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Large magneto (thermo) dielectric effect in multiferroic orthorhombic $LuMnO_3$

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We have investigated the relation between ferroelectric and magnetic orders of orthorhombic (*o*-) $LuMnO_3$ ceramics. The increase of dielectric constant ε exceeds 82% near incommensurate to commensurate E-type antiferromagnetic (AFM) spin ordering transition temperature T_L, reflecting a large magneto (thermo) dielectric response. Meanwhile, distinct anomalies and thermal hysteresis behavior are observed near this temperature in both temperature dependence of ε and specific heat C_p, indicating a strong coupling between FE and magnetic orders in *o*-$LuMnO_3$. Comparing to *o*-$HoMnO_3$, $TmMnO_3$, and $YbMnO_3$ with similar E-type AFM ground state, *o*-$LuMnO_3$ has the largest magneto (thermo) dielectric effect © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4722299]

I. INTRODUCTION

Multiferroic materials have attracted much attention in recent years since they are of both academic and technological importance.[1–5] The strongly coupled electric and magnetic degrees of freedom open the possibility of integration between the ferroelectric (FE) and magnetic properties, resulting in magnetoelectric (ME) or magnetodielectric (MD) effects. The MD effects showing anomaly dielectric behaviors correlating with magnetic transitions were observed in some exotic magnetic materials in recent years.[6–8] They are expected to lead to unprecedented device applications, in which the magnitude of dielectric constant can be controlled by the magnetic field. Still, few multiferroics are known and most of their MD effects are weak. Exploring multiferroic compounds with a large MD effect is vital to either fundamental studies or prospective applications. The rare-earth manganites $RMnO_3$ (R = La-Lu), as a typical single phase multiferroic system exhibiting strong correlation between FE and magnetic properties, deserves careful investigations.

The $RMnO_3$ (R = rare earth) have been found to crystallize into either an orthorhombically distorted perovskite structure (space group *Pbnm*) or a layer-like non-centrosymmetric hexagonal structure (space group $P6_3cm$), depending on the radius of rare-earth ions.[9,10] However, the hexagonal phase can be transformed into the metastable orthorhombic phase through high-pressure.[11–13] In particular, in these transformed compounds for R = Ho-Lu, an incommensurate (IC) antiferromagnetic (AFM) order occurs at Néel temperature $T_N \approx 40$ K.[14] It transforms into E-type AFM order at lock-in transition temperature T_L, with a modulation wave vector $k = 1/2$ along b direction.[15–17] A large ε enhancement of about 42% is revealed in *o*-$HoMnO_3$ between T_L and T_N.[18] Interestingly, it is due to the onset of ferroelectricity found within the E-type AFM phase in *o*-$HoMnO_3$.[19,20] The origin of ferroelectricity is different from that induced by spiral spin order in $TbMnO_3$ (Ref. 21) in that the polarization is believed to mainly come from the exchange interaction of Mn e_g states. Very recently, large polarization is also reported to be observed for R = Er-Lu with E-type AFM phase.[22] It is natural to expect a large MD effect in R = Tm, Yb, and Lu due to their large spontaneous polarization. Therefore, we focus our research on the origin and strength of MD effect in *o*-$RMnO_3$ and find an 82% increase of thermodielectric constant ε and 18% decrease of ε under 9 T around T_L for *o*-$LuMnO_3$, which are both larger than those reported in *o*-Y(Ho)MnO_3.[18] The largest MD effect observed in *o*-$LuMnO_3$ is of importance in the design of future information technology devices.

II. EXPERIMENT

The polycrystalline samples of *o*-$RMnO_3$ (R = Ho, Tm, Yb, and Lu) used in this study were transformed from their hexagonal phases under high pressure. The hexagonal manganites were first synthesized from R_2O_3 and Mn_2O_3 by solid state reactions as described elsewhere.[20,23] Then, the hexagonal powders encapsulated in gold foil to prevent contamination were heated at 1423 K for 20 min (1173 K and 30 min for R = Ho)[20] at 5 GPa, and rapidly cooled down to room temperature before releasing the pressure. The high-pressure products were single phase without trace of impurity within the resolution of the powder x-ray diffraction (XRD).

The XRD experiments were performed with M18AHF diffraction meter (MAC SCIENCE, Japan) employing Cu K_α radiation. The magnetic measurement was preformed in a Quantum Design (SQUID) magnetometer. The specific heat was measured in Quantum Design PPMS using the

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heat-pulse method from 2 to 200 K. The dielectric constant was measured using AH 2550 A Ultra-precision Capacitance Bridge and HP 4275A multi-frequency LCR meter with the frequency of 1 kHz.

