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Multiferroic Properties of $\text{CaMn}_7\text{O}_{12}$

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We report that $\text{CaMn}_7\text{O}_{12}$ is a new magnetic multiferroic material. The appearance of a ferroelectric polarization coinciding with the magnetic phase transition (~ 90 K) suggests the presence of ferroelectricity induced by magnetism, further confirmed by its strong magnetoelectric response. With respect to other known magnetic multiferroics, $\text{CaMn}_7\text{O}_{12}$ displays attractive multiferroic properties, such as a high ferroelectric critical temperature and large polarization. More importantly, these results open a new avenue to search for magnetic multiferroics in the catalogue of doped oxides.

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I. INTRODUCTION

Multiferroics, with coexisting ferroelectric (FE) and magnetic orders that are mutually coupled, have attracted considerable interest for their technological relevance and fundamental science challenges.¹⁻³ To avoid the natural exclusion between ferroelectricity and magnetism,⁴ there are several routes to achieve multiferroicity. Based on the microscopic origin of the FE polarization (P), multiferroics can be classified into two families.⁵ Type-I multiferroics, where ferroelectricity and magnetism have different origins, often present high critical temperatures (T_C 's) and polarizations. However, the coupling between magnetism and ferroelectricity is usually weak. In contrast, type-II multiferroics (i.e. magnetic multiferroics), where the ferroelectricity is caused by a particular magnetic order, are more interesting and important since both orders tend to be strongly coupled.

Since the discovery of TbMnO_3 ,⁶ several magnetic multiferroics have been found. However, in the spiral spin multiferroics, the FE polarizations are regulated by the Dzyaloshinskii-Moriya (DM) interaction,^{7,8} which originates from the spin-orbit coupling and, thus, is very weak. This problem can be partially overcome in exchange-striction multiferroics. For instance, the predicted FE P in the E-type AFM manganites is of the order of $10000 \mu\text{C}/\text{m}^2$,^{9,10} which has been recently confirmed in experiments.¹¹⁻¹³ However, the FE T_C 's of the E-type AFM manganites remain low (typically ~ 30 K)¹¹ due to the magnetic frustration, namely the competition between nearest-neighbor (NN) and next-nearest-neighbor (NNN) exchange interactions.^{14,15}

Among all the magnetic multiferroics, the narrow-bandwidth perovskite manganites define a very fertile field. In recent years, the undoped REMnO_3 case ($RE = \text{Rare Earth}$) has been intensively studied, both theoret-

ically and experimentally. In addition, recent theoretical calculations predicted that *doped* manganites may provide additional magnetic multiferroic phases with even better physical properties.^{16,17} The expected spin structures of the new multiferroics are rather complex, involving zigzag-chains, and they are stabilized by mechanisms that do not involve superexchange frustration, such as electronic self-organization into stripes¹⁷ or correlation effects,¹⁶ that may be strong enough to obtain a high FE T_C . Also, the origin of the FE P in these systems involves several aspects: not only a DM contribution from noncollinear spin pairs can be present, but also additional components triggered by spin dimmers and charge-orbital ordering are available.^{16,17} Clearly, it would be important to test the general prediction of multiferroic complex states in real doped manganites.

In this manuscript, we will study the quadruple manganite $\text{CaMn}_7\text{O}_{12}$, which is an ideal candidate to host new magnetic multiferroic phases. From the structural point of view, $\text{CaMn}_7\text{O}_{12}$ belongs to the quadruple $(\text{AA}'_3)\text{B}_4\text{O}_{12}$ family, which becomes more explicit by writing the chemical formula as $(\text{Ca}^{2+}\text{Mn}_3^{3+})(\text{Mn}_4^{3.25+})\text{O}_{12}^{2-}$.¹⁸ This perovskite-derived structure consists of a three-dimensional array of corner-sharing BO_6 octahedra, which are considerably tilted due to the small size of the A-site ($\text{Ca}^{2+}\text{Mn}_3^{3+}$), as shown in Fig. 1(a). Therefore, the B-site Mn-O-Mn bond is short and bended, giving rise to a very narrow bandwidth system with robust DM interaction, considered very important in multiferroic manganites. In addition, different from normal perovskite manganites, the Jahn-Teller (JT) distortion (Q_2 mode) in $\text{CaMn}_7\text{O}_{12}$ is weak.¹⁹ This weak Q_2 mode and a moderate Jahn-Teller Q_3 mode can stabilize some multiferroic phases (such as the predicted "SOS" phase)¹⁷ which are difficult to form in normal narrow bandwidth perovskite manganites with strong JT

