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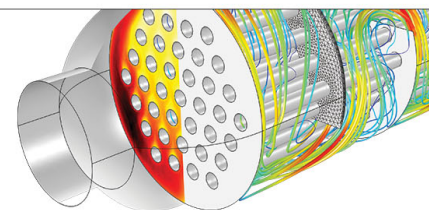
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Effect of Mn substituents on the domain and local structures of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ single crystals near a morphotropic phase boundary

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The ferroelectric domain and local structures of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}x\%\text{BaTiO}_3$ (NBT-BT) and 0.14 at. %Mn substituted $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}x\%\text{BaTiO}_3$ (Mn:NBT-BT) single crystals with $x=5.5$ near a morphotropic phase boundary have been investigated by transmission electron microscopy. Increased ferroelectric ordering and enhanced in-plane octahedral tilting were observed for Mn:NBT-BT compared with NBT-BT. Bragg-filtered lattice images revealed that the size of the in-phase tilt domains of Mn:NBT-BT were on the order of 2 to 8 nm, with a tendency of alignment along $\{110\}$. © 2011 American Institute of Physics. [doi:10.1063/1.3573801]

Lead-free piezoelectrics have attracted much attention due to environmental concerns.¹⁻³ $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ -based (NBT) perovskite solid solutions are considered as an important lead-free ferroelectric (FE). The system has been shown to have high piezoelectric properties of $d_{33}=500$ pC/N. It thus has the potential to replace the widely used Pb-based piezoelectric ceramics.^{2,4}

The $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}x$ at. % BaTiO_3 solid solution (NBT- $x\%$ BT) is a very complex system which has a morphotropic phase boundary or MPB for $5.5 < x < 6.5$. The MPB is a temperature independent boundary between rhombohedral (R) and tetragonal (T) FE phases.^{5,6} Studies have shown that NBT-based solid solution is one Pb-free FE that has a MPB. This is beneficial for piezoelectrics that need to operate over a wide temperature range.⁵ Recent piezoresponse force microscopy (PFM) studies of the domain structure of NBT- $x\%$ BT have shown with increasing x , as the MPB is approached, that (i) the size of polar nanoregions is decreased and their self-organization enhanced; and (ii) the formation of proper ferroelastic domains is suppressed, and rather improper ones are favored that form below the FE Curie temperature to elastically accommodate the FE domains.^{7,8}

It is known near the MPB of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\%\text{PbTiO}_3$ (PMN- $x\%$ PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\%\text{PbTiO}_3$ (PZN- $x\%$ PT) crystals that high piezoelectric properties are achieved by low symmetry monoclinic (M) phases that structurally bridge R and T phases.⁹⁻¹³ However, to date, no intermediate bridging M phases have been found in NBT-BT; thus the mechanism of piezoelectric property enhancement remains in question. Near the MPB of NBT-BT, x -ray investigations have revealed the coexistence of R and T phases, where application of E along the (001) direction induces the T phase.^{6,14} It is worth noting that the highest d_{33} values for NBT-BT have been reported in Mn-modified systems, where d_{33} was increased to 480 pC/N from 280 pC/N by Mn. This enhancement has been attributed to an increase in the resistivity by Mn;⁴ however, the effect of

Mn substitution on the local structure of NBT-BT crystals has not yet been reported.

Here, we have studied the domain structure, octahedral tilting, and lattice structure of NBT- $x\%$ BT and Mn:NBT- $x\%$ BT with $x=5.5$ using bright field and lattice imaging, and selected area electron diffraction (SAED). We find the following with Mn substitution: (i) increased tendencies of FE ordering and in-plane octahedral tilting; (ii) formation of structural modulation across domain boundaries, which may help relax elastic stress between FE domains; and (iii) an increase in the number of in-phase oxygen tilted regions, with a size of about 2 to 8 nm and with a tendency of alignment along $\{110\}$.

Single crystals of NBT- $x\%$ BT were grown by a self-flux technique.⁴ Samples for transmission electron microscopy (TEM) were prepared by mechanical polishing, followed by a dimple grinder thinning process, and finally by argon ion thinning. Studies were performed using a Philips EM 420 electron microscopy working at 120 kV and a FEI TITAN 300 electron microscopy operating at 200 kV, with a double-tilt sample holder. All electron diffraction patterns were indexed using pseudocubic unit cell notations.