III. RESULTS AND DISCUSSION

As we will show later that the largest MD effects is observed for $R = $ Lu, thus, we will focus our study on this sample. The crystal structure of high pressure synthesized *o*-$LuMnO_3$ can be indexed very well into the orthorhombically distorted perovskite with space group *Pbnm*. The obtained lattice parameters $a = 5.19712(7)$ Å, $b = 5.78837(9)$ Å, and $c = 7.29535(5)$ Å are close to the previously reported results based on a neutron powder diffraction data.[17]

Figure 1 presents the temperature (T) dependence of magnetic susceptibility $\chi(T)$ under different magnetic fields H. At high temperatures above 100 K, the reciprocal susceptibility $1/\chi$ plotted in the inset of Fig. 1 follows the Curie-Weiss law, with Curie temperature $\theta \approx -61.7$ K. The effective paramagnetic moment μ_{eff} is estimated to be 4.95 μ_B per formula unit, very close to the theoretical value of 4.9 μ_B for the Mn^{3+} high-spin state. At lower temperatures, a clear anomalous peak in $\chi(T)$ at $H = 1$ kOe is observed at about 40 K, indicating the onset of the IC magnetic ordering of Mn^{3+} ions at T_N, consistent with the temperature reported previously.[17] The data of $\chi(T)$ under $H = 30$ kOe are almost identical to that under 1 kOe, and the shift of T_N is negligible with increasing H. They are analogous to the case of *o*-$YMnO_3$, suggesting that the IC AFM phase is rigid with respect to magnetic fields.[18] However, the hysteresis behavior observed in the $\chi(T)$ of *o*-$YMnO_3$ near the lock-in transition is negligible in our data of *o*-$LuMnO_3$. We revealed such behavior in the specific heat C_p data of *o*-$LuMnO_3$ between cooling and warming cycles presented in the lower right inset of Fig. 2. As can be seen from the data, clear features are exhibited at two magnetic transition temperatures in the cooling curve: the paramagnetic to IC AFM transition is indicated by a small kink appearing at $T_N \approx 40$ K and the lock-in transition a peak at $T_L \approx 37$ K. The latter shows a clear thermal hysteresis behavior, verifying its first order nature.[14]

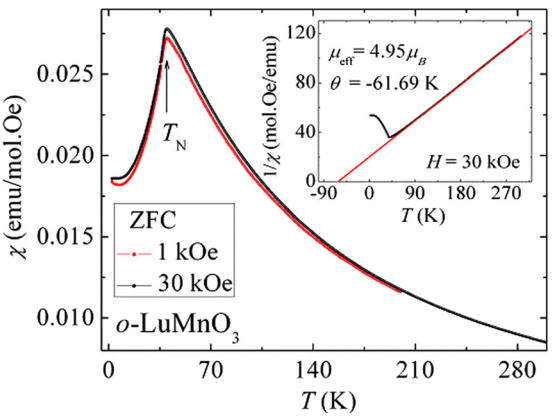

FIG. 1. T dependence of magnetic susceptibility $\chi(T)$ for *o*-$LuMnO_3$ under different magnetic fields. The kink represents the Néel temperature T_N. Inset: the inverse of susceptibility and the high-T Curie-Weiss fit (red solid line).

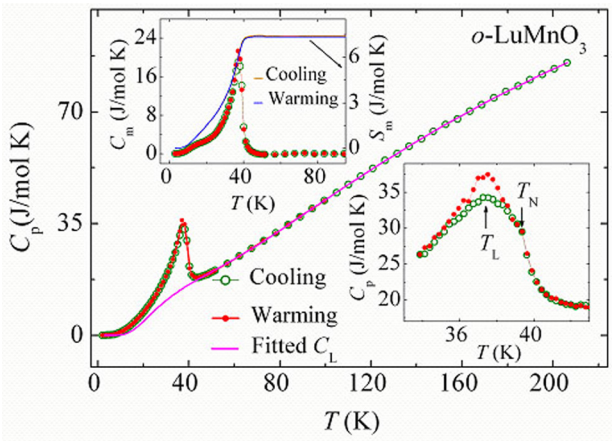

FIG. 2. Specific heat data with respect to temperature at zero-field in both cooling and warming processes. The magenta solid line shows the lattice specific heat C_L obtained from the fit of Einstein models. Upper inset: magnetic specific heat C_m and magnetic entropy S_m as a function of temperature. Right lower inset: T dependent specific heat C_p curves measured under zero-field in smaller temperature interval.

