



Tuning electric polarization via exchange striction interaction in $\text{CaMn}_7\text{O}_{12}$ by Sr-doping

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ABSTRACT

Magnetoelectric (ME) materials displaying magnetically induced polarization have attracted considerable interest due to their potential applications in spintronics and various fast electrically controlled magnetic devices. $\text{CaMn}_7\text{O}_{12}$ (CMO) stands out for its giant spin-induced ferroelectric polarization. However, the origin of the induced electric polarization in CMO remains highly controversial and continues to be a subject of ongoing debate. In this paper through room temperature X-ray powder diffraction (XRPD), temperature-dependent magnetization, and thermally stimulated depolarizing current (TSDC) measurements, we provide experimental evidence for a route to tune the magnetically induced polarization by modifying the exchange-striction in CMO via Sr-doping. Our findings demonstrate that the large and broad current density peaks observed near the first magnetic phase transition ($T_{\text{N1}} \sim 90$ K) indicate contributions to the TSDC from both extrinsic dipolar thermally stimulated relaxation processes and intrinsic pyroelectric current, the later arising from magnetically induced polarization changes. We suggest that the reduction in induced electric polarization in CMO originates from an increase in the $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ bond angle due to Sr^{2+} doping, which weakens the exchange-striction interaction. Meanwhile, the Dzyaloshinskii–Moriya (DM) effect determines the direction of the induced electric polarization. Our result sheds light on understanding the intriguing giant-induced polarization in CMO and similar compounds with complex magnetic structures.

1. Introduction

Magnetoelectric (ME) materials, which exhibit coupling between electric polarization and magnetic ordering, have recently attracted significant attention due to their potential applications in spintronics and electrically controlled magnetic devices [1–8]. Magnetically induced ferroelectrics, known as type-II multiferroics, are among the most promising magnetoelectrics due to the coupling between electric and magnetic ferroic orders [9–16]. However, most candidates exhibit weak induced-electric polarization, generally occurring at low temperatures, which limits their potential for further applications [17,18].

In this context, $\text{CaMn}_7\text{O}_{12}$ (CMO) emerges as a singular multiferroic

material with a quadruple perovskite structure and the extended formula $(\text{CaMn}_3^{3+})(\text{Mn}_3^{3+}\text{Mn}^{4+})\text{O}_{12}$, where $\frac{3}{4}$ of the A-sites are occupied by Mn^{3+} ions and $\frac{1}{4}$ by Ca^{2+} , while the B-sites are occupied by both Mn^{3+} and Mn^{4+} below 440 K. At room temperature, the CMO exhibits a distorted perovskite structure with trigonal symmetry belonging to the $R\bar{3}$ space group. Moreover, this material displays two antiferromagnetic (AFM) helical spin orderings (named AFM I and AFM II) at $T_{\text{N1}} = 90$ K and $T_{\text{N2}} = 48$ K [19], respectively. Notably, in the recent past, a relatively large magnetically-induced spontaneous polarization ($\sim 2870 \mu\text{Cm}^{-2}$) was observed in CMO below T_{N1} [19–21]. However, since the direction of electric polarization in CMO lies perpendicular to the rotation plane of Mn spins in the helical magnetic structure the induced

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electric polarization in CMO cannot be explained by the spin-current model [21].

In the last decade, there has been considerable debate in the literature regarding the origin of induced-electric polarization in multiferroic CMO [21–26]. Two models have been distinguished for explaining the origin of magnetically-induced polarization in CMO: (i) the first one proposes a combined effect involving exchange striction and Dzyaloshinskii-Moriya (DM) interactions [20], with exchange-striction interaction being responsible for the large induced ferroelectric polarization (P) in CMO [24,25,27], (ii) the second model argues that, the spontaneous polarization observed arises from the combination of $p-d$ hybridization and exchange-striction [23,25].

Recently, Lu *et al.* investigated the origin of the giant spin-induced electric polarization in $\text{AMn}_7\text{O}_{12}$ ($\text{A}=\text{Bi}_{0.5}\text{Ag}_{0.5}$) [26]. Their findings strongly suggest that the giant electric polarization observed in the $\text{A}^{2+}\text{Mn}_7\text{O}_{12}$ perovskite family does not depend on orbital ordering. Instead, the exchange-striction model is the most plausible explanation for the ME coupling mechanism in this material. This new evidence strongly contradicts the idea previously proposed by Perks *et al.*, which suggested that orbital ordering plays a crucial role in stabilizing the chiral magnetic structure in CMO [22]. This points out that the predominant mechanism for inducing electric polarization in CMO is more likely due to exchange-striction interaction, where the spontaneous polarization is strongly coupled to the helical magnetic order. Otherwise, some studies have shown that the high values of electric polarization observed in CMO originate from thermally stimulated currents (TSC) [28,29]. All these issues highlight that the mechanism behind the multiferroicity in the compound remains controversial.

Regarding this, we point out some experimental findings that suggest the electric polarization observed below T_{N1} cannot purely originate from extrinsic effects: (i) a strong magnetoelectric coupling is observed just below T_{N1} [19,30]; (ii) an anomaly in the dielectric constant is observed at T_{N1} [19]; (iii) recently, the exchange-striction interaction at the first magnetic transition, investigated by XRPD, has been recognized as crucial for the emergence of simultaneous electric polarization [24]; (iv) a significant dependence of electric polarization on A-site cation doping was observed below T_{N1} [26,30,31]: and, according to A. Nonato *et al.* the phonon anomalies observed at $T_{\text{N1}} \sim 90$ K are evidences for spin-phonon coupling in CMO [32].

