Magnetic and electric properties of CaMn$_7$O$_{12}$ based multiferroic compounds: effect of electron doping

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Abstract
The mixed valent multiferroic compound CaMn$_7$O$_{12}$ is studied for its magnetic and electric properties. The compound undergoes magnetic ordering below 90 K with a helimagnetic structure followed by a low temperature magnetic anomaly observed around 43 K. This study shows that the magnetic anomaly at 43 K is associated with thermal hysteresis indicating the first order nature of the transition. The compound also shows field-cooled magnetic memory and relaxation below 43 K, although no zero-field-cooled memory is present. A clear magnetic hysteresis loop is present in the magnetization versus field measurements, signifying the presence of some ferromagnetic clusters in the system. We doped trivalent La at the site of divalent Ca expecting to enhance the fraction of Mn$^{3+}$ ions. The La doped samples show reduced magnetization, although the temperatures associated with the magnetic anomalies remain almost unaltered. Interestingly, the spontaneous electrical polarization below 90 K increases drastically on La substitution. We propose that the ground states of the pure as well as the La doped compositions contain isolated superparamagnetic like clusters, which can give rise to metastability in the form of field-cooled memory and relaxation. The ground state is certainly not spin glass type, as is evident from the absence of zero-field-cooled memory and frequency shift in the ac susceptibility measurements.

(Some figures may appear in colour only in the online journal)

1. Introduction
In recent times there has been tremendous interest in multiferroic materials for their versatile technological importance [1–4]. A multiferroic possesses both ferroelectricity and magnetic order, and it is particularly important when the magnetic and electric phenomena remain intercoupled. This magnetoelectric (ME) effect is quite promising for memory devices, and at the same time has fundamental importance.

Ferroelectricity and magnetism in a material are generally mutually exclusive, and even when they occur together in a material they have their different sources. As a result the ME coupling is found to be quite weak. Examples of such multiferroics are found among transition metal oxides such as BiFeO$_3$, BiMnO$_3$, etc [5, 6]. However, in the last decade several other transition metal oxide based materials were discovered where the magnetic order itself is responsible for the development of ferroelectric polarization [7]. Such materials are often referred to as magnetic multiferroic, and examples include rare-earth manganites (TbMnO$_3$, DyMnO$_3$, YMnO$_3$, TbMn$_2$O$_5$, etc) [8, 9], vanadate (Ni$_3$V$_2$O$_8$) [10], chromate (CoCr$_2$O$_4$), etc. The existence of direct coupling between magnetic and electric polarizations in these materials is of fundamental importance. However, the ME coupling strength is still rather weak in these materials and the value of the spontaneous electric polarization ($P$) is a few
orders of magnitude smaller than those of conventional proper ferroelectrics, along with a low value of ferroelectric transition temperature. Consequently they are not useful for practical applications.

Very recently, a new magnetic multiferroic, CaMn$_7$O$_{12}$, has been reported in the literature which shows large ferroelectric polarization (2870 $\mu$C m$^{-2}$) below the helical magnetic ordering temperature of 90 K [11, 12]. CaMn$_7$O$_{12}$ belongs to the quadrupole (AA)$_3$B$_2$O$_{12}$ family of manganites and has a perovskite derived crystal structure with trigonal space group $R\bar{3}$ [13, 14]. In this structure, Mn has three crystallographically inequivalent sites with Wyckoff positions 9e, 9d and 3b. The 9e and 9d sites are occupied by Mn$^{3+}$ ions (three Mn ions at each site per formula unit), and the 3b site is occupied by one Mn$^{4+}$ ion [11, 12, 15, 16]. As is evident, the compound is mixed valent with the Mn$^{3+}$ to Mn$^{4+}$ ratio being 6:1. The Mn$^{3+}$ (9d) and Mn$^{4+}$ (3b) remain in a charge ordered state below 250 K [16].

