

Ferroelectric transition with off-center magnetic Mn<sup>4+</sup> ions in Sr<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub>

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## 1 Introduction

Most ferroelectric perovskites discovered so far are non-magnetic without  $d$  electrons on off-center transition metal ions, as exemplified by BaTiO<sub>3</sub> and Pb(Zr,Ti)O<sub>3</sub>. 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  $n \neq 0$ . 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  $AMnO_3$  ( $A=Ca, Sr, \text{ and } Ba$ ), where the magnetic ( $d^3$ ) Mn<sup>4+</sup> 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 ( $\sim 6$  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<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> ( $0 \leq x \leq 0.5$ ). As  $x$  increases from 0 to 0.4, the lattice constant at 300 K monotonically increases from 3.807 to 3.856 Å 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  $c$ -axis. Figure 1(b) shows a magnetoelectric phase diagram for Sr<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> as a function of  $x$ . The ferroelectric transition temperatures  $T_C$  were determined as the temperatures where the tetragonal distortion vanishes. The G-type antiferromagnetic phase is stable for the entire doping range ( $0 \leq x \leq 0.5$ ), although the transition temperature  $T_N$  gradually decreases from 230 K ( $x=0$ ) to 185 K ( $x=0.5$ ). For  $x \geq 0.45$ , a novel multiferroic phase

thus appears below  $T_N$  ( $< T_C$ ), associated with the antiferromagnetic ordering of off-center Mn<sup>4+</sup> 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<sup>4+</sup> 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  $T_N$  [ $\sim 175.4(5)^\circ$ ], but becomes close to 180° below  $T_N$  [ $\sim 179.1(5)^\circ$ ]. This may correspond to the spontaneous polarization change by several  $\mu\text{C}/\text{cm}^2$ , indicating huge magnetoelectric coupling in the present system.

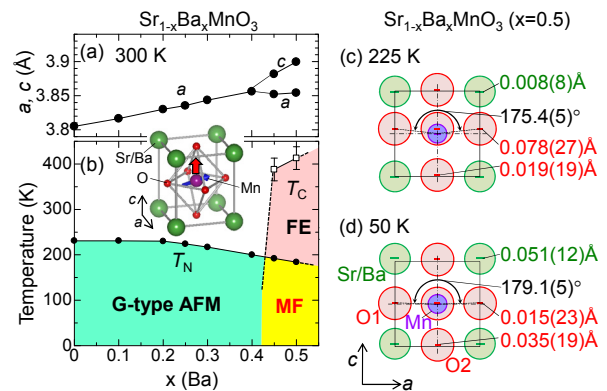


Fig. 1: (a) Lattice constant and (b) phase diagram for Sr<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> as a function of  $x$ . PM, AFM, PE, FE, and MF denote paramagnetic, antiferromagnetic, paraelectric, ferroelectric and multiferroic phases, respectively. Detailed crystal structures at (c) 225 K and (d) 50 K are deduced from the single-crystal x-ray diffraction.

## References

[1] H. Sakai *et al.*, Phys. Rev. Lett. **107**, 137601 (2011).

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