Figures 1(a) and 1(b) show bright-field images for NBT- $x\%$ BT and Mn:NBT- $x\%$ BT with $x=5.5$, respectively. Two types of domain structures can readily be discerned. For NBT-5.5%BT, polar nanodomains are clearly evident, as previously reported.⁷ The average size of these polar nanodomains was about 20–50 nm. Prior studies of pure NBT single crystal have shown a polar nanodomain size of 50–100 nm,¹⁵ thus it appears that the polar nanodomain size is reducing with increasing x at. % BT on approaching the MPB. Upon Mn substitution, the morphology of these domains was notably changed. More highly ordered domain structures became evident, which were aligned along $\{110\}$. It is worth noting that similar types of domains have been found on the tetragonal side of the MPB for PMN- $x\%$ PT, i.e., the so-called normal micron-sized T domains.^{16,17} However, there are two notable differences of the domain state between Mn:NBT-5.5%BT and the T phase of PMN-PT, which are as follows: (i) Mn:NBT-5.5%BT displays relaxor

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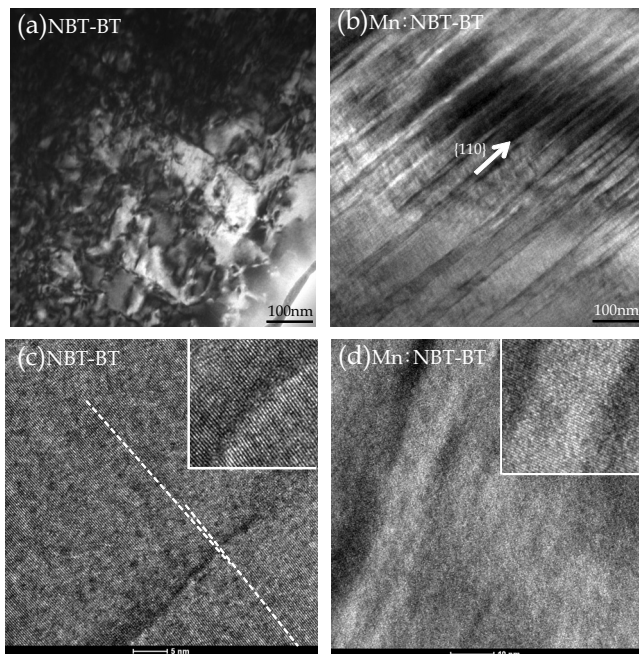


FIG. 1. TEM bright field images of (a) NBT-5.5%BT and (b) Mn:NBT-5.5%BT, which reveal enhanced FE ordering for NBT-5.5%BT with Mn substitution; lattice images taken across octahedral tilt boundaries for (c) NBT-5.5%BT, and (d) Mn:NBT-5.5%BT, the insets show the magnified region across the boundaries.

FE features, not normal FE ones;⁴ and (ii) the stable crystal structure in Mn:NBT-5.5%BT was R, where as that of PMN-*x*%PT was T. Clearly, the development of micron-sized domains in Mn:NBT-5.5%BT is due to Mn substitution. We can ascertain this from the fact that there were no changes in crystal structure for NBT-5.5%BT with Mn based on our x-ray studies. Furthermore, this infers that the change in domain stability arise due to changes in defect distributions and their interaction with domains. Figures 1(c) and 1(d) show lattice images obtained near domain boundaries for NBT-5.5%BT and Mn:NBT-5.5%BT, respectively. For NBT-5.5%BT, planar defects along $\{110\}$ twin boundaries can be seen, as previously reported for NBT.¹⁵ However, for NBT-5.5%BT, the lattice planes were found to be tilted with respect to each other across this boundary, as illustrated by dashed lines in the figure and by a higher resolution image shown in the inset of the figure. This tilt clearly shows that the lattice is elastically relaxed across the boundary. For Mn:NBT-5.5%BT, the lattice was found to be coherent

across the boundaries, as can be seen in Fig. 1(d), also the inset of the figure. In this case, the lattice planes of different regions were not found to exhibit a tilt with respect to each other. Clearly, Mn substitution not only makes significant changes in the polar domain structure and superlattice reflections but also to the mechanism of stress accommodation between octahedral tilt regions.

An electron diffraction pattern for NBT-5.5%BT taken along $[001]$ is shown in Fig. 2(a). Weak $1/2$ (ooe) superlattice reflections can be seen, as marked by arrows; where o designates odd values of the Millers indices, and e even. These findings are consistent with prior reports for NBT-5.5%BT ceramics.¹⁸ It is believed that these $1/2$ (ooe) reflections originate from oxygen octahedra tilts in the NBT-5.5%BT system of limited spatial correlation.^{19–23} These small tilted regions may have a local tetragonal distortion within the average R structure. For Mn:NBT-5.5%BT, SAED patterns taken along $[001]$ and $[110]$ are shown in Figs. 2(b) and 2(c), respectively. These patterns clearly revealed intense $1/2$ (ooe) and weak $1/2$ (ooo) reflections as marked by arrows and rings, respectively. These results show that a coexistence of in-phase $1/2$ (ooe) and out-of-plane $1/2$ (ooo) octahedral tilted regions is stabilized by Mn substitution, this is indicative of a mixture of R and T phases. It is noted that an orthorhombic (O) perovskite phase can also exhibit both superlattice spots simultaneously.²⁴ For NBT, the orthorhombic phase was only observed near 230 °C, bridging between R and T ones.^{21,22} To date, no O phase in NBT-based solution has been observed at room temperature, either by TEM or x-ray studies. Therefore, the possibility that these superlattice are due to an orthorhombic phase in Mn:NBT-BT can be reasonably excluded. The strong intensity of the in-phase tilts with Mn may indicate an enhanced local tetragonal distortion within the R phase, which is coincidental with a significant enhancement of d_{33} with Mn.⁴

