Perovskite Manganites Hosting Versatile Multiferroic Phases
with Symmetric and Antisymmetric Exchange Strictions

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Complete magnetoelectric (ME) phase diagrams of orthorhombic $R$MnO$_3$ with and without magnetic moments on the $R$ ions have been established. Three kinds of multiferroic ground states, the $ab$-cycloidal, the $bc$-cycloidal, and the collinear $E$-type phases, have been identified by the distinct ME responses. The electric polarization of the $E$-type phase dominated by the symmetric spin exchange on the magnetically induced multiferroics [1, 2], which can be classified into two types; one is driven by antisymmetric exchange striction in the commensurate collinear spin structure. Since orthorhombic ($o$-) perovskite $R$MnO$_3$ ($R$ = rare earth and $Y$) contains both the types, it provides an ideal laboratory to compare the respective magnetoelectric (ME) properties and extract the essential ingredients for the development of the magnetically induced multiferroics.

The ferroelectricity with a cycloidal spin order in $o$-R MnO$_3$ has been found for $R =$ Gd, Tb, Dy, and Eu$_{1-x}$Y$_x$ [3, 4, 5, 6, 7, 8]. Upon the application of magnetic field $B$ along the $a$ axis in the $ab$-cycloidal phase (in $Pbnm$ notation) of Eu$_{1-x}$Y$_x$MnO$_3$, the spin-cycloidal plane rotates from $ab$ to $bc$, accompanied by the polarization $P$ rotation from $a$ to $c$ [3, 9, 10]. The origin of the ferroelectricity has been discussed in terms of the spin-current model or the inverse Dzyaloshinskii-Moriya (DM) interaction represented by the relation, $P \sim \sum A e_{ij} \times (S_i \times S_j)$ [11, 12, 13, 14, 15, 16], in which $e_{ij}$ is the unit vector connecting the neighboring spins ($S_i$ and $S_j$) and both the spin-orbit and super-exchange interaction are relevant to the coefficient $A$. On the other hand, $o$-R MnO$_3$ with $R =$ Ho, Tm, Yb, Lu shows a commensurate collinear spin order with a propagation vector $q = (0, 1/2, 1)$, which is so-called $E$-type antiferromagnetic order [14, 15, 16, 17]. This phase is allowed to possess $P$ along $a$ due to symmetric exchange striction, which is independent of the spin-orbit interaction. Sergienko et al. proposed the emergence of substantially large $P$ up to 0.12 C/m$^2$ in the $E$-type phase with considering the ferromagnetic nearest-neighbor interaction $J_1$ mediated by $\epsilon_g$ electrons as a major source of the exchange striction [18, 19].

It has been a long standing problem how to enhance the correlation between magnetism and ferroelectricity in a solid. Possible solutions can be found in recent studies on the magnetically induced multiferroics [1, 2], which can be classified into two types; one is driven by antisymmetric exchange striction in the commensurate collinear spin structure, typified by TbMnO$_3$ [3, 4, 5, 6], and the other is driven by symmetric exchange striction in the incommensurate collinear spin structure. Since orthorhombic ($o$-) perovskite $R$MnO$_3$ ($R$ = rare earth and $Y$) contains both the types, it provides an ideal laboratory to compare the respective magnetoelectric (ME) properties and extract the essential ingredients for the development of the magnetically induced multiferroics. The ferroelectricity with a cycloidal spin order in $o$-R MnO$_3$ has been found for $R =$ Gd, Tb, Dy, and Eu$_{1-x}$Y$_x$ [3, 4, 5, 6, 7, 8]. Upon the application of magnetic field $B$ along the $a$ axis in the $ab$-cycloidal phase (in $Pbnm$ notation) of Eu$_{1-x}$Y$_x$MnO$_3$, the spin-cycloidal plane rotates from $ab$ to $bc$, accompanied by the polarization $P$ rotation from $a$ to $c$ [3, 9, 10]. The origin of the ferroelectricity has been discussed in terms of the spin-current model or the inverse Dzyaloshinskii-Moriya (DM) interaction represented by the relation, $P \sim \sum A e_{ij} \times (S_i \times S_j)$ [11, 12, 13, 14, 15, 16], in which $e_{ij}$ is the unit vector connecting the neighboring spins ($S_i$ and $S_j$) and both the spin-orbit and super-exchange interaction are relevant to the coefficient $A$. On the other hand, $o$-R MnO$_3$ with $R =$ Ho, Tm, Yb, Lu shows a commensurate collinear spin order with a propagation vector $q = (0, 1/2, 1)$, which is so-called $E$-type antiferromagnetic order [14, 15, 16, 17]. This phase is allowed to possess $P$ along $a$ due to symmetric exchange striction, which is independent of the spin-orbit interaction. Sergienko et al. proposed the emergence of substantially large $P$ up to 0.12 C/m$^2$ in the $E$-type phase with considering the ferromagnetic nearest-neighbor interaction $J_1$ mediated by $\epsilon_g$ electrons as a major source of the exchange striction [18, 19].

