Ferroelectric transition with off-center magnetic Mn$^{4+}$ ions in Sr$_{1-x}$Ba$_x$MnO$_3$


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1 Introduction
Most ferroelectric perovskites discovered so far are non-magnetic due to d electrons on off-center transition metal ions, as exemplified by BaTiO$_3$ and Pb(Zr,Ti)O$_3$. This empirical “$d^0$-ness” rule can be explained in terms of the stabilization of the ferroelectric distortion by forming a covalent bond between empty d orbitals of transition metal and filled 2p orbitals of oxygen. In contrast, magnetism requires d$^n$ states in transition metal ions with n≠0. Such incompatibility between ferroelectric and magnetic properties has been one of the most important challenges in designing new multiferroic materials. Recently, however, several first-principles calculations predicted the ferroelectric ground states in perovskite A$\text{MnO}_3$ (A=Ca, Sr, and Ba), where the magnetic (d$^n$) Mn$^{4+}$ ions move off-center due to strong Mn-O bond covalency. Experimentally, these manganites with a cubic perovskite structure have not been explored, since the hexagonal polymorphs become more stable with increasing the A-site ionic radius. In this study, we have developed a two-step crystal growth technique, consisting of a floating-zone method and high-pressure oxygen annealing (~6 GPa) [1]. This enabled the synthesis of single crystals with the perovskite structure up to 50% Ba substitution.

2 Results and Discussion
Figure 1(a) shows the dependence of lattice constant a on Ba concentration x for Sr$_{1-x}$Ba$_x$MnO$_3$ (0≤x≤0.5). As x increases from 0 to 0.4, the lattice constant at 300 K monotonically increases from 3.807 to 3.856Å with keeping the cubic symmetry. Around x=0.45, the crystal structure changes from cubic to tetragonal, indicating ferroelectric distortion with an elongation of the a-axis. Figure 1(b) shows a magnetoelectric phase diagram for Sr$_{1-x}$Ba$_x$MnO$_3$ as a function of x. The ferroelectric transition temperatures Tc were determined as the temperatures where the tetragonal distortion vanishes. The G-type antiferromagnetic phase is stable for the entire doping range (0≤x≤0.5), although the transition temperature Tc gradually decreases from 230 K (x=0) to 158 K (x=0.5). For x ≥ 0.45, a novel multiferroic phase thus appears below $T_N$ (<$T_c$), associated with the antiferromagnetic ordering of off-center Mn$^{4+}$ ions.

To further investigate the atomic displacements in the ferroelectric lattice for x=0.5, we have performed the single-crystal structural analysis by using synchrotron x-ray diffraction at BL8A. Figures 1(c) and (d) show the detailed crystal structures at 225 K (above $T_N$) and at 50 K (below $T_N$), respectively. All the reflection points are well assigned based on the non-centrosymmetric tetragonal P4mm space group at both temperatures. Noteworthy is that the magnitude of shift of Mn$^{4+}$ ion from the center of the surrounding oxygens is dramatically suppressed below $T_N$. In particular, the Mn-O-Mn bond significantly deviates from 180° above $T_N$ (~179.4(5)°), but becomes close to 180° below $T_N$ (~179.1(5)°). This may correspond to the spontaneous polarization change by several μC/cm$^2$, indicating huge magneto-electric coupling in the present system.

References

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