AIP | Applied Physics Letters

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Citation: Applied Physics Letters **95**, 162903 (2009); doi: 10.1063/1.3253412
View online: http://dx.doi.org/10.1063/1.3253412
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/95/16?ver=pdfcov
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Influence of dc-bias on phase stability in Mn-doped $Na_{0.5}Bi_{0.5}TiO_3$-5.6 at. %$BaTiO_3$ single crystals

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(Received 8 July 2009; accepted 1 October 2009; published online 20 October 2009)

Mn-doped $Na_{0.5}Bi_{0.5}TiO_3$-5.6 at. %$BaTiO_3$ (Mn:NBT-5.6%BT) single crystals were grown by a top-seeded solution growth method. Tetragonal and rhombohedral phases were found to coexist in the as-grown condition. The dielectric and structural properties were studied as a function of temperature under dc electrical bias. An induced phase stability change from rhombohedral to tetragonal phases occurred under an electric-field applied along the ⟨001⟩ direction. © *2009 American Institute of Physics*. [doi:10.1063/1.3253412]

Lead-free piezoelectric materials have attracted much attention in recent years from the view point of environmental protection.[1,2] However, the piezoelectric performance of lead-free materials is still inferior to that of lead-containing ones thus determination of a mechanism by which to realize higher piezoelectricity in lead-free systems is an important topic at the present time. Since the time ultrahigh piezoelectric coefficients were first reported in oriented $(1-x)Pb(Mg_{1/3}Nb_{2/3}O_3)$-$xPbTiO_3$ and $(1-x)Pb(Zn_{1/3}Nb_{2/3}O_3)$-$xPbTiO_3$ crystals,[3] many investigations have focused on monoclinic bridging phases around the morphotropic phase boundary (MPB).[4–11] Recently, a monoclinic M_C phase has been reported in ⟨001⟩ field-cooled $BaTiO_3$ single crystals,[12] indicating that ultrahigh piezoelectricity in Pb-free systems might be achieved via domain engineering.

Solid solutions of $(1-x)Na_{0.5}Bi_{0.5}TiO_3$-$xBaTiO_3$ (abbreviated as NBT-x at. %BT) are potentially important lead-free piezoelectric materials, as they have a rhombohedral (R) to tetragonal (T) phase transition at a MPB near $0.06<x<0.08$. Accordingly, enhanced piezoelectric properties might be possible, if domain-engineered low symmetry states can be stabilized.[13] However, electric field dependent phase transition studies of NBT-x at%BT have not previously been reported, this may simply be because of difficulty in obtaining large single crystals of high resistance. Recently,[14] the authors have developed Mn-doped NBT-x at%BT (i.e., Mn:NBT-5.6at. %BT) crystals with notably higher resistivity, enabling near complete ferroelectric poling.

Here, in this letter, we report an investigation of the electric field dependence of the relative phase stability in ⟨001⟩ oriented Mn:NBT-5.6at. %BT single crystals. Our findings show an electric field induced R→T phase stability change.

Single crystals of Mn:NBT-x at. %BT were grown by a top-seeded solution growth method from a 1 at % Mn-doped $Na_{0.5}Bi_{0.5}TiO_3$-10%$BaTiO_3$ solid flux. The concentration of Ba and Mn ions in the as-grown condition was determined by inductive coupled plasma atomic emission spectrometry to be 5.6 and 0.14 at. %, respectively. Pseudocubic ⟨100⟩ oriented Mn:NBT-5.6at. %BT crystal wafers with dimensions of $3\times3\times0.7$ mm^3 were cut from the boule and subsequently electroded on both surfaces with gold. Temperature dependent dielectric constant measurements were performed using a LCR meter (HP 4284A) under dc electric fields of E=0, 8, and 12 kV/cm in the temperature range of 30 to 200 °C. Temperature dependent (200) line scans were taken using a Philips MPD high-resolution x-ray diffraction (XRD) system under fields of 0 and 11.4 kV/cm. The x-ray wavelength was that of Cu K_α=1.5406 Å and the x-ray generator was operated at 45 kV and 40 mA.