Generally, the specific heat of an insulator only consists of spin and lattice contributions. Therefore, the lattice specific heat C_L of our *o*-$LuMnO_3$ sample shown as magenta solid line in Fig. 2 is estimated from three Einstein modes and is subtracted from the total specific heat C_p to have the net magnetic specific heat C_m. The C_m and the magnetic entropy S_m calculated from the integral $S_m = \int (C_m/T) dT$ are shown in the upper inset of Fig. 2. The total change in the entropy below T_N is 6.43 and 6.52 J/mol K for the cooling and warming processes, respectively, which are smaller than the spin only value in the high spin Mn^{3+} states ($S = 2$): $N_A k_B \ln(2S + 1) = N_A k_B \ln 5 = 13.38$ J/mol K, where N_A and k_B are Avogadro's constant and Boltzmann's constant, respectively. This "missing" entropy suggests that the lattice is distorted during the lock-in transition owing to the occurrence of the coexisting FE phase transition. Our finding proves a close coupling between FE and E-type AFM orders.

To further explore the correlation between magnetic and dielectric properties, the temperature dependent dielectric constant $\varepsilon(T)$ for *o*-$LuMnO_3$ were measured, as illustrated in Fig. 3, in both cooling and warming cycles. Distinct thermal hysteresis behavior is observed below T_N because of the first order nature of the lock-in transition. Moreover, the ε rapidly increases below T_N and pass through maximum at T_L, showing pronounced steep λ-type peak feature in both cooling and warming courses. The relative enhancement of dielectric constant $\Delta\varepsilon/\varepsilon_N$ ($\Delta\varepsilon = \varepsilon_L - \varepsilon_N$) from T_N to T_L is more than 82%, which is higher than that of *o*-Y(Ho)MnO_3.[18] The larger increase of ε probably reflects a larger MD response in this compound. Furthermore, T_L are deduced from the peak temperature of $\varepsilon(T)$ in both cooling and warming processes in the Fig. 3 after Ref. 20, consistent with the magnetic specific heat peak temperatures in the Fig. 2, again indicating the strong connection between magnetic and dielectric properties.

For practical applications, the magnetic field sensitivity of dielectric properties is of important interest. We, therefore, show the magnetic field dependent dielectric constant of *o*-$LuMnO_3$ as well as other *o*-$RMnO_3$ ($R = $ Ho, Tm, and

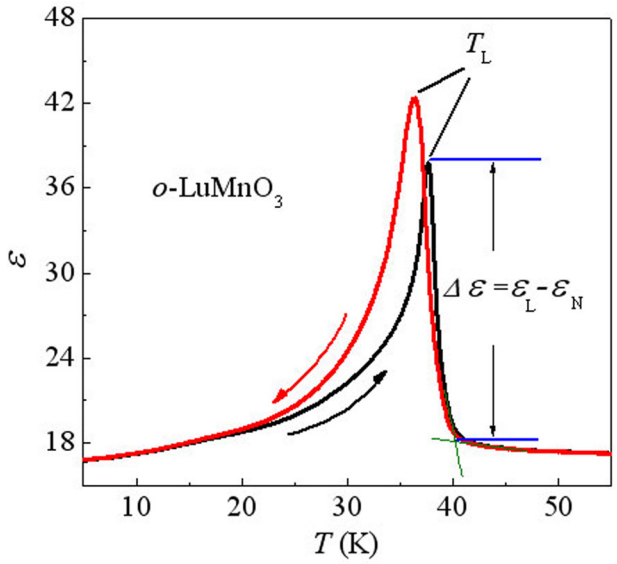

FIG. 3. T dependence of dielectric constant ε (T) at 1 kHz for o-$LuMnO_3$ sample, in both cooling and warming cycles. $\Delta\varepsilon$ is the difference between the dielectric constant at T_L (ε_L) and at T_N (ε_N).

Yb) samples at selected fields near T_L for comparison, as displayed in Fig. 4. It is found that, in all the samples (except o-$HoMnO_3$), the dielectric peak intensity at T_L is suppressed by the application of magnetic fields and shifts to lower temperature with increasing magnetic field. Especially for o-$LuMnO_3$, the field-induced changes in ε are larger than those in both (o-) $TmMnO_3$ and $YbMnO_3$ samples. To further quantitatively compare the magnitude of the MD effect, we display the isothermal MD changes (derived from the data in the Fig. 4) for o-$RMnO_3$ (R = Ho-Lu) at various temperatures near T_L in the Fig. 5. The relative MD change is defined as MD (%) = $[\varepsilon(H)- \varepsilon(0)]/\varepsilon(0)$, where $\varepsilon(H)$ is the magnetic field dependent ε, and $\varepsilon(0)$ is the ε value at zero-field. For (o-)