distortion. Furthermore, in this quadruple structure, the A-site $\text{Ca}^{2+}\text{Mn}^{3+}$ are fully ordered, different from the random distribution of A-site cations in standard chemically doped perovskites. The reduction of quenched disorder provides an extra advantage to stabilize complex spin patterns at a relatively high temperature (T).

Quadruple perovskite manganites have not been much studied,^{18,20,21} particularly with regards to their multiferroicity. Imamura *et al.* and Mezzadri *et al.* reported room- T ferroelectricity (evidenced from the cation displacements) in $\text{BiMn}_7\text{O}_{12}$.^{22,23} However, its polarization is difficult to measure due to its low resistivity at room- T . Since the ferroelectricity in $\text{BiMn}_7\text{O}_{12}$ is caused by the well-known $6s^2$ lone pair of Bi^{3+} instead of a magnetic order, then this material is not a magnetic multiferroic. As for $\text{CaMn}_7\text{O}_{12}$, Sánchez-Andújar *et al.* reported a magnetodielectric effect at low T .²⁴ However, it has been well recognized that a magnetodielectric effect may be unrelated to a true magnetoelectric coupling.²⁵

II. METHODS

Polycrystalline samples of $\text{CaMn}_7\text{O}_{12}$ were prepared using the standard sol-gel method. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ (50%) were chosen as reagents and treated in the same way as reported in previous literature.^{27,28} To avoid the impurities Mn_2O_3 , Mn_3O_4 or maybe CaMnO_3 , the obtained sol-gel precursors were ground and then heated in air at $800^\circ\text{C}/48\text{ h}$, $925^\circ\text{C}/48\text{ h}$, and $950^\circ\text{C}/48\text{ h}$, respectively, with intermediate grindings. The resultant powders were pressed into pellets and sintered in air at 970°C for 60 h. As a result of a careful preparation, the samples are found to be in a single phase, as shown in Fig. 1(b). The average grain size (diameter) is $\sim 1.0\ \mu\text{m}$ according to the scanning electron microscope (SEM) micrograph (not shown).

The sample crystallinity was characterized by X-ray diffraction (XRD) with $\text{Cu } K\alpha$ radiation at room temperature. The dc magnetic susceptibility (χ) as a function of T was measured using the Quantum Design superconducting quantum interference device (SQUID), and specific-heat measurements using the “physical properties measurement system” (PPMS) were performed. To measure the dielectric constant ε and polarization P , gold pastes were used as electrodes while the varying T and magnetic field H environment was provided by PPMS. The $\varepsilon - T$ data were collected using the HP4294 impedance analyzer at various frequencies. The polarization P as a function of T was measured using the pyroelectric current method plus a careful exclusion of other possible contributions, such as those from the de-trapped charges. The samples were first poled under selected electric fields from 120 K to 8 K, and then the pyroelectric currents, using the Keithley 6514A electrometer, were integrated by warming the sample at different ramping rates of $2 \sim 6\ \text{K}/\text{min}$, respectively. At present, this pyroelectric currents process is the most widely used