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The rich variety of magnetic phases of $o$-R MnO$_3$ reflects the $J_1$-$J_2$ competition that varies as a function of $R$-ion radius under the staggered orbital ordering of $3x^2-r^2$ and $3y^2-r^2$ type orbitals; As GdFeO$_3$-type lattice distortion becomes large, the antiferromagnetic next-nearest-neighbor interaction $J_2$ in the $ab$ plane becomes competitive with the ferromagnetic interaction $J_1$. So far, ME phase diagrams of $o$-R MnO$_3$ have been made for $R$ from La to Dy or Eu$_{0.5}$Y$_{0.5}$ (see Figs. 1(a) and 1(b)) [6, 8, 9, 14, 15, 20, 21, 22]. However, since $o$-R MnO$_3$ with a smaller $R$ ion than Dy needs a high pressure (HP) technique to synthesize, a complete ME phase diagram of $o$-R MnO$_3$ including the neighboring area between the cycloidal and the $E$-type phases is absent. In fact, although the ferroelectricity in the $E$-type phase has been confirmed for $o$-R MnO$_3$ with $R =$ Y, Ho [23], and Tm [17], intrinsic ME properties inherent to the Mn-spin arrangement alone remain unclear because of the intervention by the magnetic $R$ ions. Besides, the reported $P$ values vary widely depending on the materials. As a result, quantitative estimations of $P$ of the $E$-type phase and its microscopic origin are under intensive debate.

This Letter reports complete ME phase diagrams of a series of $o$-R MnO$_3$ with nonmagnetic $R$ ions ($R =$ Eu$_{1-x}$Y$_x$ and Y$_{1-y}$Lu$_{y}$) together with the system containing the magnetic $R$ ion ($R =$ Dy, Ho, Er, Tm, Yb). By using high-quality polycrystalline samples of $o$-R MnO$_3$, we have confirmed substantially large $P$ of nearly 5000 $\mu$C/m$^2$ for the $E$-type phases, yet one order of magnitude smaller than the predicted values [18, 19], and clearly demonstrated the generic transition of the

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multiferroic ground state from the $ab$-cycloidal, to $bc$-cycloidal, and eventually to the $E$-type phase upon decreasing the size of the $R$ ion. Furthermore, we found an enhanced ME response characteristic of a bicritical phase boundary formed by the different multiferroic phases.