The compound undergoes two magnetic transitions, one at $T_1 = 90$ K and the other at $T_2 = 45$ K [11, 15]. Below 90 K, the magnetic structure is helical with incommensurate magnetic propagation vectors $q_1 = (0, 1, 0.963)$ [12]. The magnetic structure is found to be more complex below $T_2$ and it may be represented by two coexisting propagation vectors, namely $q_2 = q_1 \pm (0, 0, \delta)$, where $\delta \sim 0.08$. The compound shows giant ferroelectric polarization along the $c$ axis below 90 K [11, 12]. The magnetic nature of this electrical polarization is also confirmed by the strong ME effect observed below 90 K, which shows about 30% change in $P$ under an applied magnetic field of $H = 90$ kOe [11, 17].

Based on a recent density functional theory (DFT) calculation, it has been argued that giant P and ME in CaMn$_7$O$_{12}$ arise from the symmetric exchange-striction in the presence of a strong Dzyaloshinskii–Moriya (DM) type magnetic interaction between certain Mn$^{3+}$ and Mn$^{4+}$ ions [18].

It is understood that the magnetic and ferroelectric anomalies in CaMn$_7$O$_{12}$ are strongly governed by the mixed valent nature of manganese. In this work we carefully examined the nature of the magnetic transitions as well as their evolution with changing Mn$^{3+}$ and Mn$^{4+}$ ratio. We substituted trivalent La at the divalent Ca to tune the Mn$^{3+}$/Mn$^{4+}$ ratio. Our study indicates interesting magneto-thermal irreversibility across the low temperature magnetic transition along with drastic change in the magnetic and ferroelectric properties.

2. Experimental details

Ceramic samples of CaMn$_7$O$_{12}$ and some La doped compositions (Ca$_{1-x}$La$_x$Mn$_7$O$_{12}$, $x = 0.04$ and 0.08) were prepared by the sol–gel method using polyethylene glycol gel. The gel produced by the method was first heated at 250 °C in an oven. The products were heated consecutively at (i) 800 °C, (ii) 925 °C and (iii) 950 °C each for 16 h. Finally, the powder samples were pelleted and heated at 970 °C for 60 h. Room temperature powder x-ray diffraction (XRD) data of the samples were recorded using Cu Kα radiation. Energy dispersive spectrometry (EDS) on the samples was performed in an FEI Quanta 200 scanning electron microscope. The pure and $x = 0.04$ samples were also investigated through core level x-ray photo-electron spectroscopy (XPS) at room temperature using Al Kα radiation on a laboratory based commercial instrument (Omicron). The magnetic measurements were performed on a vibrating sample magnetometer from Cryogenic Ltd UK, as well as on a Quantum Design SQUID magnetometer. The pyroelectric current of the sample was measured using a Keithley electrometer (model 6517B) in a helium closed cycle refrigerator. The ac dielectric measurements were performed using an Agilent E4980A precision LCR meter in the temperature range 10–300 K.

3. Sample characterization

The XRD patterns (not shown here) indicated that all the samples crystallize in the trigonal $R\bar{3}$ crystal structure. No extra unindexable reflection was found in the XRD patterns indicating that the samples are all single phase in nature. We have determined the lattice parameters of the samples considering a hexagonal unit cell as described in table 1. The hexagonal lattice parameters $a$ and $c$ decrease systematically with La doping.

We performed careful EDS measurements to find the elemental ratios of the studied samples. The EDS showed a homogeneous concentration of the constituent elements within the accuracy of the method. We carried out EDS at 8–10 different regions of the samples with an effective scanning area of 0.34 × 0.34 mm². The mean atomic ratios (La + Ca):Mn were found to be 1.75 (±0.067) and 1.694 (±0.09) in the $x = 0.04$ and 0.08 samples respectively. The error values indicated in the brackets are the standard deviations of the elemental ratios measured at different parts of a particular sample. The (La + Ca):Mn values are quite close to the expected stoichiometric value of 1.7. The Ca:La atomic ratios were found to be 1:0.05 (expected 1:0.04) and 1:0.088 (expected 1:0.08) in the $x = 0.04$ and 0.08 samples respectively. These values are quite close to the actual stoichiometry considering the fact that the percentage of La in the doped samples is small.

