

Cationic Disordering and Its Related Non-Polar Regions in Sodium Bismuth Titanate

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Sodium bismuth titanate, $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT), is known to be a typical relaxor perovskite and has been extensively investigated for its potential applications to actuators, sensors, and transducers. In order to comprehensively understand the relaxor ferroelectric property of NBT, it is necessary to verify the real atomic structure, since the origin giving rise to a relaxor characteristic is still ambiguous to date even though it is widely accepted that polar nano regions (PNRs) are surrounded by non-polar regions in a relaxor perovskite. In terms of the ordered structure in NBT, the NaCl-type ordering of Na and Bi cations (Fig. 1(a)) and the criss-cross superlattice (Fig. 1(b)) have been proposed. Once the superlattice is formed by compositional ordering of Na and Bi, the criss-cross or NaCl-type ordering structure is assumed to create a noticeable superlattice peak in the diffraction pattern. From this viewpoint, the compositional ordering/disordering of NBT has also been studied using statistical analysis tools such as XRD, neutron diffraction, and Raman spectra.¹⁻⁴

In this study, moving beyond statistical methods, we attempted to visualize the atomic structure of NBT via aberration-corrected STEM to verify the origin of a relaxor perovskite. STEM results confirm that NBT has no apparent superlattice structure (Fig. 2) although the weak diffracted spots induced by superlattice structure were observed in this study as well. Since the superlattice structure is related with PNR with a size of a few nanometers, it is challenging to visualize the ordered lattice structure. Instead, the cationic disordered structure, Na- and Bi-excess regions, was likely observed. Because Na- and Bi-excess regions are defective region and accordingly they are related with non-polar region, the spontaneous polarization was not observed (Fig. 3), as expected in PNR model. However, the charge imbalance caused by the cationic disordering appears to be compensated by the vacancy formation: Na- and Bi-excess areas hold oxygen vacancies and A-site vacancies, respectively. Therefore, in summary, the PNR in a relaxor characteristic is originated from the cationic ordering/disordering; and non-polar region is deeply related with the atomic vacancies, which are formed to compensate the charge imbalance in cation disordered regions

References

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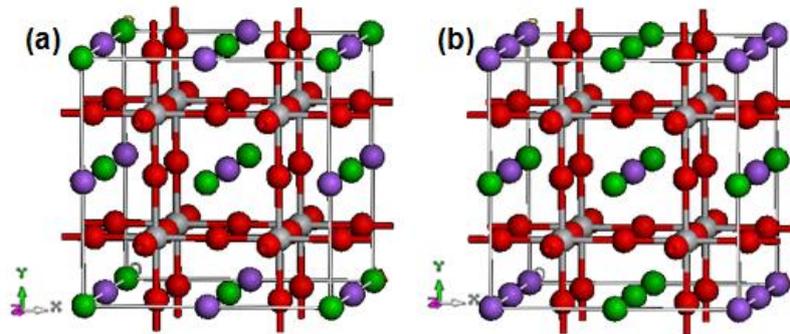


FIG. 1. (a) NaCl-type and (b) criss-cross superlattice structures of NBT, where the green, purple, gray, and red spheres represent sodium, bismuth, titanium, and oxygen atoms, respectively.

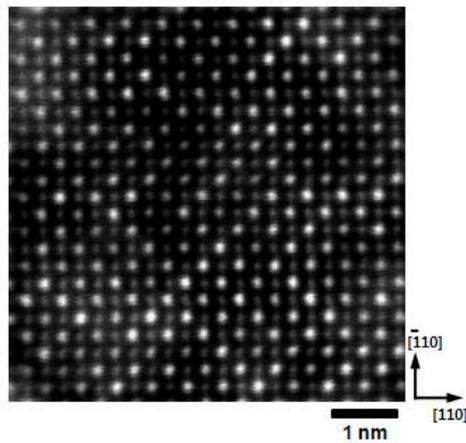


FIG. 2. HAADF-STEM image from a thin area showing cationic disordering.

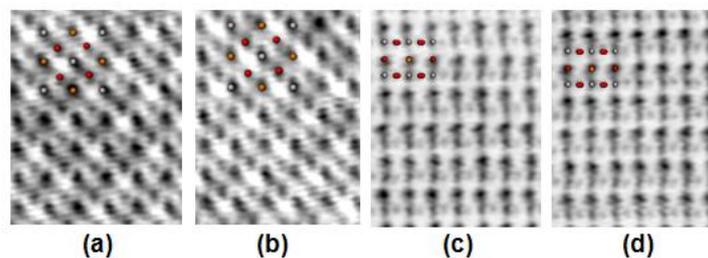


FIG. 3. (a) and (b) are the $[001]$ projected ABF-STEM images from Bi-excess and Na-excess regions, respectively. (c) and (d) are the $[110]$ projected ABF-STEM images from Bi-excess and Na-excess regions. The unit cell structure along the $[001]$ or $[110]$ projections was superimposed into each ABF image, where the orange, gray, and red spheres indicate Na-Bi, Ti-O, and O atomic columns, respectively.