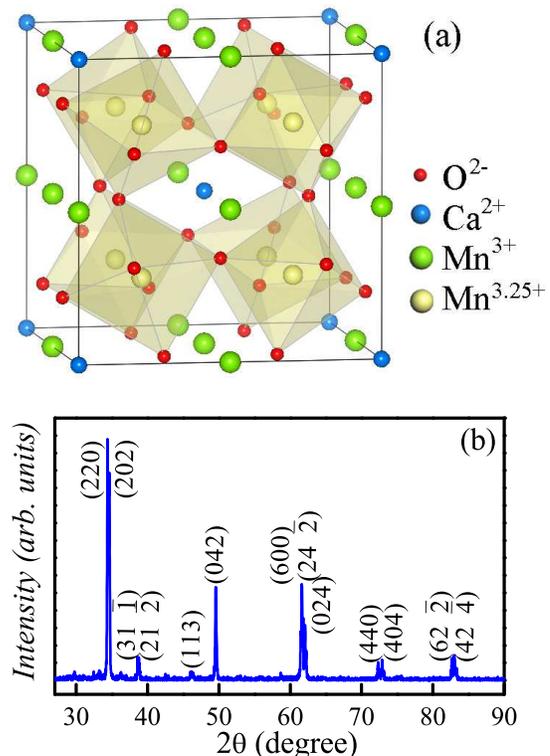


FIG. 1. (color online) (a) Sketch of the crystal structure of $\text{CaMn}_7\text{O}_{12}$. The A(A')-site $\text{Ca}^{2+}/\text{Mn}^{3+}$ cations are ideally ordered. The lattice is cubic ($\text{Im}\bar{3}$ with a lattice constant $a \approx 7.35\ \text{\AA}$) above $\sim 440\ \text{K}$, while below this temperature it distorts into a rhombohedral arrangement ($\text{R}\bar{3}$ with lattice constants $a \approx 10.44\ \text{\AA}$ and $c \approx 6.34\ \text{\AA}$).^{18,19} The $\text{Mn}^{3.25+}$ cations locate in the center of oxygen octahedra, which become (nominal) $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordered below $250\ \text{K}$.¹⁹ Due to the small size of $\text{Ca}^{2+}\text{Mn}^{3+}$, the lattice is shrunk and the oxygen octahedra are more tilted when compared with other perovskite manganites. For example, the NN distance of B-site Mn's (nominal bond length) is only $\sim 3.68\ \text{\AA}$ and the B-site Mn-O-Mn bond angle is $\sim 138^\circ$,¹⁹ both much smaller than those of standard perovskite manganites (e.g. $\sim 3.88\ \text{\AA}$ and $\sim 160^\circ$ for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$).²⁶ (b) The room- T XRD spectrum.

method to measure ferroelectricity in magnetic multiferroics, since their polarizations are usually too weak (typically 3 – 4 orders of magnitude weaker than traditional ferroelectrics) to be verified by FE hysteresis loops.

III. RESULTS AND DISCUSSION

Let us first consider the magnetic properties. The T -dependence of the magnetic susceptibility (χ) is shown in Fig. 2(a). Upon cooling, first, a small kink in χ appears at $T_{\text{N}1} \sim 90\ \text{K}$, indicating an AFM transition, in agreement with previous literature.^{19,29–31} When the sample is further cooled down to $T_{\text{N}2} \sim 48\ \text{K}$, χ rapidly grows. Below $T_{\text{N}2}$, the zero-field-cooling (ZFC) and field-cooling (FC) χ 's diverge from each other. Using the Curie-Weiss law to fit the data above $\sim 90\ \text{K}$, a good paramagnetic (PM) behavior above $T_{\text{N}1}$ is observed, as indicated by the