### Table 1. Variation of the hexagonal lattice parameters ($a_0$ and $c_0$), pseudo-cubic angle ($\alpha_{\text{cub}}$), effective paramagnetic moment ($\mu_{\text{eff}}$), magnetization in 50 kOe at 5 K ($M_{50\text{kOe}}$), coercive field at 5 K ($H_{C}^{K}$) and spontaneous polarization at 10 K ($P^{10\text{K}}$) of Ca$_{1-x}$La$_x$Mn$_7$O$_{12}$ for different values of $x$.

| $x$ | $a_0$ (Å) | $c_0$ (Å) | $\alpha_{\text{cub}}$(deg) | $\mu_{\text{eff}}$ ($\mu_B$/Mn) | $M_{50\text{kOe}}^{K}$ ($\mu_B$/f.u.) | $H_{C}^{K}$ (kOe) | $P^{10\text{K}}$ ($\mu$C m$^{-2}$) |
|-----|----------|----------|--------------------------|-------------------------------|---------------------------------|-----------------|---------------------|
| 0.0 | 10.63    | 6.31     | 91.18                    | 4.69                          | 2.99                           | 3.1             | 440                 |
| 0.04| 10.57    | 6.29     | 91.05                    | 4.78                          | 2.18                           | 0.92            | 878                 |
| 0.08| 10.51    | 6.28     | 90.93                    | 4.81                          | 1.84                           | 0.52            | 1190                |
Figure 1. Core level x-ray photo-electron spectra of (a) Mn-2p, (b) O-1s, (c) Mn-3s and (d) La-3d levels recorded at room temperature for CaMn$_7$O$_{12}$ and Ca$_{0.96}$La$_{0.04}$Mn$_7$O$_{12}$ samples.

We performed core level XPS measurements on the $x = 0.0$ and 0.04 samples at room temperature as shown in figure 1. The background subtraction and peak fitting were performed using the software XPS-PEAK 4.1. Figure 1(a) shows the Mn-2p levels of both the samples. Clear splitting is observed in the Mn-2p peak, which corresponds to 2p$_{3/2}$ and 2p$_{1/2}$ due to spin–orbit coupling. The spin–orbit splitting in the 2p level is found to be 11.7 eV for both the samples. The Mn-2p$_{3/2}$ is broad and asymmetric on the higher binding energy (BE) side. Such broadness and asymmetry have often been ascribed to the mixed valency of Mn in the sample [19]. Each 2p doublet was fitted using three components, namely Mn$^{3+}$, Mn$^{4+}$ and a satellite peak. The Mn-2p$_{3/2}$ peak is slightly shifted towards the lower BE side in the $x = 0.04$ sample.

We have looked at the energy differences between the O-1s (see figure 1(b)) and Mn-2p$_{3/2}$ levels and they are found to be $\Delta E_{2p-1s} = 112.4$ and 112.0 eV for the $x = 0$ and 0.04 samples respectively. The lower value of $\Delta E_{2p-1s}$ in $x = 0.04$ may indicate the larger Mn$^{3+}$ fraction in the La doped sample as compared to the undoped one [20].

Figure 1(c) shows XPS spectra of the exchange split Mn-3s level for the $x = 0.0$ and 0.04 samples. The extent of splitting ($\Delta E_{3s}$) depends on the valence state of the Mn ions [21], and the Mn valence can be expressed by the empirical relation $v_{\text{Mn}} = 9.67 - 1.2\Delta E_{3s}$ [22]. We find $v_{\text{Mn}}$ to be 3.22 and 3.08 respectively for the $x = 0$ and 0.04 samples. It is to be noted that the average Mn valence of CaMn$_7$O$_{12}$ is expected to be 3.14 (considering the 6:1 ratio of the Mn$^{3+}$ and Mn$^{4+}$). The investigation indicates enhancement of Mn$^{3+}$ ions in the material on La substitution.

