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Giant magnetoelectric effect in multiferroic $HoMnO_3$ with a high ferroelectric transition temperature

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We present an example of giant magnetoelectric effect in a conventional multiferroic $HoMnO_3$, where polarization is very large ($\sim 56\ \mathrm{mC/m^2}$) and the ferroelectric transition temperature is higher than the magnetic ordering temperature by an order. We attribute the characteristic of the giant magnetoelectric effect to the ferroelectricity induced entirely by the off-center displacement of rare-earth ions with large magnetic moments. This finding suggests an avenue to design multiferroics with large polarization and higher ferroelectric transition temperature as well as large magnetoelectric effects.

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I. INTRODUCTION

Magnetoelectric multiferroics had been an interesting research field for several decades[1–4] and they were recently revived actively due to discoveries of spectacular magnetoelectric (ME) or magnetodielectric response in several materials[5–14] including orthorhombic manganites [(Gd, Tb, Dy) MnO_3, (Tb, Dy) Mn_2O_5], Kagome-staircase $Ni_3V_2O_8$, and hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$. Common features of these new materials are low ferroelectric transition temperature (T_C), small spontaneous polarization (P) (of the order of $100\ \mu\mathrm{C\,m^{-2}}$), and strong ME effects. Recent theoretical studies proposed that the ferroelectricity in these materials is induced by magnetic ordering of peculiar structures, such as noncollinear or long-wavelength magnetic structure.[15,16] Despite strong ME effects, magnetically driven ferroelectrics are not so convenient for practical applications in some sense because they have to be poled frequently by applying an electric field to maintain the single ferroelectric domain state. This is because they have too small polarization which can be easily broken into multidomain polarization and also because the ME effect arises mainly from the phase transition between the paraelectric state and the ferroelectric state.[13,14] Thus, multiferroics with a high T_C and a robust large polarization are more desirable in certain case because they easily maintains the single ferroelectric domain state once they are poled, exhibiting ME effect just by applying H.

Traditional way to achieve multiferroics with large P and high T_C is to search for conventional ferroelectrics containing magnetic ions. For example, lone-pair driven multiferroic $BiMnO_3$ ($BiFeO_3$),[17] geometrically driven multiferroic $YMnO_3$,[18] and $BaMnF_4$ ($BaCoFe_4$) (Ref. 4) have high T_C ranging from 700 to 1000 K and P larger than $10\ \mathrm{mC\,m^{-2}}$. However, in these "high T_C multiferroics," except a few cases of electric-field-induced magnetism in $BiFeO_3$ (Ref. 19) and $HoMnO_3$,[11] no examples are known that show giant ME effect, which here means a large change in the electric polarization (larger than $\sim 100\ \mu\mathrm{C/m^2}$) in a moderate magnetic field of a few tesla or less, comparable to the ME effect observed in the magnetically driven multiferroics. These high T_C multiferroics usually exhibit just slight anomalies in dielectric constants (ε) at T_M and show negligible H dependence of ε or P.[4,17,18] In this paper, we demonstrate a drastic change in P as well as ε at the magnetic transition temperatures and giant ME effects in a high T_C multiferroic $HoMnO_3$. Although the ME effect in $HoMnO_3$ was demonstrated by the magnetization in dependence on electric field,[11] the other case of the ME effect, i.e., the change in the electric polarization upon applied magnetic fields has not been fully investigated. Our crystallographic study suggests that the rare-earth Ho ions are wholly responsible for the ferroelectricity as in the case of $YMnO_3$.[20] We discussed the origin of the giant ME effect with the competing mechanism between the in-plane and interplane magnetic exchange interactions among Mn and Ho moments. Our study provides an interesting model for the behavior of polarization when the antiferromagnetic ordering of spins of ferroelectric active ions is triggered along the polarization direction. In addition, our result offers a clear-cut explanation for the ε anomalies at the magnetic transitions, of which the origin has been under debate.[21,22]