In this paper, based on X-ray powder diffraction (XRPD), temperature-dependent magnetization, and TSDC measurements, we present insights into the origin of the observed electric polarization below the first magnetic phase transition (T_{N1}). For the first time, we provide evidence of a route to tuning electric polarization via both the inverse Dzyaloshinskii-Moriya (DM) effect and exchange-striction interaction, achieved by modifying the $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ bond angle through Sr-doping in CMO. This is obtained by doping the A-site of CMO with small concentrations of Sr^{2+} (up to ≤ 0.3), which modifies the effective ionic radius of the A-site, leading to variations in the Mn-O-Mn bond angles. Our results reveal that the broad currents in the temperature-dependent TSDC around $T_{\text{N1}} \approx 90$ K have contributions from both extrinsic dipolar thermal relaxation processes and intrinsic pyroelectric currents. Additionally, our approach provides evidence that the reduction in intrinsic polarization observed below 90 K in Sr-doped CMO primarily originates from the weakening exchange-striction strength. The dependence of magnetically induced electric polarization on Sr-concentration in CMO is discussed. This study opens new horizons in understanding the mechanisms governing magnetically induced electric polarization in CMO and other complex magnetic structures.

2. Experimental details

Sr-doped CMO polycrystalline samples, $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0 \leq x \leq 0.30$) were synthesized by the Pechini method [33] following the procedure described for the undoped compound [32,34], using

SrCO_3 (Panreac, >96 %) , CaCO_3 (Panreac, >98.6 %) and $\text{Mn}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ (Aldrich, >98 %) as starting reagents. The resin initially obtained was decomposed at 400 °C, forming the precursor powder. The resulting precursor powders were grounded and then heated in air at 800 °C/60 h, 900 °C/24 h, and 950 °C/24 h, with intermediate grinding and pelletizing. The resultant powders were pressed into pellets and sintered in air at 970 °C for 60 h.

The obtained samples were characterized by X-ray powder diffraction (XRPD) at room temperature using a Siemens D-5000 diffractometer with $\text{Cu}(K_\alpha)$ radiation. The XRPD data were analyzed by the Rietveld profile analysis using the GSAS [35,36]. Their magnetic properties were studied in a Quantum Design MPMS Squid magnetometer, in which zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were recorded under a field of 1000 Oe in the temperature range of $5 \leq T(\text{K}) \leq 300$. The thermally stimulated depolarization current (TSDC) of the samples was measured using a Keithley 617 electrometer with the samples enclosed in a helium-closed cycle refrigerator. The samples were prepared as pellets with a pair of electrodes attached to the two flat surfaces of the sample, which had been sputter-coated with gold. Thermally stimulated depolarizing current (TSDC) measurements were performed during the heating process at constant rates of 4 K/min, 6 K/min, and 8 K/min. The samples were first subjected to an electric field at 100 K, followed by cooling down to 14 K using the same temperature ramp intended for the heating measurement. After reaching 14 K, the samples were short-circuited for ~ 30 minutes to prevent free charges. Finally, the depolarizing current was recorded between 14 K and 150 K with the selected temperature ramp. In addition, the direction of polarization could be inverted by switching the electric field, resulting in symmetric induced polarization curves with respect to the temperature axis.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the room-temperature XRPD patterns obtained for the $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ samples ($0 \leq x \leq 0.30$). As in the parent CMO compound, all samples exhibit the distorted perovskite structure with trigonal symmetry belonging to the space group $R\bar{3}$ (Figure S1). Nevertheless, the presence of weak extra peaks reveals the presence of small traces of Mn_3O_4 (hausmannite) (see Figure S2). It is generally challenging to obtain this compound as a completely single-phase

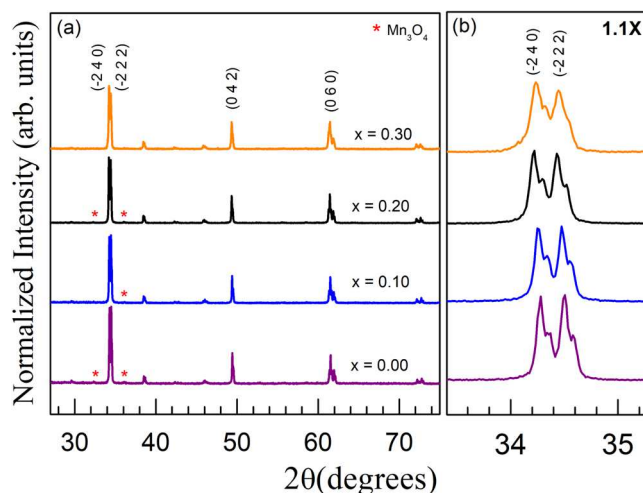


Fig. 1. (a) Room temperature XRPD patterns of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0.00 \leq x \leq 0.30$). (b) Detailed view of the most representative diffraction peaks evolution upon Sr-doping. The asterisk indicates the presence of a small amount of Mn_3O_4 (hausmannite).

material, and traces of impurity have also been reported by other authors [37,38]. However, quantitative analysis of our XRPD data by the Rietveld refinement reveals that these impurities, when observed, are consistently at low concentrations ($\text{Mn}_3\text{O}_4 < 2\%$). Detailed structural parameters for the $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0 \leq x \leq 0.30$) are shown in Table SI of the supplementary material.

Fig. 1(b) clearly shows that the inclusion of Sr in the crystal structure of CMO does not induce additional structural distortions, and the compounds retain their trigonal symmetry (S.G: $R\bar{3}$). Additionally, Sr-doping results in an increase of the a and c lattice parameters and consequently expansion of the cell volume (see Fig. 2), as substitution of the smaller Ca^{2+} by the larger Sr^{2+} [39] implies an increase in the average effective A-site ionic radius.