The presence of La in the $x = 0.04$ sample is confirmed by the observation of La-3d doublet peaks at energies of 855.3 eV (3d$_{5/2}$) and 838.5 eV (3d$_{3/2}$). Each doublet is further split into two components; this occurs due to the charge transfer from the ligand 2p level to the La 4f level [23]. The spin–orbit splitting between the 3d$_{5/2}$ and 3d$_{3/2}$ lines is found to be close to 16.8 eV, which is expected for the La$^{3+}$ state.

4. Results

4.1. Magnetization studies on CaMn$_7$O$_{12}$

Figure 2 shows the dc magnetization ($M$) as a function of temperature ($T$) measured in zero-field-cooled-heating (ZFCH), field-cooled-heating (FCH) and field-cooling (FC) protocols. The ZFCH and FCH data diverge from below about $T_2 = 43$ K. The signature of the high-$T$ magnetic transition is also evident from a kink around 90 K, as shown in the inset of figure 2. However, no signature of the emergence of thermo-magnetic irreversibility is observed at this transition. The 43 K transition is more prominent and it is associated with the large enhancement of $M$. We also observe the signature of thermal hysteresis just below $T_2$ between the FCH and FC data. Interestingly, the FC and FCH data show rather unusual behaviour as far as the thermal hysteresis is concerned. On cooling below $T_2$ they join up at around 38 K and then separate out again to form another hysteresis loop between 38 and 15 K. In other words, we observe two separate thermal hysteresis loops below $T_2$. The existence of thermal hysteresis between 43 and 38 K clearly indicates the first order nature of the magnetic transition, which is also supported by the structural anomaly reported around $T_2$ previously [14, 17]. Notably, ac dielectric permittivity data show an upturn below around 40 K [17], which may be connected to the hysteresis
Figure 2. The temperature dependence of the zero-field-cooled-heating (ZFCH), field-cooling (FC) and field-cooled-heating (FCH) magnetization data of the CaMn$_7$O$_{12}$ sample measured in the presence of 100 Oe of field. The inset shows an enlarged view of the anomaly at 90 K.

observed in our $M(T)$ data between 38 and 15 K. A clear change in slope was reported in the $P(T)$ data around 45 K followed by a flat region below 35 K [11]. Such anomalies are also apparent in the $M(T)$ data of our measurements. The anomalous thermal hysteresis observed in our data may indicate the existence of multiple first order phase transitions in the sample.

The concomitant occurrence of structural and magnetic anomalies at $T_2$ indicates the magneto-structural nature of the transition. First order magneto-structural coupling can show intriguing effects as a function of $T$ or $H$. There are examples where such a transition can give rise to metastability, arrested dynamics, glassiness, etc [24–26]. We investigated the thermo-magnetic curves of CaMn$_7$O$_{12}$ measured in different protocols (see figure 3). We cooled the sample down to 5 from 200 K at different applied fields (100 Oe, 1 and 30 kOe) and measured $M$ while heating in 100 Oe. It is clearly evident that cooling in higher fields produces larger values of $M$. The field applied during cooling induces some magnetic domains/clusters which are oriented favourably along $H$. Such favourably oriented magnetic clusters persist even when the field is lowered and the sample is heated back.