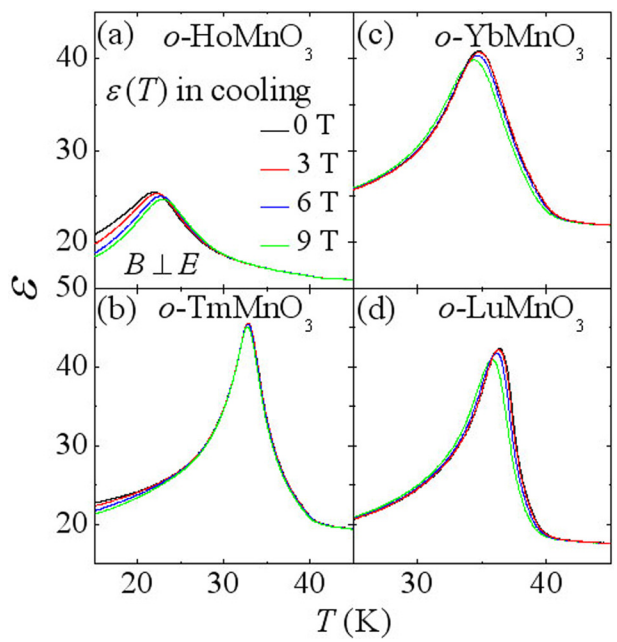

FIG. 4. ε(T) under different magnetic fields for o-$RMnO_3$ (R = Ho, Tm, Yb, and Lu) in the cooling process. In particular, the R = Ho data come from Ref. 20.

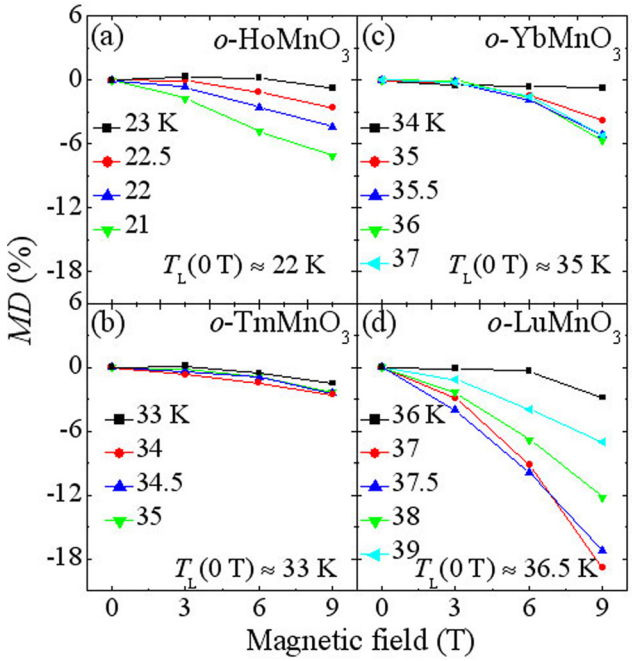

FIG. 5. The isothermal MD (derived from the data in the Fig. 4) as a function of the magnetic field at various temperatures near T_L.

$HoMnO_3$, $TmMnO_3$ and $YbMnO_3$ samples, their MD around T_L are less than 8%, 3%, and 6% at 9 T, respectively. While, in o-$LuMnO_3$, it exceeds 18% at 9 T, which is also larger than the values reported for (o-) $YMnO_3$ and $HoMnO_3$.[18] Our results suggest that o-$LuMnO_3$ has the largest MD effect than any other o-$RMnO_3$ (R = Y, Ho, Tm, and Yb) compounds. It may be related to the most significant suppression of the dielectric peak intensity near T_L in o-$LuMnO_3$.

IV. CONCLUSIONS

In summary, we have proved the existence of a large magneto (thermo) dielectric effect in o-$LuMnO_3$ by dielectric constant ε, magnetic susceptibility χ, and specific heat C_p measurements. An increase of ε in the o-$LuMnO_3$ going beyond 82% below $T_N \approx 40$ K is found, where ε peaks at the lock-in transition temperature T_L at which a change from incommensurate to commensurate E-type AFM ordering takes place. The magnetic-field causes a change as large as about 18% in the dielectric constant of o-$LuMnO_3$ under 9 T in the vicinity of T_L, much larger than that in (o-) $HoMnO_3$, $TmMnO_3$, and $YbMnO_3$ samples.

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