

Enhanced multiferroicity in Mg-doped $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$

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Polycrystalline $\text{Ca}_{3-x}\text{Mg}_x\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$) samples are prepared in order to investigate the A-site doping effect of $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$). Compared with $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$), the ferroelectric polarization and Curie point of $\text{Ca}_{3-x}\text{Mg}_x\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($x \sim 0.3$, $y \sim 1.0$) at the maximal doping $x \sim 0.3$ are significantly enhanced. The magnetic order of $\text{Ca}_{3-x}\text{Mg}_x\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($x \sim 0.3$, $y \sim 1.0$) and thus ferroelectric order are more robust than the undoped compound. The slight lattice shrinking as a result of Mg substitution may contribute to the enhancement of exchange striction, leading to the changes in magnetic and ferroelectric properties. © 2010 American Institute of Physics. [doi:10.1063/1.3292584]

Recent discoveries of multiferroics that display a coupling between magnetic and ferroelectric (FE) orders have caused a resurgence in the field of magnetoelectric effect.^{1,2} Among these materials, a recently synthesized Ising chain magnet $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$, abbreviated as CCMO hereafter) has attracted great interest.³⁻⁹ CCMO can be viewed as doped $\text{Ca}_3\text{Co}_2\text{O}_6$ (CCO) where a half of Co^{2+} ions are replaced by Mn^{4+} ions. CCO is a spin-chain compound consisting of parallel one-dimensional Co_2O_6 chains built by successive alternating face-sharing CoO_6 trigonal prisms and CoO_6 octahedra along the hexagonal c -axis, separated by Ca^{2+} ions. Each chain is surrounded by six equally spaced chains and forms a triangular arrangement on the a - b plane.¹⁰

For CCMO, all the Mn^{4+} ions locate at the oxygen-octahedron sites while Co^{2+} ions occupy the prism sites.¹¹ Alternating high-spin (HS) Mn^{4+} and HS Co^{2+} ions form the Ising chain with an up-up-down-down ($\uparrow\uparrow\downarrow\downarrow$) spin order in the ground state, making CCMO an alternating-spin Ising ferrimagnet (ASIF).^{3,9} Due to the exchange striction from the superexchange interaction between the nearest-neighbor spins along the chain, bonds between parallel spins are stretched while those between antiparallel ones are shortened, which is responsible for the FE polarization.⁷ Therefore, a maximized exchange striction would assure a maximized polarization. To proceed along this line, a simple approach to improve ferroelectricity is to reduce the lattice volume so that the exchange interaction can be enhanced so as to strengthen the exchange striction.^{7,12}

It is well known that the lattice volume can be modulated by doping ions of different radius, which allows us to reduce the lattice parameters through partially substituting Ca^{2+} with smaller ions, such as Mg^{2+} which has an ionic radius of only 2/3 of Ca^{2+} , namely, 0.66 Å. The reason for us to adopt A-site doping is that it would make little difference in the intrachain magnetic order, which is the prerequisite for ferroelectricity in CCMO.

Furthermore, it was reported that for $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$, the magnetic long-range order is absent exactly at $y=1.0$ where the best Co/Mn ionic order is achieved.⁵ Thus, a stoi-

chiometric Co:Mn=1:1 may not benefit the ferroelectricity, indicating a tiny change of the Co/Mn ratio around one would influence significantly the FE property of CCMO. Earlier works on CCMO mainly focused on the Mn-substitution of Co (Ref. 11) and the microscopic mechanism of ferroelectricity.³⁻⁹ While CCMO single crystal (actually $y \sim 0.96$) has a polarization P as high as $\sim 90 \mu\text{C}/\text{m}^2$, no work on the ferroelectricity of polycrystalline CCMO samples has been reported so far. Also, no much work on the A-site doping in CCMO in terms of exchange striction/polarization enhancement has been done. In this letter, we report our experiments on the effect of Mg-doping at the A-site of ceramic CCMO, which seems to be a persuasive case to approve the simple strategy of polarization enhancement mentioned above.

Polycrystalline $\text{Ca}_{3-x}\text{Mg}_x\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$, abbreviated as CMCM hereafter) and CCMO samples were prepared by the codeposition method. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in de-ionized water and K_2CO_3 was used to deposit these ions. The deposition was then washed with de-ionized water for three times. After drying at 80 °C for 12 h, the precipitation was calcined at 700 °C for 24 h, pressed into pellets and calcined at 1000 °C for 24 h.

The samples were then characterized by x-ray diffraction (XRD) at room temperature and the concentration of Co and Mn was determined by means of electron microprobe analysis. The dc magnetic susceptibility χ was measured in a superconducting quantum interference device and the dielectric constant was measured using HP4294 impedance analyzer at frequency $f=100$ Hz. For measuring polarization P , the samples were first poled in an electric field $E=16.7$ kV/cm from 200 to 2 K and then P as a function of temperature T was obtained by integrating the pyroelectric current at a T -varying rate of 2 K/min. Details of such measurement and data processing were reported in earlier letter.¹³ We prepared a series of samples with different doping levels x and the highest value excluding identifiable impurity phase is $x \sim 0.3$. It was shown that higher doping corresponds to better properties in terms of ferroelectricity enhancement. Hereafter, we refer CMCM to the doping level $x \sim 0.3$.