The presence of thermo-magnetic irreversibility and the cooling field effect encouraged us to investigate the possible metastable character below $T_2$. The inset of figure 3(a) shows the time ($t$) variation of $M$ in the ZFC condition at 5 K. The sample was first cooled in the absence of $H$ down to 5 K and subsequently 100 Oe of the field was applied and then $M$ was measured as a function of $t$. The sample shows large relaxation, where $M$ changes by more than 8% in 3600 s. Such large relaxation is generally observed in disordered magnetic systems or in spin glasses. The relaxation data can be well fitted by the Kohlrausch–Williams–Watt (KWW) stretched exponential model ($\sim \exp[-(t/\tau)\beta]$) [27, 28], where $\tau$ is the characteristic relaxation time and $\beta$ is the shape parameter. This model has been widely used to analyse the data for spin glass and other disordered magnets [29]. The value of $\beta$ was found to be 0.37 for the present CaMn$_7$O$_{12}$ sample. The exponent $\beta$ in the KWW model signifies the number of intermediate states through which the system should evolve, and it approaches 1 when the number of such intermediate states diminishes [30]. Glassy and disordered magnetic systems are found to show $\beta$ values over a wide range between 0.2 and 0.6 and the value of $\beta$ for the present composition falls well within the range.

We performed a magnetic memory experiment [31, 32] to further elucidate the metastable state. For the memory measurement, the sample was first cooled in the presence of $H = 1$ kOe with intermediate stops of 3600 s each at 12 K and 8 K (curve $M_{\text{stop}}$ in figure 3(b)). At each stop, $H$ was reduced to zero. After reaching 2 K, the sample was heated back in 1 kOe (curve $M_{\text{mem}}$ in figure 3(b)), and the signature of stops is clearly imprinted in the heating curve at respective temperatures in the form of dips. This prominent signature of memory clearly indicates that the system evolves through multiple metastable states as one cools it below $T_2$.

However, it should be noted that the above memory measurement was performed in the field-cooled condition and a positive signature of memory can be present in an assembly
of noninteracting superparamagnetic particles due to their individual relaxation under an applied field [33, 34]. An elegant way to distinguish a superparamagnet from a glassy magnetic system is the measurement of zero-field-cooled memory. In this protocol, the sample was first cooled in zero field with intermediate stops and subsequently the sample was heated back in the presence of a small applied field and \( M(T) \) data were recorded. For the present sample, although the field-cooled memory was very strong, we failed to observe any signature of zero-field-cooled memory (not shown here). We also measured the ac susceptibility of the sample around \( T_2 \) at different driving frequencies \( (f) \). The signature of magnetic transition at \( T_2 \) is apparent in the real part of the ac susceptibility \( (\chi'_M(T)) \) in the form of a peak. However, we do not see any shift in the peak position with \( f \) (see the inset of figure 3(b)). The negative results for zero-field-cooled memory and the absence of \( f \) dependence of \( \chi'_M(T) \) rule out the possibility of a low-\( T \) glassy magnetic state of CaMn\(_7\)O\(_{12}\).

### 4.2. Effect of La doping in CaMn\(_7\)O\(_{12}\)

CaMn\(_7\)O\(_{12}\) is a mixed valent compound and it is well known that the Mn valency plays a crucial role in deciding the electronic and magnetic properties of the sample. We tried to vary the Mn valency by doping La at the Ca site. Since La remains in the 3+ state as opposed to the 2+ state of Ca, it is expected that doping would enhance the Mn\(^{3+}\) fraction at the cost of Mn\(^{4+}\). Figure 4(a) shows a comparison of the ZFC \( M(T) \) data recorded for Ca\(_{1-x}\)La\(_x\)Mn\(_7\)O\(_{12}\) samples with \( x = 0.0, 0.04 \) and 0.08. The transition at \( T_2 \) is present in the doped samples; however, it is slightly shifted to lower \( T \) with increasing \( x \). The most important change due to doping is the drastic reduction of the value of \( M \) (see table 1). The peak value of \( M \) decreases from 3.33 emu g\(^{-1}\) in the pure sample to 0.65 emu g\(^{-1}\) for \( x = 0.08 \). This decrease is also visible in the isothermal \( M \) versus \( H \) data depicted in figure 4(b). The coercivity of the magnetic hysteresis curve becomes reduced with increasing \( x \). This indicates that the FM-like contribution present in the sample below \( T_2 \) is becoming reduced due to La doping at the Ca site.