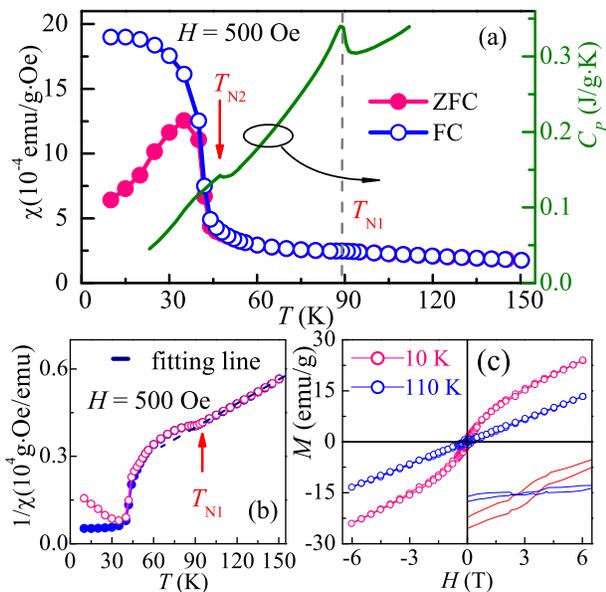


FIG. 2. (color online) (a) The magnetic susceptibility (χ , left axis, FC and ZFC) and specific heat (C_p , right axis) versus T . (b) Inverse of χ (FC and ZFC) versus T . The Curie-Weiss law provides a good fit above T_{N1} . (c) The magnetic hysteresis loops at two typical T 's. The loops show PM behaviors (linear $M - H$ relationship without a coercive field) above T_{N1} and a weak FM-like signal (with a coercive field ~ 450 Oe) at a low T . The inset in the fourth quadrant is a zoomed view near $H = 0$. The horizontal and vertical scales are $[-3000, 3000]$ Oe and $[-5, 5]$ emu/g, respectively.

dashed line in Fig. 2(b). The extrapolated Curie-Weiss temperature Θ is ~ -50 K. Such a Curie-Weiss behavior and a negative Θ confirm the PM-AFM transition at T_{N1} . The phase transitions at T_{N1} and T_{N2} are further confirmed by the specific heat C_p , which exhibits sharp anomalies at both T 's, as shown in Fig. 2(a). In addition, magnetic hysteresis loops were measured, as shown in Fig. 2(c), indicating a weak ferromagnetic (FM) signal at low T 's.

The dielectric and FE properties were the main focus of this effort. First, the dielectric constant ϵ as a function of T , was measured at frequency $f = 1$ kHz, as shown in Fig. 3(a). A small but clear anomaly in $\epsilon(T)$ was identified at 90 K indicating a FE transition, coinciding with T_{N1} , the AFM transition point. Even more interesting, as shown below a FE polarization emerges at this AFM transition, suggesting the presence of ferroelectricity induced by magnetism. In other words, $\text{CaMn}_7\text{O}_{12}$ is here shown to be a magnetic multiferroic material. The reliability of the measured $P(T)$ is evidenced by the pyroelectric current (I) as a function of T with different warming rates: 2 K/min, 4 K/min, and 6 K/min, as indicated in Fig. 3(a). The peaks of the three $I - T$ curves do not shift along the T -axis, and the integral of $I(t)$ for the three curves are almost identical (not shown), indicating that the de-trapped charges, if they exist, do not contribute appreciably to the measured current and, then, the intrinsic pyroelectric current is dominant. We also

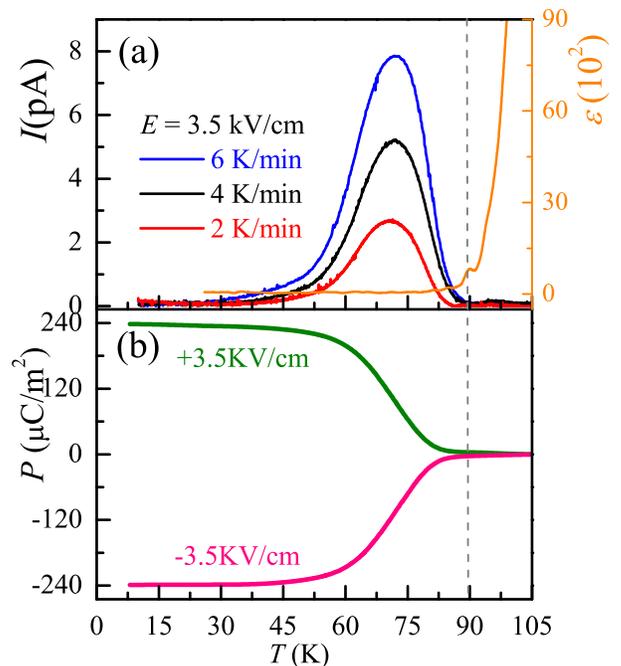


FIG. 3. (color online) (a) The pyroelectric currents, under different warming rates, (I , left axis) and the dielectric constant (ϵ , right axis) vs. T . The poling electric field is 3.5 kV/cm. Note that there is a peak in the $\epsilon - T$ curve at T_{N1} . (b) The (symmetric) FE polarizations under positive and negative poling electric fields.

measured $P(T)$ under positive and negative poling electric fields $E = \pm 3.5$ kV/cm, respectively. The polarity of P is determined by the sign of E , as shown in Fig. 3(c), confirming the existence of ferroelectricity in $\text{CaMn}_7\text{O}_{12}$.

