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Phase coexistence and Mn-doping effect in lead-free ferroelectric (Na_{1/2}Bi_{1/2})TiO₃ crystals

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Phase transformations of (001)-cut (Na_{1/2}Bi_{1/2})TiO₃ (NBT) and 1 at. % Mn-doped NBT (Mn-NBT) crystals have been investigated by means of dielectric permittivity, conventional x-ray diffraction (XRD), and high-resolution synchrotron XRD and reciprocal space mapping. An R–R+T–T–C transition sequence was observed in NBT and Mn-NBT upon zero-field heating. R, T, and C are rhombohedral, tetragonal, and cubic phases, respectively. R+T represents that the ferroelastic T phase coexists with the ferroelectric R phase. The Mn dopant can enhance dielectric response and reduce the dielectric loss in the high-temperature region due to the increased degree of ordering.

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The lead-free sodium bismuth titanate Na_{1/2}Bi_{1/2}TiO₃ (NBT) materials are relaxor ferroelectrics because of the random placement of Na⁺ and Bi³⁺ ions on the perovskite A sites. They have attracted attention because of their ferroelectric (FE) and piezoelectric properties, which are comparable to those for the tetragonal Ti-rich PZT but smaller than for (1–x)Pb(Mg_{1/3}Nb_{2/3})O₃–xPbTiO₃ (PMN–PT) and (1–x)Pb(Zn_{1/3}Nb_{2/3})O₃–xPbTiO₃ (PZN–PT).¹ A critical drawback for PMN–PT and PZN–PT is the concern of lead-containing toxicity. The NBT related crystals have higher Curie temperatures, which enable them to be used at higher temperatures.

It has been known that NBT undergoes a transition sequence from the high-temperature cubic (C) to a tetragonal (T) and then a FE rhombohedral (R) phase.^{2–7} There is no dielectric anomaly at the C to T phase transition, suggesting that the intermediate T phase is ferroelastic.⁷ Neutron scattering indicates that the transition between T and R phases is characterized by a region of phase coexistence.^{6,7} Based on the x-ray diffraction (XRD) result, a coexistence of R and T phases was proposed in the region of ~250–300 °C.⁸ The broad dielectric maximum, characteristic of many relaxor ferroelectrics, was attributed to an over-damped infrared soft mode with a central-mode type dispersion.⁹

Recent results showed that Mn dopant can enhance piezoelectric coefficient and dielectric properties.^{10,11} The piezoelectric coefficients (*d*₃₃) and electromechanical coupling factors (*k*_t) are 60–80 pC/N and 0.20–0.30, and 120–145 pC/N and 0.45–0.55 for (001) NBT and 1 at. % Mn-doped NBT, respectively.^{10,11} It was found that Ce dopant can improve the FE properties of Na_{1/2}Bi_{1/2}TiO₃–BaTiO₃.¹² How Mn dopant affects dielectric response and structure is still not understood completely in the lead-free relaxor FE crystals.

NBT and 1 at. % Mn-doped NBT single crystals were grown by using the top-seeded solution method. The samples were cut perpendicular to a ⟨001⟩ direction. A Wayne–Kerr Analyzer PMA3260A was used to obtain the real (ϵ') and imaginary (ϵ'') parts of dielectric permittivity upon zero-field heating. The sample surfaces were coated with platinum films as electrodes.

A Rigaku Model MultiFlex x-ray diffractometer with Cu K α_1 and K α_2 radiations was used for *in situ* (002) XRD. The XRD spectra were fitted with a sum of Gaussian and Lorentzian terms. *In situ* high-resolution (002) synchrotron XRD and reciprocal space mapping were performed at the National Synchrotron Radiation Research Center (in Taiwan) with photon energies of 10.0 and 8.0 keV ($\lambda=1.2408$ and 1.550 Å), respectively, and beam size of 0.58×0.15 mm². A series of rocking ($\Delta\omega$) scans were performed to form the (002) reciprocal space mapping.

The 2 θ reflection and *d* spacing obey the Bragg law, i.e., $2d_{hkl} \sin \theta_{hkl} = n\lambda$, where (*hkl*) is crystallographic orientation. For the eight R domain types, one *d* spacing is expected from the (002) reflection, i.e., $1/d^2 = 4 \sin^2 \alpha_R / [a_R^2 (1 - 3 \cos^2 \alpha_R + 2 \cos^3 \alpha_R)]$.¹³ *a*_R and α_R are lattice parameters of the R phase. Two *d* spacings are expected from the six T domain types for the (002) reflection, i.e., $d_{(200)} = a_T/2$ and $d_{(002)} = c_T/2$, where *a*_T and *c*_T are lattice parameters of the T phase.

Figure 1 shows frequency-dependent dielectric permittivity (ϵ') and dielectric loss ($\tan \delta = \epsilon''/\epsilon'$). The ϵ' exhibits a frequency dispersion below about 250 and 240 °C for NBT and Mn-NBT, respectively, followed by a rapid rise without dispersion. The dielectric maximum temperatures (*T*_m) of NBT and Mn-NBT appear in the region of 310–315 °C. Mn-NBT has higher ϵ' and smaller dielectric loss in the high-temperature region than NBT. Above 450 °C NBT shows a upward frequency-dependent dielectric dispersion, which could be from the phase-shifted conductivity.¹⁴ This conductivity at 500 kHz obeys $1.81 \times 10^5 \exp[-(1.12 \text{ eV})/k_B T]$ (S/m). For a different NBT

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FIG. 1. (Color online) Dielectric permittivity ϵ' and dielectric loss ($\tan \delta$) of (001) unpoled NBT and Mn-NBT upon heating. Dielectric loss was taken at $f=0.5$ MHz.

crystal we obtained $2.25 \times 10^4 \exp[-(1.09 \text{ eV})/k_B T]$ (S/m) for the high-frequency envelope of the conductivity.¹⁵ The near equality of activation energies indicates that the difference in the pre-exponential factors reflects a difference in carrier concentrations. If the carriers are oxygen ion vacancies, the lower conductivity for Mn doping may mean that this doping reduces the oxygen vacancy concentration.