It is to be noted that all the samples \( (x = 0.0, 0.04 \) and 0.08) show paramagnetic behaviour above about 120 K. The Curie–Weiss fitting \( (\chi = M/H = C/(T - \theta)) \), where \( \chi \) is the dc magnetic susceptibility, \( C \) is the Curie constant and \( \theta \) is the Weiss temperature) to the data indicates that the effective paramagnetic moment per Mn \( (\mu_{\text{eff}}/Mn) \) increases with La doping (see table 1). This is expected as La doping enhances the Mn\(^{3+}\) fraction at the cost of Mn\(^{4+}\), and the former spin state has a larger value of the isolated magnetic moment \( (4.9 \ \mu_B) \) than the latter \( (3.87 \ \mu_B) \). Using these moment values along with the calculated \( \mu_{\text{eff}}/Mn \) from the Curie–Weiss law, one can estimate the effective valency of Mn in the samples. For the \( x = 0.0, 0.04 \) and 0.08 samples, the effective valency values of Mn were found to be 3.22, 3.12 and 3.09 respectively. These are close to the values expected for nominal stoichiometric compositions \( (3.15, 3.14 \) and 3.13), and they match well with the \( v_{\text{Mn}} \) calculated from XPS data.

It has already been shown in the literature that CaMn\(_7\)O\(_{12}\) shows spontaneous electrical polarization below \( T_1 \). We have presented here the polarization data as calculated from the measured pyroelectric current densities \( (P) \) of the samples. In order to record \( P \), we used a capacitor type assembly with a pair of electrodes attached to two flat surfaces of the sample using silver epoxy. The sample was first cooled down to 10 K in the presence of an electric field, \( E_{\text{cool}} = 3.1 \ \text{kHz} \). After reaching 10 K, \( E_{\text{cool}} \) was set to zero and \( P \) was measured while the sample was heated at a constant rate of 4 K min\(^{-1}\). One can calculate \( P \) by integrating \( J_P(t) \). Here, we assumed that \( P \) vanishes for all the samples as soon as \( T \) goes above 120 K [35, 36]. The measured \( J_P \) and \( P \) have been shown in figures 5(a) and (b) respectively as a function of \( T \). Clearly, a drastic increase in the value of \( P \) is observed in the La doped samples (see table 1). The peak value of \( J_P \) increases by a factor of 2.5 in the \( x = 0.08 \) sample as compared to the undoped one. Consequently, \( P \) is found to be higher in the La doped compositions. For all the samples, \( P \) rises with decreasing \( T \) below \( T_1 \) and eventually saturates at low \( T \). The magnitude of this saturated \( P \) in our study is found to be higher in the pure CaMn\(_7\)O\(_{12}\) \( (∼440 \ \mu\text{C m}^{-2}) \) for \( E_{\text{cool}} = 3.1 \ \text{kHz} \) compared to a previous report on a polycrystalline sample \( (∼240 \ \mu\text{C m}^{-2}) \) for \( E_{\text{cool}} = 3.5 \ \text{kHz} \) [11]. However, the observed value is certainly much smaller than reported single crystal
Figure 5. (a),(b) The temperature dependence of the pyroelectric current density ($J_p$) and the spontaneous electrical polarization ($P_s$) respectively for Ca$_{1-x}$La$_x$Mn$_7$O$_{12}$ ($x = 0.0, 0.04$ and $0.08$) samples.

