Ferroelectric transition and soft-phonon dynamics associated with off-center displacement of magnetic ions in perovskite $Sr_{1-x}Ba_xMnO_3$

Since ferroelectricity was discovered in perovskite $BaTiO_3$ in 1940s, a variety of ferroelectric oxides have been extensively studied in terms of electronic device engineering as well as academic interest. Most of the perovskite ferroelectrics ABO_3 so far identified, however, consist of non-magnetic *B* (transition metal) site with no *d*-orbital electrons (Fig. 1(a)). Typical examples include $Pb(Zr,Ti)O_3$ and $KNbO_3$. The requirement of the d^0 electronic configuration in the off-center transition metal ions can be interpreted in terms of the covalent bonding [1]. Since electrons can virtually hop from the filled 2*p* orbital in oxygen to the empty *d* shells in the transition metal ions, the d^0 states are energetically stabilized by forming a covalent bond (Fig. 1(b)). This empirical rule for the ferroelectric perovskites, however, has been a severe restriction in designing new multiferroic materials where magnetism and ferroelectricity coexist. Since magnetic ordering in contrast requires the partial occupation of the *d* shell of the transition metal ions, mutually exclusive conditions are necessary for the emergence of both ferroelectricity and magnetism [2].

Against this empirical rule, a few multiferroic perovskites have been investigated, as exemplified by $TbMnO_3$ with the spiral magnetic order [3] and $BiFeO_3$ with an off-center Bi (*A* site) ion [4]. However, they show only small polarization or otherwise weak magnetoelectric coupling. Recently, several first-principles calculations have pointed out the possible ferroelectric ground state with large polarization (tens of $\mu C/cm^2$) for $AMnO_3$ (*A*=Ca, Sr, and Ba), accompanied by the Mn^{4+} ion displacement due to strong Mn-O bond covalency [5]. In reality, cubic $SrMnO_3$ is a typical Mott insulator with G-type (staggered in all three directions) antiferromagnetism and to be paraelectric down to the lowest temperature. Although the ferroelectric instability was predicted to be promoted with increasing the ionic radius of the *A* site ions, no ferroelectric transition was experimentally observed up to 20% Ba substitution for Sr. For a larger radius of the *A* site ion, the hexagonal polymorph becomes so stable that the cubic perovskite structure cannot be synthesized by the conventional solid-state reaction.

To overcome this problem, we have developed a two-step crystal growth technique, consisting of a floating-zone method and high-pressure oxygen annealing (~6 GPa) [6]. This enabled the synthesis of single crystals with the perovskite structure up to 50% Ba substitution.

Figure 2(a) shows the dependence of lattice constant *a* on Ba concentration (*x*) for $Sr_{1-x}Ba_xMnO_3$ ($0 \leq x \leq 0.5$). 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 2(b) shows a magnetoelectric phase diagram for $Sr_{1-x}Ba_xMnO_3$ as a function of *x*. The ferroelectric transition temperatures T_C were determined as the temperatures where the tetragonal distortion vanishes (Fig. 2(d)). 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^{4+} ions.

Spontaneous electric polarization, P_S, along the *c*-axis was clearly observed in the *P*-*E* hysteresis curve, as shown in Fig. 2(c). The measured P_S value at 2 K is ~4.5 $\mu C/cm^2$ in a specimen with heavily-twinned tetragonal domains, suggesting the intrinsic P_S value of 13.5 $\mu C/cm^2$ for a single domain. The values of P_S and T_C for $x=0.5$ are almost comparable with those for $BaTiO_3$ ($P_S=26$ $\mu C/cm^2$ and $T_C=406$ K). Since there are no lone pairs in Sr^{2+}/Ba^{2+} ions, the observed ferroelectricity is attributed to the displacement of the magnetic Mn^{4+} ion with d^3 configuration.

The long-range ordering of Mn^{4+} spins has strikingly large effects on the spontaneous polarization and lattice distortion, as shown in Fig. 2(d). The *c*/*a* value, which reaches 1.012 around room temperature, begins to decrease with decreasing temperature around 225 K ($>T_N$) probably due to the antiferromagnetic fluctuation, and then steeply drops at T_N. Below 150 K, the *c*/*a* value is almost constant (~1.0035),

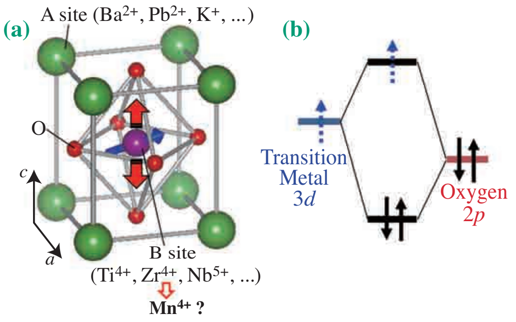

Fig. 1. **(a)** Crystal structure of perovskite oxides. For most proper ferroelectrics, the transition metal ions in the B sites are nonmagnetic. **(b)** Energy diagram of covalent bonding between transition metal 3*d* and oxygen 2*p* orbitals. Partially occupied 3*d* states in transition metal ions are energetically unfavorable in forming a covalent bond. (d^0-ness rule)

