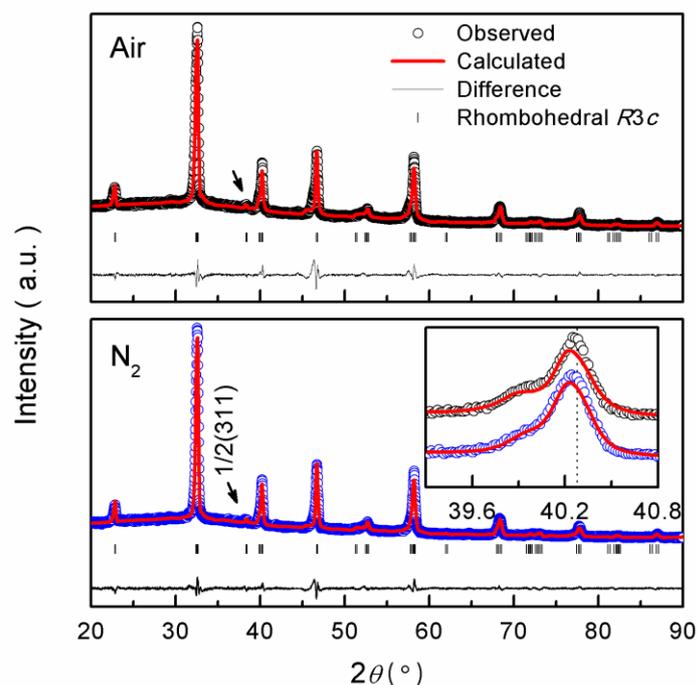
Fig. S1 Rietveld fitting for XRD patterns of A-BNTG and N-BNTG refined as $R3c$ cell since the 1/2(311) superlattice reflection is the characteristic of the rhombohedral phase. The inset illustrates the enlarged drawing of (111) pseudocubic peak. The fitting can fully describe the measured diffraction patterns with better quality as listed in Table S1. Quantitative refined lattice parameters indicate a slight increase in a, and decrease in c as compared N-BNTG with A-BNTG, showing the similar trend with the previous study[24].

Table S1 Structural parameters from the $R3c$ refinement of A-BNTG and N-BNTG at ambient temperature.

	Symmetry	a, b (Å)	c (Å)	Volume	Profile fit	
A-BNTG	$R3c$	5.4814	13.5492	352.551	R_p 4.18	χ^2 3.78
N-BNTG		5.4846	13.5358	352.618	R_p 4.04	χ^2 2.76
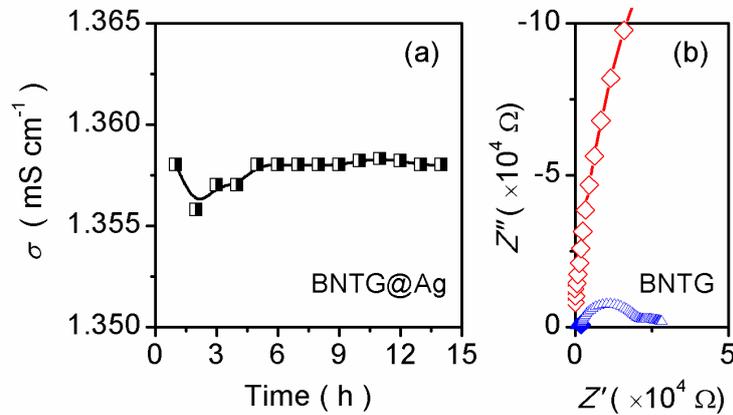
Fig. S2 (a) Cycle stability of grain conductivity of N-BNTG@Ag for 14 h at 502 °C. (b) Complex impedance Z^* of N-BNTG without Ag addition for two cycles at 500 °C. Dramatic change is observed in N-BNTG without Ag addition during cycling. Even, most of them exhibits an original resistive grain. Thus, Ag addition in BNTG is helpful to obtain its high conductivity and improve the stability, especially the properties repeatability since it is really highly sensitive to stoichiometry and synthesis processes for acceptor-doped BNT.
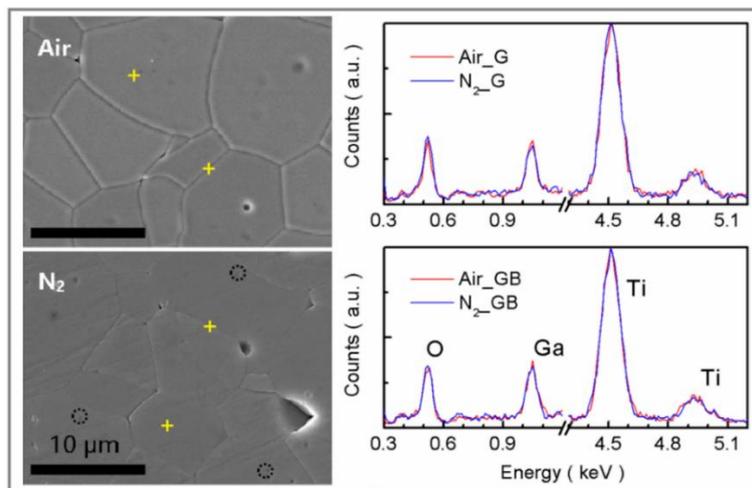
Fig. S3 SEM micrographs of A-BNTG and N-BNTG, which are polished and thermally etched at 850 °C for 30 min, with the micropore on the surface marked by black circles. All samples are dense with the relative density more than 94%, and have an average grain size of approximately 12 μm in