The real part of the complex permittivity shows a $T$-independent flat region at low $T$, followed by a thermally activated rise at high $T$. Such activated behaviour is quite common among ceramics and it is contributed by mobile charge carriers in the presence of grains and grain boundaries. If we compare the $\epsilon'$ with $P_s$, this flat portion actually corresponds to the region where spontaneous polarization is present. Very similarly to $P_s$, the magnitude of $\epsilon'$ in the flat region increases with La doping. Interestingly, the flat region in $\epsilon'$ at low-$T$ is not exactly flat, rather it shows a shallow minimum, which was earlier reported for a pure sample [12]. It was also found that a magneto-capacitive effect is visible around this shallow minimum. In our case, the minimum shifts to higher $T$ with increasing La doping. This is on a par with the polarization data, where the temperature corresponding to the appearance of spontaneous polarization shifts to higher $T$ with $x$.

5. Discussion

The multiferroic compound CaMn$_7$O$_{12}$ is an improper ferroelectric, where spontaneous electrical polarization occurs due to the helical spin ordering below $T_H = 90$ K [11, 12, 18]. Our magnetization measurements indicate clear thermal hysteresis around $T_2$, which signifies a first order phase transition (FOPT). Previous x-ray and neutron diffraction studies [14] have indicated that the system undergoes a structural transition around $T_2$, which is associated with a sharp change in lattice parameters. The observation of thermal hysteresis is in line with the previously reported structural anomaly. Although $P_s$ develops just below $T_1$, it shows a change in slope around $T_2$, which is clearly associated with the FOPT occurring at this point.

In our magnetic study, we observe an interesting magneto-thermal anomaly, which is reflected in the $M(T)$ and $M(H)$ data measured during heating in 100 Oe after field-cooling in different $H$ through $T_2$. The sample shows a strong signature of field stop magnetic memory below $T_2$. These observations suggest a metastable ground state of this material. Recent neutron diffraction data revealed that CaMn$_7$O$_{12}$ has a complex magnetic structure below $T_H$ with a possibility of multiple magnetic propagation vectors, and it is difficult to determine the exact magnetic structure without single crystal neutron diffraction data. The rise in $M$ below $T_2$ may be an indication of the formation of superparamagnetic like clusters. On field-cooling, the number of such clusters is enhanced and they become oriented favourably along $H$. This is the likely origin of the enhanced value of $M$ in the heating data if the sample is cooled in higher $H$. The superparamagnetic nature of the sample is also supported by the observation of a clear loop in the $M(H)$ data, which would have been unlikely to occur had the sample been a pure helimagnet.

Superparamagnetism is generally associated with an assembly of noninteracting magnetic nanoparticles, and the field-cooled memory is observed below the blocking temperature due to the Néel type relaxation superparamagnetic moment of individual particles [34, 37]. This investigation was carried out on bulk ceramic samples where the particle size was too large ($\sim$1–10 $\mu$m) to have appreciable Néel relaxation. However, evidence for superparamagnetic clusters has been reported in several bulk magnetic systems (such
as manganites, nickelites, etc) [38–42]. Therefore, it is possible that nanosized magnetic clusters can form in bulk CaMn$_7$O$_{12}$ in the backdrop of a helimagnetic structure and the relaxation of individual nano-clusters is primarily responsible for the observed field-cooled memory. The complete absence of zero-field-cooled memory rules out the possibility of a spin glass or cluster glass like ground state, indicating the lack of substantial spin frustration among different magnetic specimens. Considering the fact that metastability occurs below $T_2$ only, the formation of spin clusters can be strongly associated with the first order nature of the transition. In the presence of disorder, there can be coexisting parent and product phases across the FOPT [43]. CaMn$_7$O$_{12}$ contains both Mn$^{4+}$ and Mn$^{3+}$, and near a phase boundary one could have the chance for the formation of isolated local magnetic clusters through a double exchange mechanism.