3.2. Magnetic phase transitions in Sr-doped $\text{CaMn}_7\text{O}_{12}$

Fig. 3 shows the low-temperature zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of Sr-doped CMO samples, measured in an applied field of 1000 Oe. Qualitatively, the magnetic behavior of these Sr-doped samples is similar to that observed for undoped CMO compound [28,30,40]. The first magnetic phase transition (T_{N1}) is clearly visible in the H/M (T) curve, exhibiting a linear temperature behavior above $T_{N1} = 90$ K (see inset of Fig. 3a). As the temperature decreases below T_{N1} , the magnetization abruptly increases, marking the second magnetic transition at ~ 42 K. At this temperature, a clear divergence between the ZFC and FC curves is also observed in the Sr-doped samples. It is important to highlight that the temperature dependence of optical phonons exhibits anomalous behavior at 41 K in pure polycrystalline CMO, providing evidence of distortions occurring at this temperature through spin-phonon coupling [32,41]. Thus, the two magnetic transitions, at $T_{N1} = 90$ K and at $T_{N2} \sim 42$ K, are observed and confirmed by the temperature dependence specific heat (C_p) from reference [19], which exhibits distinct anomalies at both temperatures, as shown in the inset of Fig. 3(a). These results suggest that the magnetic phase sequence is rather similar among the studied compounds. However, Sr-doping induces different magnetic features below T_{N2} , revealing changes in the magnetic moment while maintaining a similar magnetic structure. This result is in good agreement with those previously reported for $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0 \leq x \leq 0.50$), where neutron diffraction confirmed that the helical magnetic structure remains incommensurate at all values of x , while the fundamental magnetic wavevector increases upon Sr-substitution [42].

Since most samples present traces of Mn_3O_4 impurities (e.g., samples with $x = 0.0, 0.1$, and 0.2), it is important to consider their potential influence on the observed magnetic properties. Mn_3O_4 is a ferrimagnetic material with a Curie temperature (T_c) of approximately 43 K, which is

close to the Néel temperature ($T_{N2} \approx 42$ K) reported for the main phase [43]. Even in trace amounts, Mn_3O_4 can contribute to the overall magnetic response, particularly if the main phase exhibits weak antiferromagnetic signals [44]. Therefore, the anomaly observed near $T_{N2} = 42$ K can primarily originate from Mn_3O_4 impurity. On the other hand, our XRD analysis confirms that no traces of Mn_3O_4 impurities were identified in the CSMO03 sample. This confirms that the weak anomaly observed around $T_{N2} = 42$ K in the CSMO03 sample originates from the intrinsic properties of the main phase rather than from secondary phases.

Additionally, another anomaly is observed in the magnetization curve at approximately $T_{N^*} \sim 55$ K. This anomaly becomes more evident when analyzing the derivative of the H/M (T) curve, as shown in Fig. 3 (b). Notably, this anomaly in H/M (T) curve is more pronounced in the CMO sample with a Sr-concentration of $x = 0.30$, suggesting a significant change in the magnetic exchange interactions within the AFM II magnetic lattice due to Sr-doping. Indeed, the second AFM II transition is drastically affected by Sr doping in CMO, being observed at $T_{N2} = 62$ K for the $\text{SrMn}_7\text{O}_{12}$ compound [29]. Additionally, this anomaly is also observed in the real part of the dielectric constant below 60 K, highlighting the interplay between dielectric properties and spin configuration (see Figure S3).

In the temperature range of the paramagnetic phase, the magnetic susceptibility of the Sr-doped samples is described by the Curie-Weiss law ($\chi = \frac{C}{T-\theta}$, where C is the Curie constant, T is the absolute temperature, and θ is the Curie temperature) (see Figure S4). Such modeling enables the direct calculation of the Curie-Weiss constant, allowing us to estimate the effective magnetic moment as $\mu_{\text{eff}} = 2.83C^{\frac{1}{2}}\mu_B$ [45]. Table 1 presents the constant parameters obtained for all Sr-doped samples, as well as the estimated effective magnetic moments. We found the effective magnetic moment of Sr-doped CMO samples to be very close to the expected value of $12.61 \mu_B$ for six Mn^{3+} ions and one Mn^{4+} ion. Furthermore, the Curie-Weiss behavior and the negative θ value indicate a predominance of antiferromagnetic interactions in all Sr-doped samples.

It is important to highlight that the CSMO03 sample exhibits a magnetic curve profile that differs from the other samples. It is observed that the difference between the ZFC and FC curves is much smaller in the CSMO03 sample. The maximum value is reached at 18 K, whereas in the other samples, this maximum is observed around ~ 25 K for ZFC curves. These changes suggest that the magnetic interactions and/or domain behavior below ~ 42 K in the CSMO03 sample have a distinct dynamic compared to the other samples. The shift in the peak temperature of the ZFC curve and the reduced divergence between ZFC and FC curves may indicate variations in magnetic ordering or the size distribution of magnetic domains. The distinct dynamics in CSMO03 might be linked to a lower concentration of FM and anti-FM clusters or a different type of interaction between the domains, which could influence the freezing temperature or the strength of inter-domain coupling [30,46].