Under the poling field $E = 3.5$ kV/cm, the measured P reaches up to $\sim 240 \mu\text{C}/\text{m}^2$ at 8 K. However, the real saturated FE P is much larger due to the high coercive field. For example, by using a larger poling field $E = 7$ kV/cm (the highest field we can apply in the current stage), the FE P increases to $\sim 450 \mu\text{C}/\text{m}^2$ at 8 K. The E -dependence of P at 8 K is presented in Fig. 4(b). Since the $P - E$ curve does not saturate up to $E = 7$ kV/cm, a larger saturated P is to be expected, which could be measured with higher poling fields (or using thin films).^{12,13} In addition, a tiny anomaly in the pyroelectric current emerges at T_{N2} under $E = 7$ kV/cm, as shown in Fig. 4(a), which gives rise to a small increase of P . However, this anomaly at T_{N2} is not distinct under $E = 3.5$ kV/cm, as shown in Fig. 3(a).

The existence of magnetic multiferroicity has been further confirmed by the presence of a strong magnetoelectric (ME) response, as shown by the magnetic field, H , dependence of P . During the measurement, the sample is cooled from 120 K to 8 K under various H 's and using a fixed $E = 3.5$ kV/cm. As shown in Fig. 4(c), the measured P is suppressed by the applied H , e.g. it decreases to $\sim 160 \mu\text{C}/\text{m}^2$ at 8 K under $H = 9$ T, while T_c is almost unchanged which suggests a robust magnetic transition. The ME response, defined as $(P(0) - P(H))/P(0) \times 100\%$,

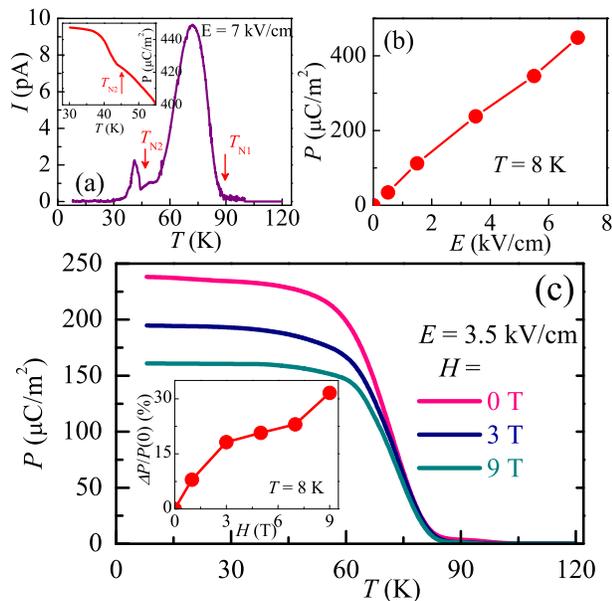


FIG. 4. (color online) (a) The pyroelectric currents under a large E . An anomalous contribution appears around T_{N2} . Inset: The corresponding FE P around T_{N2} . (b) The FE P at 8 K vs. E , which does not saturate up to 7 kV/cm (the maximum field we can apply to the bulk sample). (c) The suppression of FE P by a magnetic field. Inset: the magnetoelectric response ratio.

reaches up to 30% under $H = 9$ T (see inset of Fig. 4(c)). Considering the polycrystalline nature of the sample, this ME response is large (i.e. comparable with those of $REMnO_3$ ($RE=Eu_{1-x}Y_x$ and Lu) polycrystals),¹¹ implying the presence of magnetism-induced ferroelectricity.