Figure 1 shows the temperature dependent dielectric constant ε_r and loss factor tan δ for ⟨100⟩ oriented Mn:NBT-5.6at. %BT crystals taken on heating under E=0, 8, and 12 kV/cm. Our investigations focused on a secondary ferroelectric transition in the range of 100 to 200 °C, which was below the dielectric maximum T_c at 280 °C. Below the secondary transition, the dielectric constant can be seen to become strongly frequency dispersive near 130 °C, somewhat analogous to that of relaxor ferroelectrics.[21] Upon increasing the field, four observations can be made. First, the temperature of the secondary dielectric constant maximum was increased; from ~130 °C for E=0 kV/cm to ~150 °C for E=12 kV/cm. Second, the magnitude of the dielectric constant near this second maximum increased dramatically, from ~4000 for E=0 kV/cm to ~12 000 for E=12 kV/cm. Third, for E≥12 kV/cm, the secondary transformation sharpened dramatically, becoming frequency independent. Fourth, for E≥8 kV/cm, a tertiary dielectric anomaly was found near 105 °C, indicating an additional step in the phase transformational sequence. Taken together, these data under different E indicate the following general trends. Under zero and moderate biases, the secondary phase transformation is diffuse. With increasing field, the transformation becomes gradually sharper and a tertiary step in the structural sequence becomes apparent. Near a critical bias, the diffuse characteristics are overridden and a sharp transition is induced; please note that there are similarities between this induced transition and the relaxor-to-normal transformation in relaxor ferroelectrics.[22,23] After the dielectric measurements, we then cooled the Mn:NBT-5.6at. %BT crystal to room temperature at a rate of 2 °C/min under E=12 kV/cm applied along the ⟨100⟩. The piezoelectric d_{33} constant was then measured and determined to be 230 pC/N.

We next performed structural studies by XRD about the (200) and (220) zones at room temperature for as-grown

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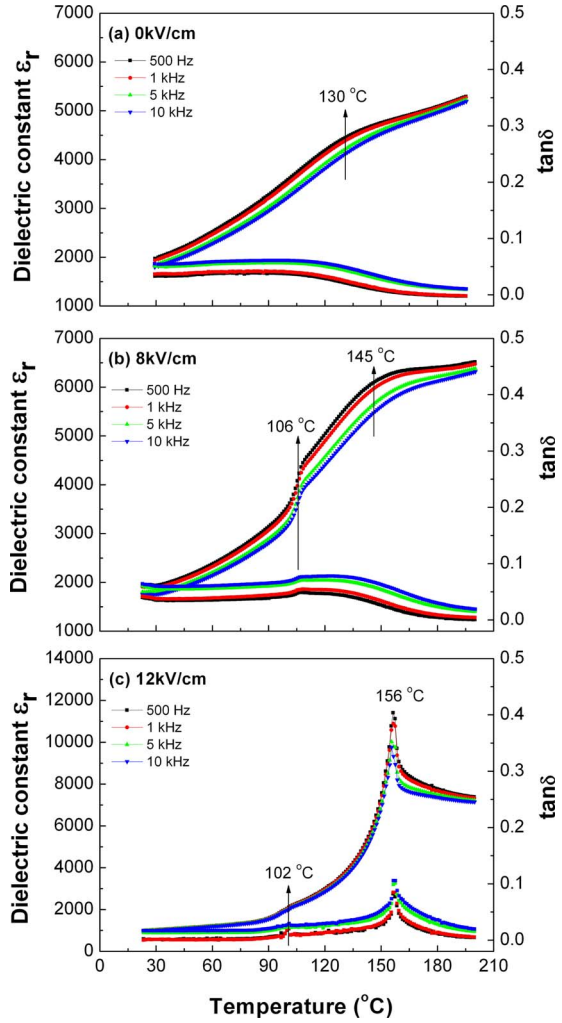

FIG. 1. (Color online) Temperature dependent dielectric constant ε_r and loss factor tan δ for ⟨100⟩ oriented Mn:NBT-5.6%BT crystals taken heating under E=0, 8, and 12 kV/cm.