Extensive studies have been recently performed on hexagonal manganites, especially on $HoMnO_3$, due to its rich phase diagram and the strong spin-lattice coupling.[21,23,24] However, any direct observation on the evolution of the spontaneous P (which is in fact one of the most important order parameters in multiferroics) has not been successfully made. Earlier attempt detected only slight anomalies at the spin reorientation temperatures by the ac ME effect measurement but did not observe any noticeable change in P at the spin reorientation transitions.[25] $HoMnO_3$ exhibits ferroelectric ordering with $T_C \approx 900$ K and antiferromagnetic (AFM) ordering at $T_N \approx 70$ K.[11,18] Owing to the detailed studies in optical second-harmonic generation (SHG) (Refs. 11, 22, 26, and 27) and the neutron scattering,[28–30] the magnetic structure had been well established. Thus, $HoMnO_3$ is a prototypical system in which one can study the effect of magnetic structures on the dielectric properties and the electric polarization.

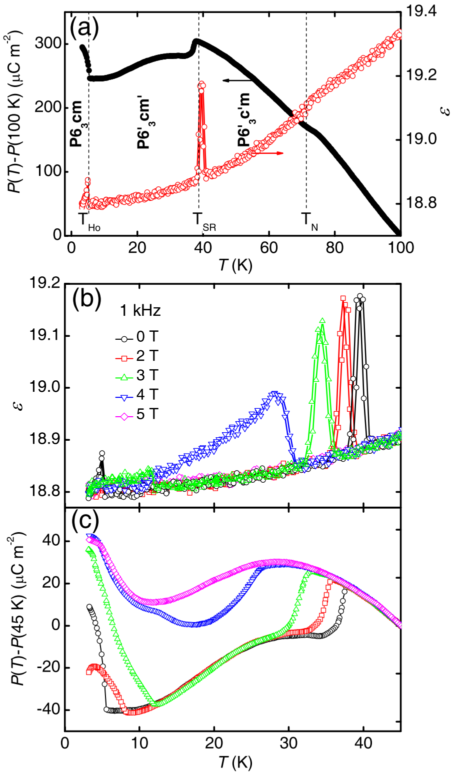

FIG. 1. (Color online) (a) T dependence of P (solid circle) and ε (open circle) for HoMnO$_3$ in zero H. Vertical dashed lines indicate magnetic phase boundaries. (b) T dependence of ε along the c axis in various H applied along the c axis. (c) T dependence of P along the c axis in H.

II. EXPERIMENT

HoMnO$_3$ single crystal was grown using a typical optical floating zone furnace. We used thin rectangular specimens with a cross sectional area of 5–10 mm^2 and a thickness of 0.2 mm. The dielectric constants and polarization were measured with a Quantum Design PPMS (physical property measurement system) down to 1.8 K. The dielectric constants were measured with a 1 kHz ac electric field applied along the c axis. The polarization was calculated by integrating the pyroelectric current which was measured while heating the sample at a rate of 4 K/min. Before pyroelectric current measurement, the sample was cooled down from 900 to 3 K in a varying electric field of 1–10 kV cm^{-1} along the c axis. Neutron powder-diffraction measurements on polycrystalline HoMnO$_3$ were performed with the NPDF instrument at Lujan Neutron Scattering Center, Los Alamos National Laboratory.

III. RESULT AND DISCUSSION

In Fig. 1(a), we show P and ε along the c axis as a function of temperature (T) for HoMnO$_3$ single crystal that was grown using an optical floating zone furnace. The long-range antiferromagnetic Mn^{3+} ordering in the ab plane at $\sim$72 K is evidenced by the slight anomalies both in ε and P. The slight kink in P can be associated with the overall expansion of the lattice along the c axis through the indirect spin-lattice coupling mechanism.[24] Upon further cooling, HoMnO$_3$ exhibits successive spin reorientation transitions at T_{SR} and T_{Ho} [Fig. 1(a)]. It has been known by optical SHG and the neutron scattering that Mn spins are reoriented in plane by 90° at $T_{SR} \approx 38$ K and Ho spins orders antiferromagnetically along the c axis at $T_{Ho} \approx 5$ K.[26,30] The most striking feature in Fig. 1(a) is the drastic change in P. P decreases abruptly at T_{SR} and increases back again at T_{Ho} upon cooling with a lower value of P in the $P6_3'cm'$ phase.