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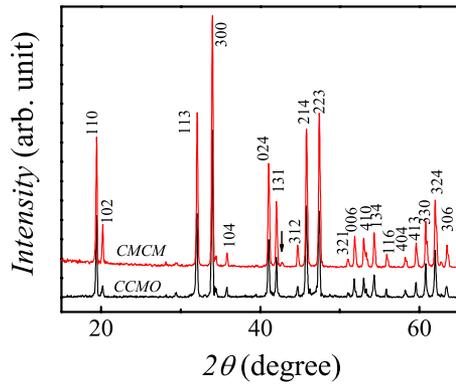


FIG. 1. (Color online) XRD spectra for samples CCMO and CMCM. The arrow indicates the peak of MgO.

Figure 1 shows the XRD patterns of the as-prepared CMCM and CCMO. All the reflections from the CCMO sample are in good agreement with earlier report.¹¹ Similar to CCMO, CMCM has a hexagonal symmetry in the $R\text{-}3c$ space group (K_4CdCl_6 -type structure) but one trace peak from impurity MgO seems identifiable. The relative intensity of MgO peak is less than 1%, indicating that most Mg^{2+} ions successfully enter into the Ca^{2+} -sites. Besides, considering the fact that MgO has no ferroelectricity and magnetism, it as an impurity phase, if any, would not affect our investigation. From the XRD data, as expected, it is evaluated that the lattice parameters of CMCM are $a=9.110$ Å, $c=10.547$ Å, indeed smaller than CCMO ($a=9.124$ Å, $c=10.567$ Å).

We then look at the ferroelectricity. It is identified that the higher Mg-doped samples have larger $P(T)$. The measured $P(T)$ data for CCMO and CMCM under a field $E=16.7$ kV/cm are presented in Fig. 2(a). While the measured P of CCMO at $T=2$ K is ~ 3 $\mu\text{C}/\text{m}^2$ and then drops

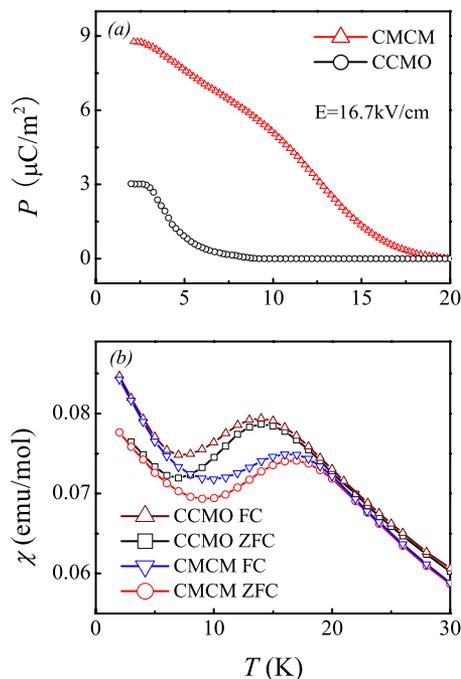


FIG. 2. (Color online) (a) Polarization P of polycrystalline CCMO and CMCM as a function of T . The samples were poled from 200 to 2 K under an electric field of 16.7 kV/cm. (b) Magnetic susceptibility χ as a function of T under $H=100$ Oe for both CCMO and CMCM.

rapidly with increasing T until $T\sim 9$ K where P disappears, CMCM has its $P\sim 8.8$ $\mu\text{C}/\text{m}^2$ at $T=2$ K, three times as large as that of CCMO. The temperature for P -disappearance is ~ 20 K, also higher than $T\sim 9$ K for CCMO. This indicates that the Mg-doping at Ca^{2+} site does allow a significant enhancement of polarization and its appearance temperature.

What should be mentioned here is that the measured P for the polycrystalline CCMO ($y\sim 1.0$) sample is much smaller than its single crystal counterpart at $y\sim 0.96$. First, this is a well known phenomenon also observed in other multiferroics.^{14,15} Furthermore, recent experiments revealed that the FE polarization in CCMO is very sensitive to the value of y at $y\sim 1.0$, i.e., the Co:Mn stoichiometry is critical, and it even disappears exactly at $\text{Co}/\text{Mn}=1.0$.⁵ Thus, the tiny variation of this ratio from samples prepared by different authors may affect significantly the measured P value, which does not allow a quantitative comparison of the measured P from different groups. With respect to our samples, the Co:Mn ratios for both CCMO and CMCM were measured by the electron microprobe analysis to be 0.99:1.01 within the measuring error of $\sim 2\%$, which allows a fair comparison between them so as to investigate the doping effect.