diameter. The right column shows the corresponding EDS results determined by averaging statistical data from five spectra for each different areas of grains (G) and grain boundaries (GB), respectively (labelled with yellow crosses). The elements distribution do not show much differences between A-BNTG and N-BNTG. By contrast, both the concentration ratio between Ga and O elements of A-BNTG and N-BNTG are slightly higher in grain boundaries than those in grains center, indicating the preferential segregation of Ga^{3+} to grain boundaries. As a result, the oxygen vacancies induced by the acceptor doping greatly promote the grain growth.
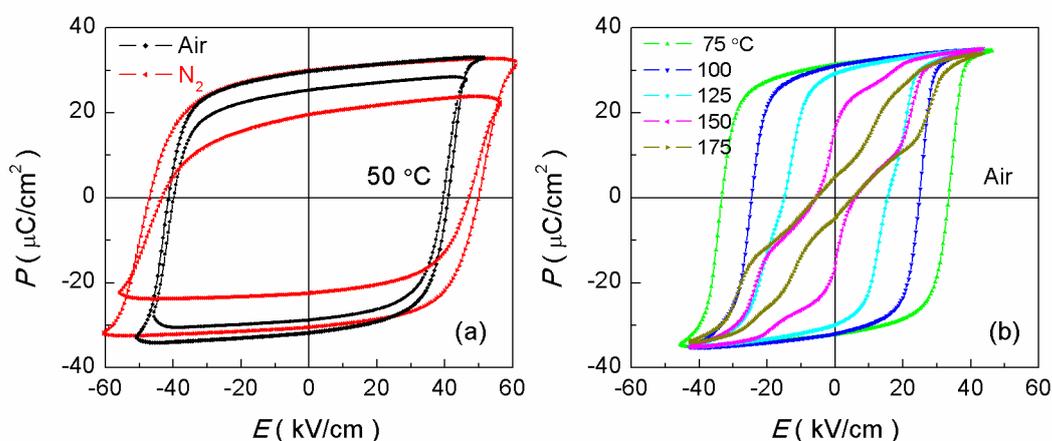
Fig. S4 (a) Polarization hysteresis (*P-E*) loops of A-BNTG and N-BNTG at different electric field at 1 Hz. (b) Evolution with temperature of *P-E* loops of A-BNTG at 45 kV cm^{-1} at 1 Hz. The polarization hysteresis loops of both samples display well-saturated typical ferroelectric behavior with the remnant polarization (P_r) of 30 μC cm^{-2}. The N-BNTG shows increased coercive field (E_c) which can be assigned to the "hard" behavior with the fact of Ga atom entering Ti-site. As the Ga incorporates in the octahedrally-coordinated perovskite B-site, the defect corresponding to oxygen vacancies is created for ionic charge compensation. Oxygen vacancies have stronger pinning effect for the ferroelectric domain switching, thereby inducing a continuous increase in E_c and a slight decline in P_r. The saturated loop of A-BNTG becomes pinched with the drop of E_c and P_r at elevated temperature, which is attributed to an electric-field-induced relaxor to ferroelectric transition, and the absence of long-range ferroelectric order. Owing to the mobility of the oxygen vacancy in N-BNTG that gradually falls behind the measured frequency as the temperature increases, we failed to get the precise *P-E* loops of N-BNTG at high temperatures above 125 °C.