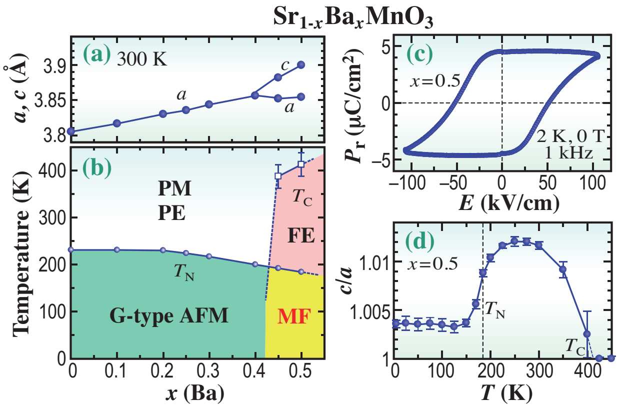

Fig. 2. **(a)** Lattice constant and **(b)** phase diagram for $Sr_{1-x}Ba_xMnO_3$ as a function of Ba concentration (x). PM, AFM, PE, FE, and MF denote paramagnetic, antiferromagnetic, paraelectric, ferroelectric and multiferroic phases, respectively. **(c)** Remnant P-E hysteresis curve for $x = 0.5$ along [001] and **(d)** temperature profile of ferroelectric distortion (c/a) for $x = 0.5$ measured by powder X-ray diffraction.

at approximately 30% of the maximum deviation from the cubic value (c/a=1). Based on a simple relation $(c/a-1) \propto P_S^2$, the P_S value above T_N is estimated to be about 1.9 times as large as that below T_N: ~25 μC/cm^2. The antiferromagnetic ordering thus can produce huge variation in P_S of the order of μC/cm^2.

The ferroelectric transition in $Sr_{1-x}Ba_xMnO_3$ is governed by a soft phonon, reflecting the displacement-type ferroelectricity. Figure 3 shows the phonon dispersion along the [110] direction for x=0–0.4, revealed by the inelastic X-ray scattering experiments at **BL35XU**. The measurements were performed on single crystals with a typical dimension of ~1×1×1 mm^3. The dispersion of the transverse optical (TO1) mode markedly varies with x, whereas those of the acoustic mode (TA) and TO2 do not change notably. In particular, the energy of TO1 mode around the zone center decreases toward zero as the doping level approaches the ferroelectric phase, showing typical soft-mode behavior. More interestingly, strong coupling between soft phonon mode and magnetism was observed. Detailed temperature dependence of inelastic X-ray scattering for x=0.3 has revealed that the soft-mode energy hardens by as much as ~50% upon the magnetic order. From Lyddane-Sachs-Teller relation, this corresponds to 60% drop in dielectric constant at T_N, suggesting significant magnetodielectric effects in paraelectric systems as well [6].

Our results confirm the violation of the empirical "d^0-ness" rule for ferroelectric perovskites and open up a promising class of new multiferroic materials with large electric polarization and huge magnetoelectric coupling. Future studies may seek a ferromagnetic ground state in further Ba-substituted compounds, which may realize switching of magnetization (polarization) with electric (magnetic) fields feasible for novel spintronics devices.

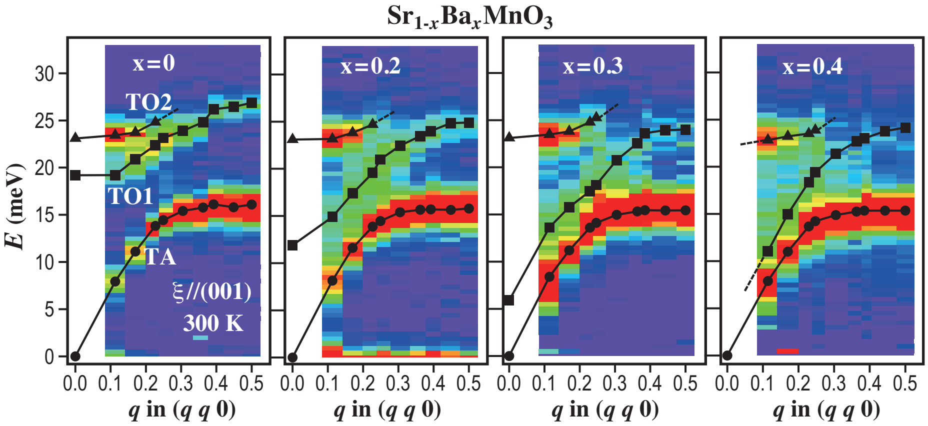

Fig. 3. Plots of the inelastic-X-ray-scattering intensity at 300 K in the energy-wave-vector (ω-q) plane in the [110] (Γ-M) direction for x = 0–0.4. The measurements were performed around the 005 Bragg reflection to detect the phonons with polarization vector ξ parallel to [001]. The closed symbols denote the phonon frequency ω_q, obtained by the fitting based on the damped harmonic oscillators. The points at q=0 were determined from the optical spectra. [6]

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