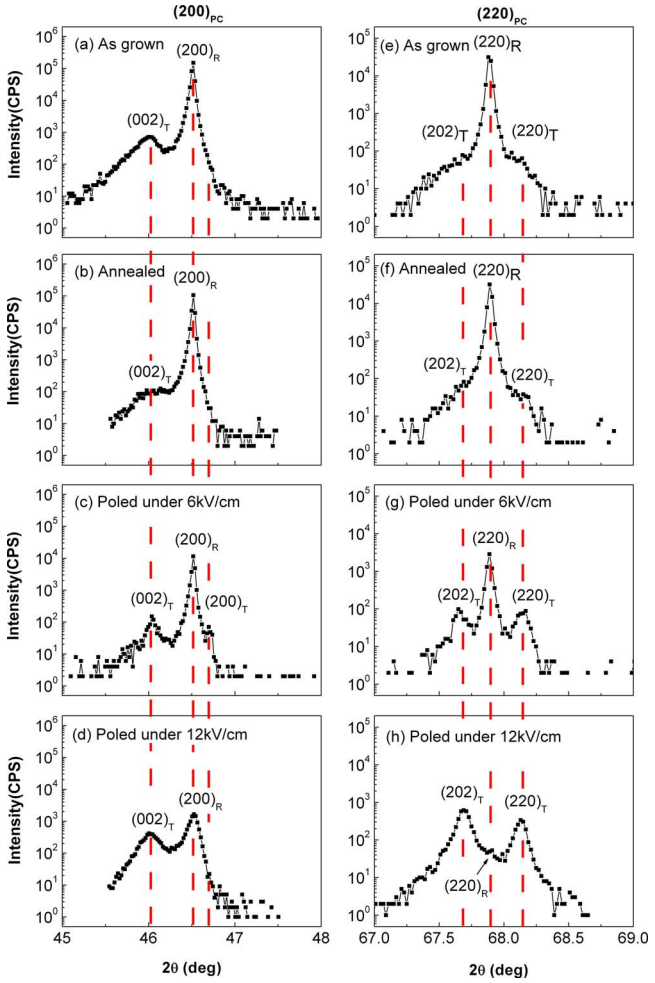

FIG. 2. (Color online) (200) and (220) x-ray line scans for Mn:NBT-5.6%BT crystals at room temperature: [(a) and (e)] as-grown crystal; [(b) and (f)] after annealing at 600 °C for 1 h; [(c) and (g)] after poling under dc E=6 kV/cm applied along ⟨100⟩ direction; [(d) and (h)] after poling under dc E=12 kV/cm applied along ⟨100⟩ direction.

Mn:NBT-5.6BT%. We annealed the crystal at 600 °C for 1 h and cooled to room temperature at a rate of 2 °C/min and again obtained (200) and (220) scans at room temperature. Finally, the crystal was heated to 200 °C and recooled to room temperature at a rate of 2 °C/min under dc biases of E=6 and 12 kV/cm, after which (200) and (220) scans were again obtained at room temperature. All of the XRD scans are given together in Fig. 2. The intensity is plotted on a logarithmic scale, so that small peaks with low intensity can be more clearly seen.

Along the pseudocubic (200) zone, an intense diffraction peak was found at 2θ=46.51° and a much weaker one was observed near 2θ=46.01°; as can be seen in the left hand column of Fig. 2. Along the pseudocubic (220) zone, an intense peak was found at 2θ=67.88°, which had two shoulders at 2θ=67.68° and 68.13°; as can be seen in the right hand column of Fig. 2. Different rows show the results for different histories. The top row is for the as-grown condition; the second row for annealed; the third and final rows for the field cooled conditions under E=6 kV/cm and E =12 kV/cm, respectively. Comparisons of the various (200) and (220) scans will reveal that none of the diffraction peak positions were changed by thermal/electrical history. However, the intensity of the diffraction peaks was notably changed.

We assign the intense peaks at 2θ=46.51° and 67.88° to the R phase. This is consistent with previously published phase diagrams,[13] where Mn:NBT-5.6BT% can be expected to lie on the R side of the MPB ($6<x<7$ at. %). Generally, there should be both (220) and (111) splittings for the R phase. However, the rhombohedral distortion is very weak in NBT crystal,[24,25] and thus its structure is very close to C. Accordingly, we could not find any splittings along (220) and (111) for either pure NBT or Mn:NBT-5.6BT% within the experimental accuracy of our system; perhaps high energy synchrotron XRD studies are needed in the future. The other diffraction peaks in Fig. 2 can be assigned to the T phase. The lattice parameters were determined to be (a_r, α) =(3.9020 Å, 89.98°) and (a_t, c_t)=(3.8897, 3.9421) Å for the R and T phases, respectively. Please note that these lattice constants were determined using both (200) and (220) scans, and that they were consistent with each other. These results show that the T and R phases coexist in Mn:NBT-5.6at. %BT: the composition lies close to the MPB (Ref. 13) ($6<x<7$ at. %) between R and T phases, but the R phase is dominant. Furthermore, from the lattice parameters, we calculated that a huge volume change of 0.39% must occur at the R→T phase stability change.