Coupling between magnetic and ferroelectric orders is more clearly manifested in Figs. 1(b) and 1(c). As H increases, T_{SR} significantly shifts to the lower T and the lower boundary of the $P6_3'cm'$ phase moves to the higher T; consequently the $P6_3'cm'$ phase shrinks and completely disappears at $\sim$5 T. We discovered that these ε anomalies are intimately associated with the P change. P demonstrates abrupt change at the T where ε shows a sharp peak, and as the peak in ε broadens out in H, the steplike change in P also becomes broad and disappear above 5 T. There have been a few explanations for the increase of ε in the intermediate phase (INT phase) between $P6_3'cm'$ and $P6_3'c'm$ a z-z ME coupling of magnetization (M) and P enabled by the Mn spin canting along the z axis,[21] the effect of unpinning between ferroelectric and AFM domain walls,[21] and the pronounced local ME effect due to massive formation of AFM domain walls observed by magneto-optical SHG.[22] Our polarization data measured using a poled HoMnO$_3$ crystal with single ferroelectric domain clearly indicate that the ε enhancement originates from the quasistatic change in P across the INT phase rather than transient effects confined within ferroelectric or AFM domain walls. Another noticeable thing in Fig. 1(c) is that the magnitude of total change in P ($\sim$80 μC m^{-2}) is almost comparable to the giant ME effect (order of 100 μC m^{-2}) observed recently in magnetically induced multiferroics.[13,14]

The evolution of ferroelectric properties across magnetic phases and the relation between ε and P are more clearly displayed in Figs. 2(a)–2(d). First, at 18 K, as expected from Figs. 1(b) and 1(c), $\varepsilon(H)$ increases sharply at $\sim$3.7 T and decreased again at $\sim$4.5 T with a plateau structure in the INT phase, accordingly $P(H)$ increases linearly in the INT phase. It should be noted that no appreciable ME effects are observed either in the low-field $P6_3'cm'$ or in the high-field $P6_3'c'm$ phase. However, a pronounced ME effect (which seemingly appears as a linear ME effect[5] with a linear ME coefficient, α_{33}, of $\sim$59 ps m^{-1}) is observed in the INT phase, which has been assumed to be of $P6_3'$ symmetry where the Mn spins rotate to an angle between 0° and 90° with respect to the a axis.[21] In fact even in this $P6_3'$ symmetry, a direct ME coupling between P and the in-plane Mn moment is not allowed.[1] The $P(H)$ at 18 K in Fig. 2(a) seems to increase linearly in the INT phase simply to connect two different P values in two well-defined phases ($P6_3'cm'$ and $P6_3'c'm$). This fact suggests that the change in P may be caused via a H-induced phase transition across a broad phase boundary (or $P6_3'$ phase) between a low-P state to a high-P state rather than via a linear ME effect in a specific symmetry that allows it.

Below T_{Ho}, ε and P show a more complicated field dependence. In Fig. 2(e), we summarized the H dependence of