3.3. Field-induced thermally stimulated currents in pure $\text{CaMn}_7\text{O}_{12}$

Fig. 4(a) shows the temperature dependence of the TSDC for the pure CMO compound under different electric field magnitudes (0.695, 3.5, 7.0, and 10.0 kV/cm). A single temperature-dependent anomaly is identified, strongly dependent on the applied DC field. As can be observed, for electric field values ≥ 3.5 kV/cm, the peak becomes broader and splits. In this case, it is observed that the temperature where the current rises (~ 100 K) does not even coincide with the magnetic transition temperature ($T_{N1} = 90$ K). Since we considered an appropriate short circuit in the CMO sample, these charges originate from TSDC during the poling process [47,48]. In this case, the observed current is not purely intrinsic to the material. In contrast, at lower fields, around 0.695 kV/cm, the shape of the current peak is quite similar to that reported for CMO by Zhang *et al.* [19], exhibiting a broad and asymmetric profile.

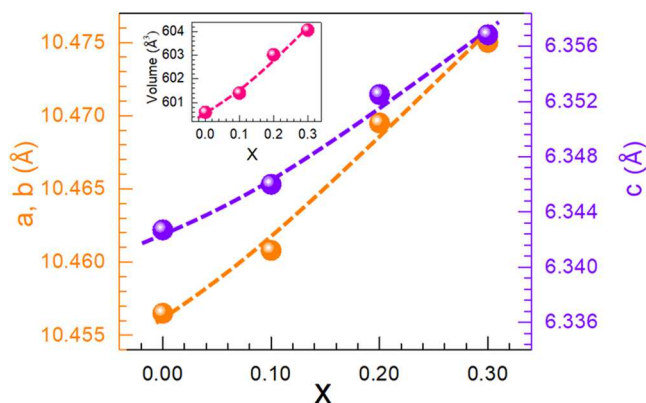


Fig. 2. Variation of the lattice parameters of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0.00 \leq x \leq 0.30$) as a function of Sr-doping. The inset shows the corresponding variation of the cell volume. Dashed lines are guides for the eyes.

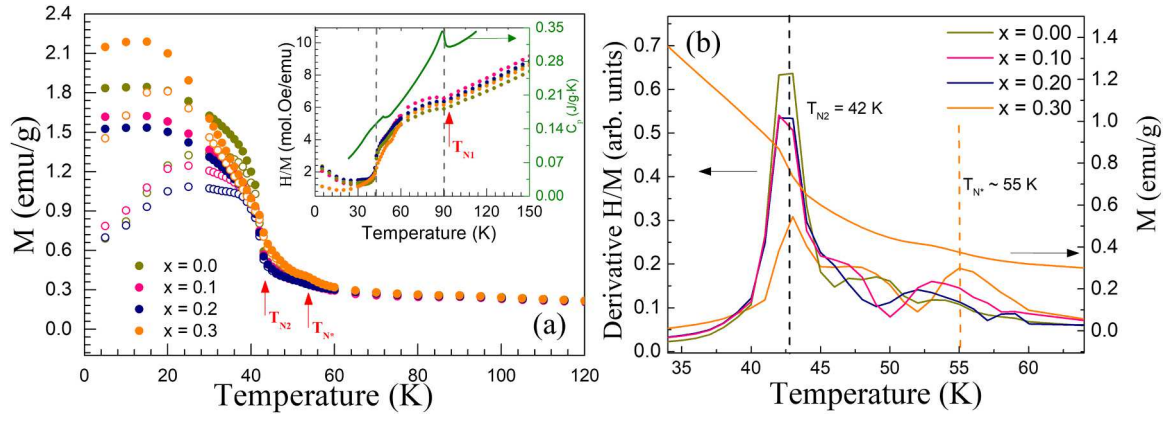


Fig. 3. (a) Temperature-dependent FC (filled circles) and ZFC (open circles) magnetization data at 1000 Oe for $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($0.00 \leq x \leq 0.30$) (indicate M in the figure). The inset shows H/M versus temperature (left axis), with vertical dashed lines indicating T_{N1} and T_{N2} . The specific heat (C_p , right axis) versus T from reference [19]. (b) Temperature-dependent derivative of the H/M for Sr-doped CMO samples, along with the M (T) curve for the sample with $x = 0.30$.

Table 1

The parameters of the Curie-Weiss Fits of Sr-doped CMO samples.

Samples	Sr-content (x)	θ (K)	C	μ_{eff} ($\mu_B/f.u.$)
CMO	0.00	-27.31 ± 0.02	20.42 ± 0.03	12.79 ± 0.01
CSMO01	0.10	-26.14 ± 0.02	19.41 ± 0.03	12.47 ± 0.01
CSMO02	0.20	-26.02 ± 0.03	20.02 ± 0.06	12.66 ± 0.02
CSMO03	0.30	-28.83 ± 0.03	21.01 ± 0.06	12.97 ± 0.02

Additionally, we performed TSDC measurements as a function of temperature at different heating rates: 4 K/min, 6 K/min, and 8 K/min, as shown in Fig. 4(d). We observe the current peaks at the same temperature, regardless of the temperature rate. This is a very important observation, as it provides clear evidence for the intrinsic nature of the current associated with the polar phase transition. Still, we do not exclude an extrinsic contribution coming from dipolar relaxation for the net current. This behavior will be discussed in more detail later. We also observed a small anomaly in the temperature dependence of the current peak around 52 K (see Fig. 4b), which is consistent with findings