Polycrystalline samples of $a$-RMnO$_3$ with $R =$ Dy and $R$ not larger than $Y$ were synthesized under HP by using hexagonal ($h$-) RMnO$_3$ as precursors. First, single crystals of $h$-RMnO$_3$ were prepared by a floating-zone method, and then heat-treated for 1 hr in the range of $1323 \sim 1373$ K under a HP of 5.5 GPa. Just for comparison between the single crystalline and polycrystalline specimens, polycrystalline samples of $a$-Eu$_{1-x}Y_x$MnO$_3$ with $x = 0.2$, 0.4, 0.6 were synthesized by heat treatment under HP using polycrystalline precursors prepared by grinding the single crystals of the $o$-phase. The grain-boundary effects on ME measurements are expected to be minimized owing to the high-quality precursors. However, as for $a$-Eu$_{1-x}Y_x$MnO$_3$ with $x = 0.75$, 0.9, the attempts to grow crystals gave the mixtures of the $h$- and the $o$-phases, which were adopted as the precursors. The linear change in the unit cell volume as a function of the $R$-ion radius ensures the successful syntheses of a series of $a$-RMnO$_3$ (Fig. 1(e)). For measurements of $P$, gold electrodes were deposited on the polished faces ($4 \text{ mm}^2$) of the platelet samples with typically 0.2 mm in thickness. As a poling procedure, an electric field of 800 V/mm was applied at 40 K, followed by cooling to 2 K. The displacement current was measured with increasing temperature at a rate of 5 K/min or sweeping $B$ at a rate of 100 Oe/sec, and was integrated as a function of time to obtain $P$. Magnetic susceptibility was measured by a SQUID magnetometer.

Figure 2 shows temperature dependence of $P$ of $a$-RMnO$_3$ prepared by the HP technique, with highlighting different responses of $P$ to external $B$ for $o$-Eu$_{0.1}Y_{0.9}$MnO$_3$ and $o$-LuMnO$_3$. As exemplified in Figs. 2(a) and 2(b), the compounds undergo a transition to an incommensurate (IC) sinusoidal phase at $T_{N1}$ where $\chi$ takes a maximum. Then, they show a second transition to the $E$-type phase at $T_{N2}$ where $P$ sets in. In Figs. 2(a) and 2(b), $P$ in zero magnetic field is plotted against temperature for nonmagnetic and magnetic $R$ ions, respectively. The compounds with $R = Eu_{0.1}Y_{0.9}$, $Y_{1-y}$Lu$_y$, Ho, Er, Tm, Yb are supposed to possess the $E$-type phase, and all the compounds but for $R =$ Er and Eu$_{0.1}Y_{0.9}$ exhibit fairly large $P$ of about 800 $\mu$C/m$^2$ at the lowest temperature. By contrast, $R = Eu_{1-x}Y_x$ ($x = 0.4$, 0.6, 0.75) and Dy sample possess relatively small $P$ values, implying the different mechanism of $P$ generation. We should note here that $o$-YMnO$_3$ and $o$-ErMnO$_3$ show the stepwise temperature dependence of $P$. The neutron diffraction studies have suggested the IC $q$ vectors of (0, 0.435, 1) and (0, 0.433, 1) for the magnetic ground states in $o$-YMnO$_3$ and $o$-ErMnO$_3$, respectively. Thus, these stepwise changes may indicate the presence of a small amount of the cycloidal or the sinusoidal phase which competes and thus coexists with the $E$-type phase. The signature for such a phase coexistence is explicitly found for $o$-Eu$_{0.1}Y_{0.9}$MnO$_3$ showing smaller $P$ and the larger effect of applied $B$ on $P$ in comparison with LuMnO$_3$ (see Figs. 2(c) and 2(d)). The possible phase coexistence in $o$-YMnO$_3$ and $o$-Eu$_{0.1}Y_{0.9}$MnO$_3$...
However, in the range of 0.4 $\theta < \pi$ the variation of $\theta$ is well systematic when the $R$-ion radius. According to the inverse $B$-induced phase transition from the $bc$-cycloidal phase to the $bc$-cycloidal phase, the system should be sub-

| FIG. 2: (Color online) Temperature dependence of polarization $P$ of $\alpha$-RMnO$_3$ with (a) nonmagnetic $R$ (Eu$_{1-x}$Y$_x$, Y$_{1-y}$Lu$_y$) and (b) magnetic $R$ (Dy, Ho, Er, Tm, and Yb) in the absence of external magnetic field $B$, and (c) $P$ of $\alpha$-Eu$_{0.1}$Y$_{0.9}$MnO$_3$ (multiplied by 2) and (d) $P$ of $\alpha$-LuMnO$_3$ measured in external $B$ perpendicular to the applied electric field and $\chi$ measured in external $B$ of 0.1 T on increasing temperature. $B$ was applied during the poling procedure as well as the measuring process.