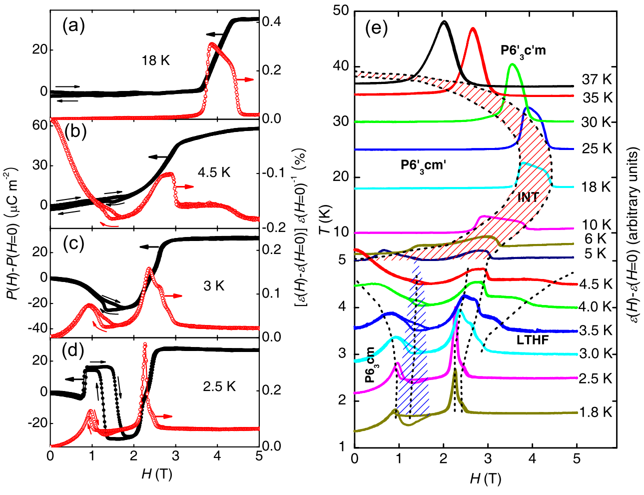

FIG. 2. (Color online) H dependence of the field-induced P and the ε change at (a) 18 K; (b) 4.5 K; (c) 3.0 K; (d) 2.5 K. The field-induced P was obtained by measuring the magnetoelectric current as a function of H, which was varied linearly with time at the uniform rate of 100 Oe s^{-1}. (e) T and H phase diagram for $HoMnO_3$ overlaid with ε change versus H for each T. Dashed lines indicate phase boundaries and hatched regions are the intermediate phase (>5 K) and the field hysteresis region (<5 K). Note that the T scale is expanded below 5 K.

TABLE I. Atomic parameters for $HoMnO_3$ refined from neutron powder-diffraction experiment at 40 K within the hexagonal space group $P6_3cm$. Refined lattice parameters are $a=6.1173(1)$ Å and $c=11.4107(2)$ Å.

		x	y	z
Ho1	$2a$	0	0	0.2747(5)
Ho2	$4b$	1/3	2/3	0.2314(4)
Mn	$6c$	0.3359(9)	0	0
O1	$6c$	0.3067(3)	0	0.1631(3)
O2	$6c$	0.6408(3)	0	0.3366(4)
O3	$2a$	0	0	0.4757(6)
O4	$4b$	1/3	2/3	0.0175(4)

ε and constructed a T versus H phase diagram. About 5 phase boundaries were identified by peak, deep, or steplike ε anomalies, which is pretty consistent with previous studies.[23,28] Complicated H-dependence of ε below T_{Ho} is also accompanied by a drastic change in P as shown in Figs. 2(b)–2(d). Below 3 K, P changes nonmonotonically as a function of H with the total change of P as large as ~58 $\mu C\ m^{-2}$ at 2.5 K. The magnetic symmetry of the low-T high-field (LTHF) phase is also still in question. There has been a proposition that the LTHF phase may be in $P6_3c'm'$ symmetry that allows linear ME effect.[26] However, no measurable linear ME effect was detected in our P versus H data at 3 and 2.5 K in high-field region (>3 T) as shown in Figs. 2(c) and 2(d).

In order to resolve the origin of the gigantic ME effect, we performed the neutron powder-diffraction study on $HoMnO_3$ in low T region. Although any noticeable crystallographic anomalies were not detected across magnetic transitions (this is generally expected because the value of P change in multiferroics usually corresponds to an average ionic displacement of the order of 10^{-4} Å), our study on the ionic structure enabled us to discuss the mechanism of the giant ME effect in terms of the origin of ferroelectricity and the magnetic exchange interaction among Mn and Ho moments. Table I shows atomic parameters for $HoMnO_3$ refined from neutron powder-diffraction experiment at 40 K. Figure 3 also displays the crystal structure based on our atomic parameters and the magnetic structure of $HoMnO_3$ for two magnetic symmetries. Recent studies have provided experimental and theoretical evidence that the electric polarization in hexagonal $YMnO_3$ is originated from a buckling of MnO_5 polyhedra and vertical shift of the Y ions with Mn ions remaining very close to the center of the oxygen bipyramids.[20,31] Our crystallographic analysis also showed that the vertical shift of rare-earth Ho ions is wholly responsible for the ferroelectricity in $HoMnO_3$ unlike the previous experimental study that indicated Mn ions considerably contribute to P by having different bond lengths between Mn and two apical oxygens in the bipyramid.[29] Our result points out that the giant change in P as a function of T and H should be related to the magnetic ordering of Ho ions that are directly responsible for the occurrence of ferroelectricity.