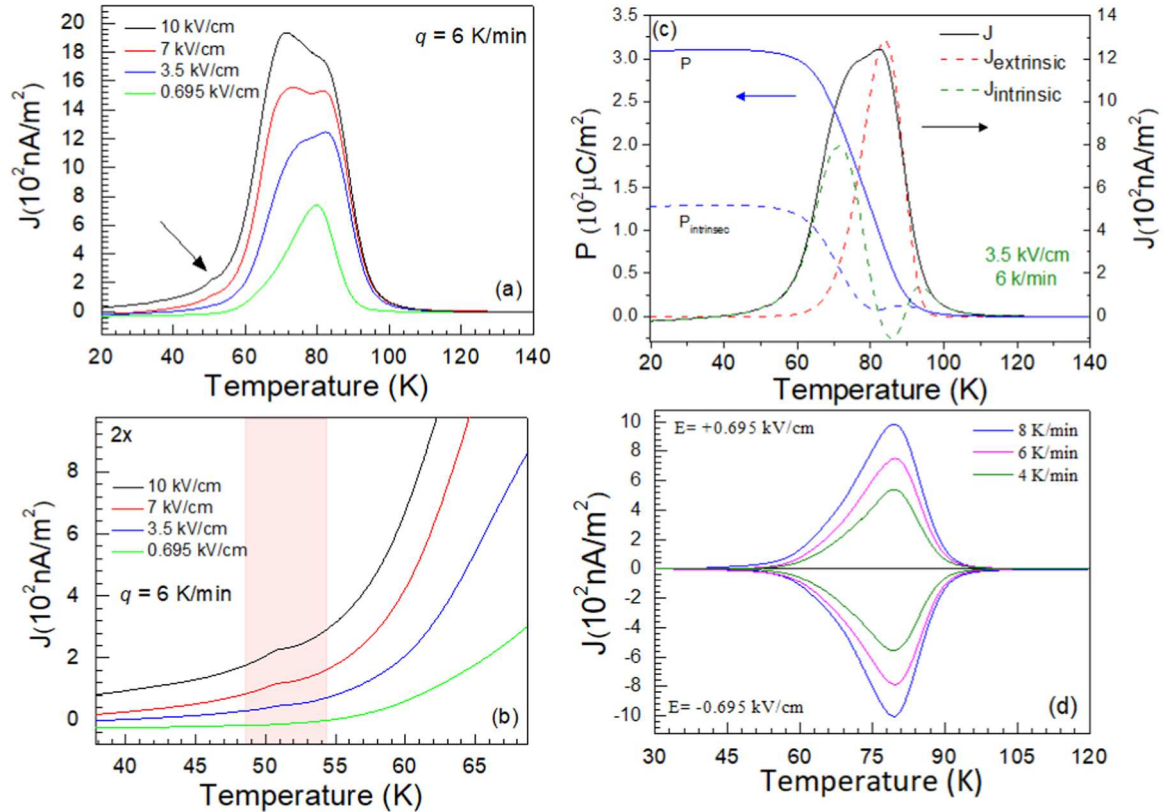


Fig. 4. (a) Thermally stimulated depolarizing current (TSDC) measured at various electric field magnitudes (0.695, 3.5, 7, and 10 kV/cm). (b) Anomaly observed in the TSDC around the transition region at $T_{N2} \sim 52$ K. (c) Temperature dependence of the TSDC density (right axis), measured with a heating rate of 6 K/min after cooling under a poling electric field of 3.50 kV/cm, along with the polarization obtained from the integration of the TSDC density data. The TSDC is decomposed by fitting the extrinsic component using Eq. 1 in the ~ 80 – 120 K temperature range (see main text). (d) The (symmetric) TSDC was measured with different heating rates (4, 6, and 8 K/min) under positive and negative poling electric fields.

reported by other authors [19,29].

The profile of the current curve for the 3.5 kV/cm field shown for pure CMO resembles what has recently been observed for $\text{BiMn}_3\text{Cr}_4\text{O}_{12}$ [49], where a TSDC peak associated with extrinsic thermally stimulated depolarization processes (e.g., Maxwell-Wagner relaxation or other defect-induced relaxations [47,48,50]) was identified. Therefore, the TSDC density (J), measured between 40 K and 120 K, can be decomposed into two components by modeling the contribution of the extrinsic density current, using the following approximate equation: [48]

$$J_{\text{extrinsic}}(T) \approx \frac{P_e}{\tau_0} \exp\left(-\frac{E}{k_B T}\right) \exp\left[-\frac{k_B T^2}{q\tau_0 E} \exp\left(-\frac{E}{k_B T}\right)\right] \quad (1)$$

where P_e is a constant, accounting for the equilibrium or steady-state polarization of the material, τ_0 is the relaxation time at infinite temperature, E is the activation energy of dipolar orientation, and $q = dT/dt$ is the heating rate. Fig. 4(c) displays the best fit of Eq. 1 to $J(T)$.

To determine the intrinsic pyroelectric contribution to the TSDC density, $J_{\text{extrinsic}}$, the extrinsic component is subtracted from the total TSDC density, J . The peak shape is not asymmetric, as one might expect, due to the approximation adopted in the employed model. This is mainly attributed to the overlapping contributions from extrinsic dipolar thermal relaxation processes and the intrinsic component, which affect the fitting accuracy. As a result, the intrinsic peak profile slightly differs from that observed in Fig. 4(d). By integrating $J_{\text{intrinsic}}(T)$, we obtain the actual ferroelectric polarization, $P_{\text{intrinsic}}(T)$ (see Fig. 4c). We found an intrinsic polarization of $\sim 127 \mu\text{C}/\text{m}^2$, corresponding to approximately 41 % of the total observed polarization ($\sim 308 \mu\text{C}/\text{m}^2$) for CMO. The intrinsic polarization value obtained through the approximate model allowed for a good approximation of the polarization value for a field of 0.695 kV/cm ($\sim 123 \mu\text{C}/\text{m}^2$). Hence, this model more effectively describes the magnetically induced polarization, as this intrinsic contribution arises below $T_{N1} = 90$ K.