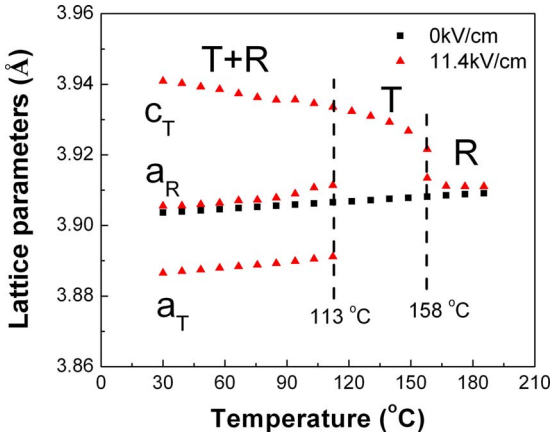

FIG. 3. (Color online) Temperature dependence of the crystal lattice parameters for Mn:NBT-5.6%BT under field of E=0 and 11.4 kV/cm.

Interestingly, the (200) pseudocubic reflection exhibited a large increase in the $(200)_r/(002)_t$ intensity ratio from 212 before annealing to 974 after annealing. This may result from one of two reasons. First, the R/T phase volume ratio might be increased by annealing. Since Mn:NBT-5.6at %BT lies close to the MPB, the T and R phases should be energetically close and thus there might be some metastability with thermal/electrical history. Second, the domain population might be altered by annealing; if this is the case, then we can conclude that the a-domain state is favored by annealing. Such a 90° domain switching by annealing might be explained by a "symmetry-conforming principle" of point defects, which was first proposed in ferroeleastic/martensite.[15–17] This model was later extended to $BaTiO_3$-based ferroelectrics[18–20] and used to explain reversible ferroelectric domain-switching in aged samples, in particular Mn-doped perovskite.[18–20] We note also near the MPB that the conforming-symmetry of the internal fields of point defects might alter slightly the relative R/T phase stability.

After field-cooling under E=6 kV/cm applied along the (001), the intensity for the T peaks was notably increased, whereas that of the R peaks was decreased: as can be seen in Figs. 2(c) and 2(g). With increase of E to 12 kV/cm, the intensity of the $(200)_r$ peak was further notably decreased, whereas that for the $(220)_r$ had nearly disappeared: as can be seen in Figs. 2(d) and 2(h). These results clearly demonstrate a change from R to T phase stability between as-grown and field-cooled conditions, although T was clearly present in both conditions.

Next, we measured the temperature dependence of the crystal lattice parameters under E=0 and 11.4 kV/cm applied along the (001). We began the investigations from the annealed condition. The results are shown in Fig. 3. For E =0 kV/cm, an intense (200) peak for the R phase was observed, whose lattice parameter increased near linearly with temperature. Under zero-field, the R phase was dominant, whereas the peak for the T phase was so weak that its position could not be determined with accuracy thus the lattice parameters for the T phase under zero-field are not shown in Fig. 3. However, in the field heating condition between 30 and 113 °C under E=11.4 kV/cm, the (200) and (220) reflections exhibited an obvious T splitting. Both T and R phases were found on heating in this temperature range, with lattice parameters as given in Fig. 3. On heating between 113 and 158 °C under E=11.4 kV/cm, the (200) pseudocubic reflection exhibited only the (002) peak for the T phase. This indicates that Mn:NBT-5.6%BT transforms into a near single c-domain T state under E≥11.4 kV/cm in this temperature range. The lattice parameter a_t was not given in the temperature range of 113 to 158 °C because we could not obtain a_t along the zones we had access to for a single c-domain Mn:NBT-5.6%BT wafer with thickness of 0.7 mm. Clearly, the tertiary phase transition observed in the dielectric constant [see Figs. 1(b) and 1(c)] is related to contributions from T domain realignment. In addition, near 158 °C, an abrupt phase transition occurred and the lattice parameters were equivalent to that for the R phase under E=0. This indicates that the Mn:NBT-5.6at. %BT crystal may have underwent a phase transition from single domain T ferroelectric to antiferroelectric, as previously suggested.[13]

In summary, the relative phase stability of Mn:NBT-5.6at. %BT crystals was investigated under dc electrical bias. T and R phases were found to coexist in the as-grown condition, with the R phase being dominant. With increasing temperature, an induced relative phase stability change from R to T phases was observed for an E-field applied along ⟨001⟩. Our results demonstrate that this T phase remains stable after removal of E in the field-cooled state.

This work was supported by the National Science Foundation (Materials world network) under Grant No. DMR-0806592, by the Department of Energy under Grant No. DE-FG02-07ER46480, by the Natural Science Foundation of China under Grant No. 50602047, and by the Shanghai Municipal Government Grant No. 08JC1420500.

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