Upon cooling, at T_{SR}, the d-f exchange interaction between Mn and Ho moments induces ordering of Ho moments in $P6_3'cm'$ phase as shown in Fig. 3.[11,30] Ho1 and Ho2 moments order along the z with a ferrimagnetic arrangement in the x-y plane leaving uncompensated moments. Thus, in this temperature range, the magnetic exchange interactions are predominantly along the z axis through the Mn-Ho and the uncompensated interplane Ho AFM exchange interaction. This is strongly supported by the recent thermal-expansion

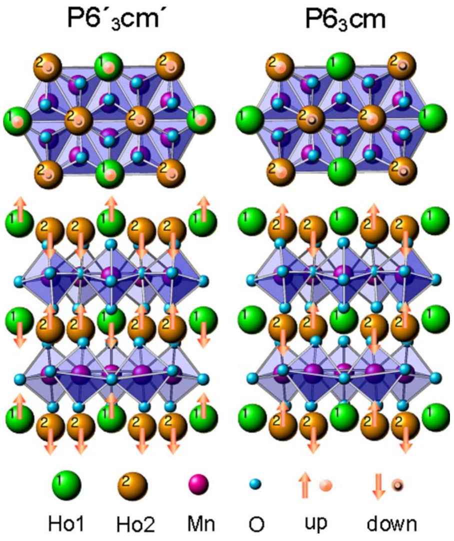

FIG. 3. (Color online) The crystallographic and magnetic structure of $HoMnO_3$ for two magnetic symmetries, $P6_3'cm'$ and $P6_3cm$. Crystallographic structure is based on the atomic parameters from our neutron powder-diffraction experiment. Magnetic structures are adopted from Refs. 11 and 30. Arrows indicate magnetic moments of Ho ion. Moments of Mn ions are not displayed.

data which showed lattice shrinkage at the magnetic transition T upon cooling along the direction of magnetic exchange interaction to gain exchange energy.[24] The lower value of P in the $P6'_3cm'$ phase suggests that the strong AFM interaction along the z accompanies a slight shift of ferroelectric active ions toward the centrosymmetric position. Note that the overall c-axis shrinkage at T_{SR} ($\Delta c/c \approx -2.4 \times 10^{-6}$) is too small to be responsible for the polarization change ($\Delta P/P \approx -10^{-3}$).[24] Upon further cooling, at T_{Ho}, the in-plane AFM ordering of Ho moments in $P6_3cm$ phase is triggered through the shorter Ho2-Ho2 exchange path (Ho1-Ho2 ≈ 3.56 Å, Ho2-Ho2 ≈ 3.53 Å).[11,30] The Ho1 moments surrounded by equal number of up and down moments of Ho2 ions, remain disordered. This onset of strong in-plane AFM Ho ordering, leaving no uncompensated in-plane moments, weakens the interplane exchange interaction along the z axis, which again allows P to restore its higher value in the $P6_3cm$ phase. This proposed mechanism of the competing in-plane and interplane exchange interactions, given by the peculiar crystallographic constraint, may explain the domelike phase diagram of $P6'_3cm'$ phase which becomes most stable at ~20 K and shrinks back as the competing in-plane Ho ordering starts to be effective and thus helps the suppression of the $P6'_3cm'$ phase at lower H in low T region as shown in Fig. 2(e).

IV. SUMMARY

We observed giant ME effect in a high T_C multiferroic $HoMnO_3$, which is intimately related to the off-center displacement of ferroelectric active Ho ions with very large moment (the largest total angular moment $J=8$ among rare-earth ions). This indicates that the highly anisotropic $4f$ electrons tightly coupled with the large rare-earth moment can play a crucial role in provoking ME effect even in conventional high T_C multiferroics.

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