At this point, it is interesting to discuss the significant role of the heating rate in influencing both the amplitude and the position of the peak. As the heating rate increases, the initial polarization must be released more quickly, while the dielectric responds more slowly. Thus,

we would expect the peak to increase in amplitude and shift to a higher temperature. By using Eq. (1) to model the current function and compare it with the curves in Fig. 4(d), we found that the expected shift to a higher temperature did not occur (see Figure S5). This indicates that the peak observed for the field of 0.695 kV/cm is likely intrinsic rather than extrinsic.

3.4. Magnetically-induced polarization in Sr-doped $\text{CaMn}_7\text{O}_{12}$

In order to check the presence of intrinsic magnetically induced ferroelectric polarization in Sr-doped CMO samples, we have studied the field-induced thermally stimulated depolarizing current. Fig. 5(a) shows the temperature-dependent current density (J_p) obtained for the Sr-doped samples, measured under a $q = 8\text{ K}/\text{min}$ heating rate. In contrast, Fig. 5(b) shows the polarization (P) obtained by integrating the current density (J_p) with respect to time. The current peaks observed for all Sr-doped CMO samples exhibit characteristics like those previously reported for pure $\text{CaMn}_7\text{O}_{12}$ [19]. We observed a broad peak below ~ 90 K in all samples, where the maximum occurs at different temperatures (T), relative to the x-value (see Figure S6). In fact, in many type II - multiferroic materials, where polarization is induced by a specific magnetic structure, the electric current peak often appears broader, as observed in $(\text{Bi}_{0.5}\text{Ag}_{0.5})\text{Mn}_7\text{O}_{12}$ [26], Y_2MnCrO_6 [51], $\text{BiMn}_3\text{Cr}_4\text{O}_{12}$ [49] and $\text{Ba}_3\text{Fe}_2\text{O}_5\text{Cl}_2$ [52]. As shown in Figure S5, we could tune and reverse the electric current values by changing the sign of the poling electric field in all Sr-doped CMO samples, and the absolute values of the current are nearly proportional to the temperature sweeping rate. However, distinct characteristics were observed in Sr-doped CMO samples, where the peak shifts occur at different heating rates, and some curves exhibit double peaks, indicating that some extrinsic contribution remains due to TSDC.

In Fig. 5(c), we observed a linear reduction in CMO total polarization (P) with increasing Sr-doping, where the sample with $x = 0.30$ exhibits only a quarter of the polarization observed in the undoped CMO compound. The reduction of polarization in Sr-doped CMO was also observed by Jain *et al.* at a Sr-concentration of $x = 0.10$ [30]. In this

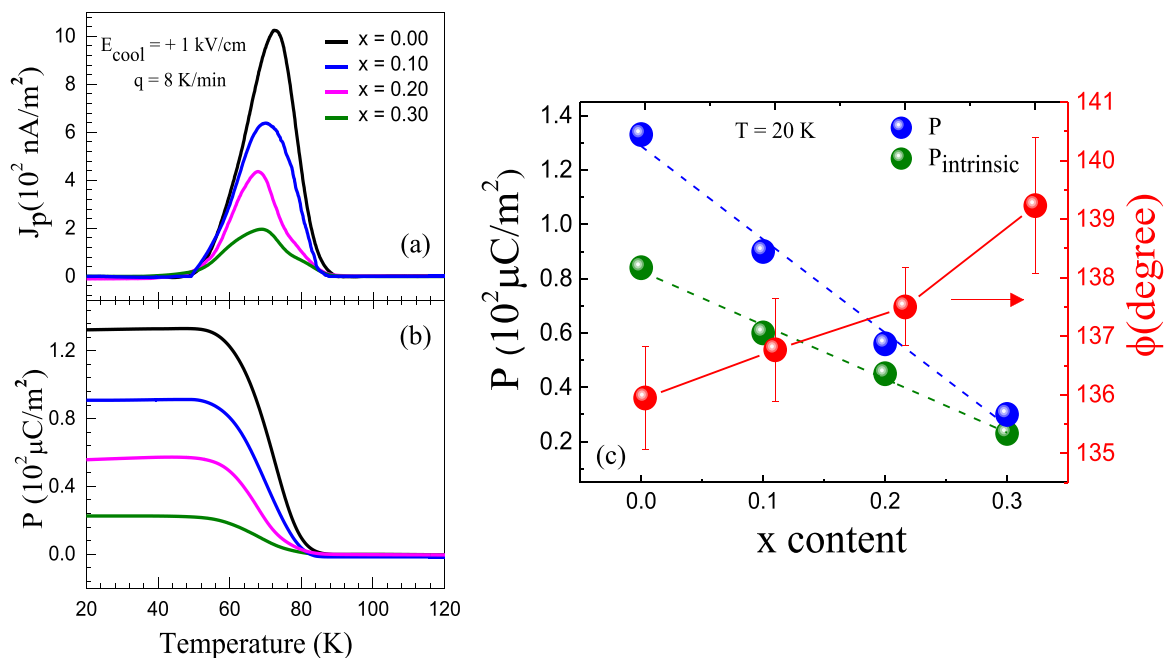


Fig. 5. Temperature dependence of (a) the current density (J_p) and (b) the total electric polarization (P) for $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ ($x = 0.00, 0.10, 0.20$, and 0.30) samples, measured under a poling field of $E_{\text{cool}} = +1$ kV/cm and a heating rate of $q = 8$ K/min. (c) Dependence of total polarization (P) and intrinsic polarization ($P_{\text{intrinsic}}$) on the Sr-content (x), along with the variation of the angle Φ between $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$. The total polarization P points in (c) were obtained from (b) at $T = 20$ K.