The (002) XRD spectra of NBT and Mn-NBT at 25 °C are given in Figs. 2(a) and 2(b), in which NBT and Mn-NBT exhibit an R-phase XRD peak. The R phase is confirmed by a single contour center in the (002) reciprocal mappings as shown in Figs. 2(c) and 2(d). In addition to the R phase, Mn-NBT exhibits a broad extra low- 2θ peak in Fig. 2(b), possibly associated with nanostructures. Nanostructures are often expected in ferroelastic and relaxor FE crystals to accommodate the lattice distortion.¹⁶ Since nanostructure is smaller than the coherent length of x-ray radiation, diffracted waves from individual nanostructure can coherently superimpose and broaden the peak.¹⁷

Figure 3 shows the temperature-dependent d spacing and lattice parameter of NBT and Mn-NBT. A two-peaks splitting

FIG. 2. (Color online) (002) XRD [(a) and (b)] and reciprocal space mapping [(c) and (d)] at 25 °C. The solid and dashed lines correlate to $K\alpha_1$ and $K\alpha_2$ radiations. The red line is the sum of fitting curves. The intensity of mapping is on a log scale.

FIG. 3. (Color online) Temperature-dependent d spacing and lattice parameter of (a) NBT and (b) Mn-NBT. The dashed lines indicate transition temperatures.

(or two d spacings) of T phase appears near 315 and 310 °C for NBT and Mn-NBT, respectively, and the sharpness of the splitting is consistent with the required first-order nature of the R–T phase transition. Our XRD and dielectric maximum peak show the same temperature for the R–T transition, and that the results of Ref. 3 that show different temperatures may be due to poling or other experimental history.

Two T-phase peaks join together near 530 and 550 °C for NBT and Mn-NBT, respectively, indicating a T–C phase transition. As shown in Fig. 1, there is no obvious dielectric anomaly near 530 and 550 °C, confirming that the T phase is ferroelastic. Overall, the d spacings and lattice parameters of Mn-NBT are smaller than those in NBT, possibly due to the smaller atomic radius of the Mn ion (0.50 Å) compared with the Ti ions (0.68 Å) on the perovskite B sites.

Note that the *in situ* (002) XRD spectra of NBT and Mn-NBT do not exhibit obvious anomalies near 250 and 240 °C, below which dielectric dispersion begins to develop. To explore possible coexistence of R and T phases and the Mn-doping effect, *in situ* (002) high-resolution synchrotron XRD was performed upon heating as shown in Figs. 4(a) and 4(b). The XRD intensity becomes much weaker in the intermediate regions of ~ 250 –315 and 240–310 °C for NBT and Mn-NBT, respectively, implying a reduction in ordering degree due to appearance of a second phase. As illustrated in Fig. 4(c), a clear low- 2θ T-phase shoulder coexists with an R phase at 290 °C in both NBT and Mn-NBT. This low- 2θ T-phase peak corresponds to the $d_{(002)}$ spacing. A two-peaks splitting of the T phase begins to develop at ~ 315 and 310 °C for NBT and Mn-NBT, respectively. Upon further heating, two T-phase peaks merge together near 530 and 550 °C for NBT and Mn-NBT, respectively, revealing a T–C phase transition. Note that the low- 2θ broad peak seen in Fig. 2 is relatively weaker in the synchrotron XRD, likely because the superimposing effect from individual nanostructures is less due to the narrow beam size of synchrotron radiation.

Figure 4(d) shows the averaged full width at half maximum (FWHM) as a function of temperature. Mn-NBT exhib-

FIG. 4. (Color online) Temperature-dependent (002) synchrotron XRD of (a) NBT and (b) Mn-NBT. (c) (002) synchrotron XRD at 290 °C. (d) Temperature-dependent averaged FWHM.

its a smaller FWHM below the ferroelastic T-phase, indicating that the Mn dopant can enhance the ordering degree of the FE phase. This FE ordering increment may explain why Mn-NBT has a higher dielectric permittivity and less dielectric loss, because a higher degree of polarization order can

improve dielectric response and reduce dielectric loss under a measuring E field.

In conclusion, coexistence of R and T phases was revealed in the intermediate region of the transition sequence in (001) NBT and Mn-NBT. The (001) unpoled NBT undergoes an R–R+T–T–C transition sequence near 250, 315, and 530 °C upon heating. Similarly, Mn-NBT has an R–R+T–T–C sequence near 240, 310, and 550 °C upon heating. The dielectric dispersion and high dielectric loss seen in NBT above 450 °C due to conductivity were reduced by the Mn dopant. The d spacings and lattice parameters of Mn-NBT are slightly smaller than those in NBT, likely due to the smaller atomic radius of the Mn ion. The modifications of dielectric properties and transition temperature are likely associated with the enhancement of FE ordering degree by the Mn dopant. The lower conductivity for Mn-NBT in the high-temperature region may mean that the Mn dopant reduces the oxygen vacancy concentration if the conductivity carriers are oxygen ion vacancies.

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