Lattice imaging was then performed on Mn:NBT-5.5%BT near the edge of the specimen along the $[001]$ zone axis. The edge was chosen so that we could try to observe the lattice planes in areas of the sample which had thicknesses on the order of the spatial coherence of the $1/2$ (ooe) octahedral tilts. Figure 3(a) shows such a lattice image and the inset shows a fast Fourier transform (FFT). The FFT reveals intense $1/2$ (ooe) reflections from in-phase octahedra tilts, consistent with the SAED patterns in Fig. 2(b). However, a FFT of similar images for NBT-5.5%BT did not reveal such $1/2$ (ooe) reflections, consistent with a much weak

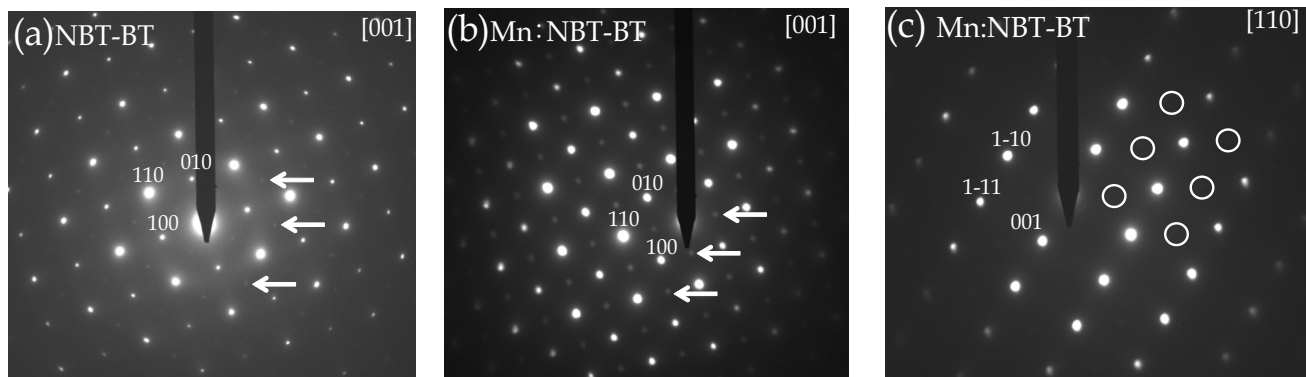


FIG. 2. SAED patterns for (a) NBT-5.5%BT taken along the $[001]$ zone axis; (b) and (c) Mn:NBT-5.5%BT along $[001]$ and $[110]$ zone axis, respectively, where intense $1/2$ (ooe) superlattice reflections can be seen in (b) as marked by arrows.

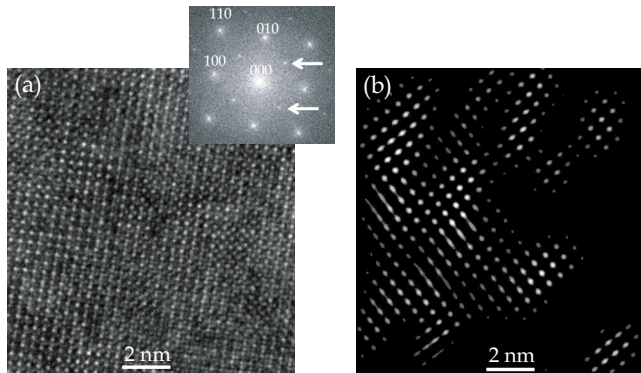


FIG. 3. (Color online) (a) Lattice image for Mn:NBT-5.5%BT taken along the [001] zone axis, and the inset shows power spectrum of the lattice image, which reveals $1/2$ (00e) super-reflections; and (b) corresponding inverse FFT image obtained using only the $1/2$ (00e) superlattice spots.

intensity in the SAED pattern. In Figs. 3(b), we show the corresponding inverse FFT image obtained by selecting only the $1/2$ (00e) super-reflections of the FFT. It clearly reveals a high intensity of small octahedral tilt regions of size 2–8 nm, consistent with a prior report for NBT-BKT-BT ceramics near the MPB.^{25,26} By comparing the intensity of the $1/2$ (00e) reflections between NBT-5.5%BT and Mn:NBT-5.5%BT, one can infer that Mn pronouncedly increases the number of in-phase tilted regions.

Our results clearly show that small amount of Mn substituents favor the formation of micro-sized FE domains in the R phase field, which contains a high density of $1/2$ (00e) octahedral tilted regions that may have tetragonal distortions of limited spatial lengths. Such local structurally inhomogeneous states that coexist over different length scales may help explain the large induced strain as high as 0.6% (Ref. 27) and enhanced d_{33} values⁴ in Mn substituted NBT-5.5%BT crystals near the MPB.

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