Ferroelectric transition and soft-phonon dynamics associated with off-center displacement of magnetic ions in perovskite Sr$_{1-x}$Ba$_x$MnO$_3$

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 $2p$ 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 magnetoelastic coupling. Recently, several first-principles calculations have pointed out the possible ferroelectric ground state with large polarization (tens of $\mu$C/cm$^2$) for $A$MnO$_3$ ($A$=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) antiferromagnetic ordering of off-center Mn$^{4+}$ ions. The 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),

$P_S=0.035$ $\mu$C/cm$^2$ and $T_C=0.035$ K.

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)
at approximately 30% of the maximum deviation from the cubic value (c/a=1). Based on a simple relation (c/a–1)×P^2, the P^2 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^2 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.

References