The results are in accord with the $E$-type phase as the magnetic ground state for both compounds, because $P$ of this phase should be proportional to $S_i \cdot S_j$ and thus to $1-aB^2$ when the magnetization is proportional to applied $B$. As clearly seen in Fig. 3(a), the $R$-ion dependence of the transition temperature $T_{N2}$, below which the system becomes ferroelectric, makes a V-shaped feature near the boundary between the $bc$-cycloidal and the $E$-type phases. This feature reminds us of the bicriticality of two competing phases separated by the first-order phase boundary in the presence of weak randomness [27]. The $bc$-cycloidal and the $E$-type phases are likely separated by the first-order phase boundary [28], and Eu$_{1-x}$Y$_2$MnO$_3$ has also weak randomness introduced via alloying the $A$ site. Since Eu$_{0.1}$Y$_{0.9}$MnO$_3$ is located on the verge of the transition from the $E$-type phase to the $bc$-cycloidal phase, the system should be sub-

On the other hand, in the $ab$-cycloidal phase of Eu$_{0.6}$Y$_{0.4}$MnO$_3$ (Fig. 3(b)) and the $bc$-cycloidal phase of Eu$_{0.25}$Y$_{0.75}$MnO$_3$ (Fig. 3(c)), $P$ changes drastically at critical $B$ of about 5 T and 3 T, respectively, which signifies the occurrence of the $P$ rotation. In fact, the study of a single crystal of Eu$_{0.2}$Y$_{0.8}$MnO$_3$ showed the $B$-induced $P$ rotation from $P_a$ to $P_c$ at 4.5 T ($B \parallel a$) [9]. However, because our samples are polycrystals, we have to consider the relative orientations between $B$, $P$, and the crystallographic axes of a single domain. To explain the drastic change in $P$ under $B$, we considered specific situations which satisfy the conditions for the occurrence of the $B$-induced $P$ rotation (hereafter we formally use
Magnetic-field $B$ visualization
Eu
relational expressions between spin rotation in a single domain both for lattice and spin. The Zeeman energy during the rotation of spin spiral inclines to be perpendicular to $c$ for the $B \perp P_m$ shown in Fig. 3(c) can be well explained. The same explanation is applicable for the $P$ rotation from $P_a$ to $P_c$ (Fig. 3(b)).

In summary, we have revealed the magnetoelectric properties of a whole series of multiferroic $\alpha$-RMnO$_3$ with both nonmagnetic and magnetic $R$ and estimated the genuine values of $P$ ($\sim 5000 \mu C/m^2$) in the $E$-type phase, which is more than 10 times as large as that of the $bc$-cycloidal phase, yet one order of magnitude smaller than the predicted values [18, 19]. Furthermore, we found the bicritical feature near the phase boundary between the competing $bc$-cycloidal and $E$-type phases.

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[26] From the ratio between the polycrystalline and the single crystalline $P$ values in $\text{Eu}_6\text{Y}_{0.6}\text{MnO}_3$, the correction coefficient to convert the observed $P$ value into the expected.
value for the single crystal was estimated to be 6. All the $P$ values in Fig. 1(c) and Fig. 3(a) are corrected with this coefficient. This estimation is consistent with the naive expectation that the polycrystalline $P$ value, even if fully poled, should be $1/3$ of the single crystalline $P$ value and even smaller since the poing for the polycrystals cannot be complete because of the random poling directions.

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