La doping at the Ca site was performed to change the Mn$^{3+}$ to Mn$^{4+}$ ratio of the sample, and it is likely that the La$^{3+}$ would enhance the percentage of Mn$^{3+}$ ions in the sample. Our XPS investigation indicates higher Mn$^{3+}$ fraction in the $x = 0.04$ sample. XPS is predominantly a surface sensitive measurement, and one should be cautious of predicting the quantitative value of the Mn$^{3+}$/Mn$^{4+}$ ratio in the bulk from the peak area of the XPS data. However, our investigation based on the analysis of several independent aspects of XPS data can at least provide supportive evidence for enhanced Mn$^{3+}$ concentration in the La doped samples. Notably, the Mn$^{3+}$/Mn$^{4+}$ ratio calculated from the effective paramagnetic moment indicates a systematic variation of Mn valency with La concentration and it is in line with the XPS analysis. It is clear from the $M(T)$ data that La doping at the Ca site causes systematic decrement of $M$ below $T_2$, although $M$ remains almost the same above $T_2$ with changing $x$. This observation supports the proposed scenario of superparamagnetic like clusters below $T_2$. La doping will reduce the Mn$^{4+}$ fraction responsible for double exchange and as a result the number of such superparamagnetic clusters will shrink.

In contrast to the value of $M$, $P$ is found to be larger in the La doped samples. We find that the small La (8%) doping can enhance $P$ by a factor of 3. This provides an easy path to enhance the functionality of this material, and is consequently important from the point of view of applications. It is expected that the ME effect in CaMn$_7$O$_{12}$ is connected to the low-$T$ spiral magnetic order, which is also present in several other multiferroics [44]. However, the nature of the electric polarization is anomalous in CaMn$_7$O$_{12}$, where $P$ lies perpendicular to the plane of the spiral magnetic structure with exceptionally large magnitude. In addition, due to the existence of proper screw type spiral magnetic structure in CaMn$_7$O$_{12}$ [45], a simple spin current model cannot alone describe the origin of multiferroicity [46, 44]. A couple of different models have been proposed for large $P$ in CaMn$_7$O$_{12}$, namely (i) ferroaxial coupling of the magnetic chirality to the structural rotation [12] and (ii) combination of exchange-striction and DM interaction [18]. At this point it is really difficult to comment on the mechanism behind the enhanced $P$ on La substitution at the Ca site. In the exchange-striction model based on DFT calculations it is found that the induced $P$ depends on the value of $\sin \alpha$, where $\alpha$ is an angle between Mn$^{4+}$ spins and the $x$ axis of a predefined coordinate system [18]. The optimum value of $\alpha$ is found to be close to 30°, which is obtained by minimizing the energy Hamiltonian comprising spin exchange interaction and DM interaction. It is likely that due to the replacement of Mn$^{3+}$ by Mn$^{4+}$, the optimum value of $\alpha$ would change, which may be responsible for the drastic enhancement in $P$.

It is to be noted that even a proper screw type magnetic structure can induce ferroelectricity through the variation in the metal–ligand hybridization in the presence of spin–orbit coupling in relatively low-symmetry crystals [46, 47]. This has been found to be quite useful in describing magnetic order induced polarization in materials such as CuFeO$_2$. Such a scenario cannot be ruled out for the observed multiferroicity in CaMn$_7$O$_{12}$. The metal–ligand (p–d) hybridization might depend upon the spin state of Mn, and hence it could contribute to the large enhancement of $P$ in electron doped samples of CaMn$_7$O$_{12}$.

In conclusion, we studied the magnetic and electric properties of CaMn$_7$O$_{12}$ and some of its La doped derivatives. We find that the low temperature magnetic transition is first order in nature and the ground state is magnetically metastable. A probable scenario of the formation of superparamagnetic like spin clusters is proposed. La doping reduces the superparamagnetic contribution at low temperature; however, it enhances the electric polarization to a large extent. Apparently, the enhanced Mn$^{3+}$ ions in the sample, at least within the doping range of this investigation, are somehow related to the enhanced polarization. This piece of information may be important for further understanding of the origin of anomalous multiferroicity in CaMn$_7$O$_{12}$. Lastly, the enhanced $P$ on La doping may be important for practical applications as far as the functionality of the materials is concerned.

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