paper, we observed for $x = 0.00$ ($T = 20$ K) a polarization of $\sim 134 \mu\text{C}/\text{m}^2$ for $E = 1.0 \text{ kV}/\text{cm}$, value which exceeds that observed by Zhang *et al.* [19] in a undoped polycrystalline CMO sample ($240 \mu\text{C}/\text{m}^2$ for $E = 3.5 \text{ kV}/\text{cm}$) when considering the same field magnitude, since P has been shown to be proportional to E in the investigated field range [19]. Of course, this polarization value is lower compared to that observed in undoped CMO single crystals ($2870 \mu\text{C}/\text{m}^2$ for $E = 4.4 \text{ kV}/\text{cm}$) [21]. The difference in polarization observed in polycrystalline samples has been attributed to the voltage-divider effect at grain boundaries, where the "effective" poling fields in ferroelectric domains are smaller than the nominal ones. Consequently, the effective poling field is greater in single crystals than in polycrystals [53].

Therefore, all these features (e.g., a large broad peak, a center peak dependent on the heating rate, and an asymmetric peak) indicate that the total polarization observed in Sr-doped CMO samples originates from both extrinsic thermally stimulated depolarization processes and intrinsic pyroelectric current contributions. By applying Eq. (1) to the observed current density across all Sr-doped CMO samples, we can effectively model the extrinsic contribution (see Figure S7). It can be observed that the samples with $x = 0.00, 0.10, 0.20$, and 0.30 Sr-content can be modeled using a single peak described by Eq. (1). All samples display current depolarization peaks with activation energies ranging from 0.14 to 0.15 eV, and relaxation times of the processes on the order of $\sim 10^{-9}$ s, in perfect agreement with that recently reported for $\text{BiMn}_7\text{O}_{12}$ [54]. Additionally, Fig. 5(c) shows that the intrinsic contribution ($P_{\text{intrinsic}}$) decreases approximately linearly with increasing Sr-concentration. This polarization is associated with the non-collinear spin ordering that occurs below 90 K, and we demonstrate a strong correlation between this intrinsic polarization and the variation of the angle Φ between $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$. As this angle increases, the induced polarization exhibits linear decay.

At this point, it is particularly important to discuss the mechanisms underlying the observed intrinsic electric polarization. Since the magnitude of electric polarization arises from the exchange-striction interaction between Mn^{3+} and Mn^{4+} ions at the B-site, we can gain insights into the exchange-striction mechanism in CMO by analyzing structural changes with Sr-doping. Our results reveal that Sr-doping significantly influences this interaction, which depends on the angle between Mn neighboring spins and the distance between these ions [55]. As shown in Fig. 5(c), Sr-doping increases the $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond

angle, resulting in a consequent reduction in the induced electric polarization. The reduction in electric polarization indicates the Sr-induced lattice expansion modifies the exchange interactions by either increasing the Mn-O bond lengths or the Mn-O-Mn bond angles, both of which are known to directly alter exchange energies in ferromagnetic and antiferromagnetic perovskite manganites [56,57]. A similar dependence was observed in the orthorhombic $\text{Gd}_{1-x}\text{Ho}_x\text{MnO}_3$ (for $x \leq 0.5$) manganite, which was investigated by Zhang *et al.* [58], where a decrease in the Mn-O-Mn angle induces an increase in the induced polarization. Moreover, these results are in good agreement with those reported by Sannigrahi *et al.*, who provided experimental evidence of exchange-striction in CMO through the observation of pronounced anomalies in the temperature dependence of Mn1-O, Mn2-O, and Mn3-O bond lengths around $T_{\text{N1}} = 90$ K [24]. Additionally, this effect was further supported by changes in the pre-edge region of the Mn-K XAS. Given that magnetostructural coupling plays a crucial role in this phenomenon, these findings reinforce that the reduction in electric polarization observed upon Sr doping in CMO in the present study originates from structural modifications induced by Sr incorporation, which impact the exchange-striction interaction.

The relationship between the structural Mn-O-Mn bond angle and the spin angles in CMO can be understood by considering the CMO spin configuration for $T_{\text{N1}} = 90$ K, as determined by neutron diffraction [22]. As shown in Fig. 6, in the B-site of the CMO trigonal structure, the Mn^{3+} ions form triangular layers above and below the Mn^{4+} ions and $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bonds with the upper layer become more acute (i.e., the angles decrease), while those with the lower layer become more open (i.e., the angles increase). As a consequence of such a pattern of displacements the central Mn^{4+} ions move upwards along the c-axis generating polarization [59]. Thus, the DM interaction plays a crucial role in determining the direction of the induced electric polarization [20]. However, at temperatures just below $T_{\text{N1}} = 90$ K, due to the magnetoelectric coupling, the magnetic ordering induces lattice deformations through the exchange-striction interaction ($\mathbf{S}_1 \cdot \mathbf{S}_2$). This effect, combined with the $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge order configuration and the ferroaxial coupling of the magnetic chirality to the macroscopic structural rotations (See Fig. 6) determines the magnitude of the observed polarization [21].