Compared with other magnetic multiferroics, the multiferroicity of $CaMn_7O_{12}$ is remarkable. First, the observed FE T_c is considerably higher than in typical magnetic multiferroics. For example, the T_c 's of orthorhombic $REMnO_3$ ($RE=Tb, Dy, Eu_{1-x}Y_x, Ho, Y, Tm,$ and Lu) are all below 35 K.¹¹ Second, the observed P (saturated value $> 450 \mu C/m^2$) is quite large as compared with other magnetic multiferroics, considering the polycrystalline nature of the sample. For $REMnO_3$, the FE P of a high-quality polycrystal is estimated to be only 1/6 of the single crystal one.¹¹ Therefore, the expected saturated P of $CaMn_7O_{12}$ single crystal can be larger than $2700 \mu C/m^2$, which is already larger than in $DyMnO_3$ ($\sim 2000 \mu C/m^2$). Even comparing with the E-AFM manganites (e.g. $\sim 600 - 900 \mu C/m^2$ for high-quality polycrystals with a poling field $E = 8$ kV/cm),¹¹ the value $450 \mu C/m^2$ (with $E = 7$ kV/cm) of $CaMn_7O_{12}$ is remarkable. The large P of $CaMn_7O_{12}$ could originate from the following two mechanisms. First, a robust DM interaction may exist in this material. As shown in Fig. 1(a), the B-site Mn-O-Mn bonds are much more bending than those in normal perovskites, which gives rise to a larger DM interaction.⁷ Second, the exchange striction^{9,10} may also exist in these materials.

Finally, it should be noted that the spin order of $CaMn_7O_{12}$ is very complex. Earlier neutron studies^{19,29,32} found that the fittings using collinear spin modes were not quite successful.^{18,19} Thus, it is crucial to carry out additional high-precision neutron investigations to figure out better the magnetic order of $CaMn_7O_{12}$, which is essential to further clarify its microscopic multiferroic mechanism.

Recently, after our first submission of this manuscript, we noticed an experimental investigation by Johnson *et al.* that also reported the existence of *magnetic multiferroicity* in this compound, and in addition they find a noncollinear spin order in this material via neutron studies.³³ Their results agree with our data quite well, as exemplified by the following facts:

- (1) The FE T_c 's are identical at T_{N1} .
- (2) The FE P reported by Johnson *et al.* is quite large: up to $2870 \mu C/m^2$ for a single crystal,³⁴ which is about 6 times our maximum value $450 \mu C/m^2$ for polycrystalline samples.
- (3) The P - T curves are also very similar.
- (4) Their neutron studies suggest that the FE P is induced by a noncollinear spin order, compatible with our report of a strong magnetoelectric response.
- (5) A small anomaly in P at T_{N2} was also noticed in their single crystal with a poling field $E = 4.4$ kV/cm.³⁴

In Ref. 33, the spin order between T_{N1} and T_{N2} has been resolved: this spin order is quite complex with a non-collinear structure (involving both the A-site and B-site Mn cations) and it contradicts earlier neutron diffraction results.²⁹ However, the magnetic order below T_{N2} remains unclear. Therefore, overall the magnetic multiferroic character of $CaMn_7O_{12}$ is nicely confirmed by Johnson *et al.*, while the clarification of the underlying microscopic mechanism still needs further experimental and theoretical careful investigations.

IV. CONCLUSION

In summary, we have found that the quadruple perovskite $CaMn_7O_{12}$ is a magnetic multiferroic material. Its multiferroic properties are interesting (large- P , high- T_c , and a strong magnetoelectric response) when compared with other known magnetic multiferroic manganites. A new physical mechanism appears to be needed to explain our results. Considered more broadly, these results for $CaMn_7O_{12}$ open a new route to pursue higher- T_c and larger- P magnetic multiferroics via the use of doped oxides. This is interesting since most previous verified multiferroic materials are actually undoped, since doping was expected to bring extra carriers and destroy the insulating behavior required by ferroelectricity. Our results show that this is not necessarily correct for narrow-bandwidth oxides. Besides further investigating the properties of $CaMn_7O_{12}$, our effort suggests that it would be important to search for additional new magnetic multiferroics in the quadruple perovskite family.

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