In the present study, Sr-doping increases such $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ angle, as shown in Fig. 5(c). Thus, when the sample reaches T_{N1} under cooling, the larger angle implies a smaller Mn^{4+} displacement, which

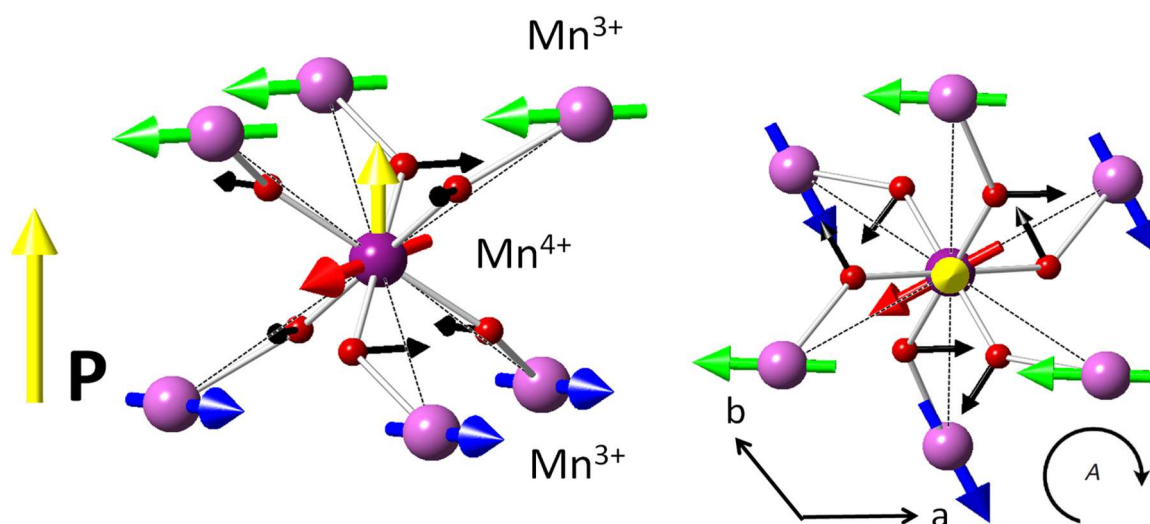


Fig. 6. Schematic representation of the $\text{CaMn}_7\text{O}_{12}$ magnetic structure at low temperatures in perspective (left) and a top view (right). The light purple spheres indicate Mn^{3+} at B-sites, while the dark purple spheres correspond to Mn^{4+} at B-sites. Black arrows indicate the direction of the oxygen displacements due to DM interaction. Green, red, and blue arrows represent the spin directions of Mn^{3+} ions in the upper plane, and of the Mn^{4+} and Mn^{3+} ions in the lower plane, respectively. The yellow arrow signals the polarization direction due to the Mn^{4+} displacement. The ferroaxial vector $\mathbf{A}$, which is along the -3 rhombohedral axis, is indicated in the top view (right). (Same schematic representation as proposed in reference [59]).

results in a lower polarization. Therefore, the $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angle can be tuned to control the polarization in CMO. Then it is expected that larger polarization values can be induced by doping CMO in such a way that the $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angles get smaller than in undoped CMO. Conversely, for samples whose $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angle has increased up to 180° , the induced polarization should be null. It is important to note that our results show a way to tune CMO polarization, as well as give sound experimental evidence that Johnson's model [59] fully describes the magnetically-induced electric polarization in CMO since the relationship between the induced electric polarization in CMO and the $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angle is defined by the ferroaxial coupling between the magnetic helical structure and the structural global rotation. Finally, based on our results, this model provides evidence that, for large $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angles, the induced electric polarization is low, which plausibly explains why $\text{SrMn}_7\text{O}_{12}$ has weak or no ferroelectricity [29].

4. Conclusions

The effects of low concentrations of Sr-doping on the structural, magnetic, and electric properties of polycrystalline $\text{CaMn}_7\text{O}_{12}$ (CMO) were investigated. Structural analysis reveals that all samples exhibit a distorted perovskite structure with trigonal symmetry, belonging to the space group $R\bar{3}$. The temperature dependence of magnetic susceptibility shows anomalies at $T_{N1} = 90$ K and $T_{N2} \sim 42$ K for all Sr-doped CMO samples, without indicating significant changes in the helical magnetic structure. Thermally stimulated depolarization currents (TSDC) measurements reveal large and broad peaks around the first magnetic phase transition ($T_{N1} = 90$ K), which are attributed to both extrinsic dipolar thermally stimulated relaxation processes and intrinsic pyroelectric currents due to the helical spin rearrangement in Sr-doped CMO samples. By modeling the extrinsic current density, we estimated the intrinsic polarization contribution in the polycrystalline in Sr-doped CMO compounds. Our results show that Sr doping in CMO strongly affects the magnetically induced polarization, leading to a significant reduction in its magnitude with increasing Sr concentration. We suggest that this reduction in induced electric polarization in $\text{CaMn}_7\text{O}_{12}$ originates from the increase in the $\text{Mn}^{3+} - \text{O} - \text{Mn}^{4+}$ bond angle, weakening the exchange-striction interaction. Meanwhile, the Dzyaloshinskii-Moriya (DM) effect determines the direction of the induced electric polarization. Finally, this result sheds light on understanding the intriguing giant-induced polarization in similar compounds with non-collinear magnetic structures.

CRedit authorship contribution statement

A. Nonato: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization. **S. Yáñez-Vilar:** Review & editing, Methodology, Investigation. **J. Mira:** Review & editing, Visualization, Resources. **M.A. Seánarís-Rodríguez:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **M. Sánchez Andújar:** review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **J. Agostinho Moreira:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition. **A. Almeida:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition. **R.X. Silva:** Review & editing, Methodology, Investigation. **C.W.A. Paschoal:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2025.180655.

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