Subsequently, we investigate the magnetic behaviors of CMCM and CCMO. The measured χ as a function of T under zero field cooling and field cooling conditions are shown in Fig. 2(b). The magnetic field is $H=100$ Oe. It is seen that the Mg-doping does not induce any identifiable change both in the low- T range ($T<5$ K) where the spins are essentially frozen, and in the high- T range ($T>20$ K) where the spin configuration is disordered. The doping-induced effect makes sense within $T=5\text{--}20$ K, where the magnetic ordering is not yet frozen. It is clearly shown that the Mg-doping suppresses the magnetic response, suggesting that the Mn-Co antiparallel order stability is enhanced. This is also partially evidenced by the fact that upon the doping the peak associated with the ASIF ordering shifts up from 14 to 16.7 K. This tendency coincides with FE ordering behavior.

Further investigation goes to $P(H)$, from which the FE stability against H can be evaluated and also the magneto-electric coupling can be identified. Figures 3(a) and 3(b) show the measured $P(T)$ under various H for CCMO and CMCM, respectively. It could be observed that for CMCM sample there is only slight suppression of P by H as high as 9 T, numerically less than 20%. However, for CCMO, the response of $P(T)$ against H is much more remarkable and a decrease of P at about 50% given a field of $H=7$ T is observed, demonstrating a higher stability of the FE order against H in CMCM than in CCMO.

To understand these observed phenomena due to the Mg-doping, as shown above, one may consult to the fact that the Mg-doping results in lattice contraction (reduced lattice parameters) and distortion. In a roughly qualitative sense, the spin-spin coupling J for the superexchange interaction in magnetic systems is usually lattice-size-dependent,¹² and shrinking lattice and distortion would result in an enhanced J , while the spin-crossover associated with Co ions so as to modulate the ASIF interaction may not be favored.¹⁶ For CCMO, according to our previous work,⁷ the exchange striction (thus polarization) becomes stronger if the intrachain interaction J is larger. We thus reasonably reach an argument that the enhanced J due to the Mg-doping is responsible for

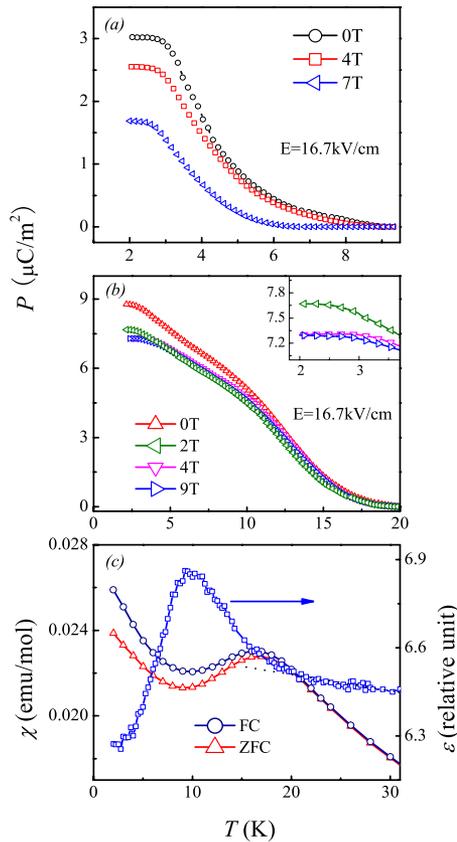


FIG. 3. (Color online) (a) Polarization P of CCMO measured under several magnetic fields (H). (b) Polarization of CMCM measured under different magnetic fields. The inset shows the locally amplified part at low T . Both CCMO and CMCM samples are poled in an electric field of $E = 16.7$ kV/cm. (c) Measured χ under $H = 100$ Oe and dielectric constant ε for CMCM. Dashed line shows the high- T linear behavior of ε .

the polarization enhancement. In addition, the slight lattice shrinking may cause an increase of the interchain dipole interaction, leading to a larger FE domain and thus a larger polarization, as theoretically predicted.⁷ What should be noted here is that a quantitative estimation of the dependence of J on the lattice unit volume and distortion remains challenging to us and further work on this issue is then appealed.

The as-obtained stronger intrachain interaction also allows a higher stability of the $\uparrow\uparrow\downarrow\downarrow$ order between the Mn-Co intrachain spin pairs,⁷ leading to the lower χ and higher ordering onset temperature. The strengthening of magnetic order results in a more stable FE order, which origins from it. This might be the reason why the Curie Point of CMCM is higher than CCMO as shown in Fig. 2(a). In addition, an external H always tends to break the $\uparrow\uparrow\downarrow\downarrow$ order and thus suppresses the polarization.³⁻⁵ Nevertheless, for CMCM, the $\uparrow\uparrow\downarrow\downarrow$ order (also FE order) is more robust against H than that for CCMO, indicating weaker response of $P(T)$ to H , as identified in Figs. 3(a) and 3(b).

Finally, we present once more in Fig. 3(c) the measured χ under $H = 100$ Oe and the T -dependence of dielectric con-

stant ε . We notice that the onset temperature of the ASIF ordering is ~ 17 K, which is signified by a broad peak.³ This temperature is roughly the same as the polarization onset point ~ 20 K, indicating the coupling between magnetic and FE orders in CMCM system. Absence of any sharp anomaly of $\varepsilon(T)$ at the magnetic transition point indicates that CMCM may be still in a frozen state undergoing slow relaxation processes.³ These phenomena seem to reveal that the Mg-doping does not change the origin of multiferroicity in CMCM.

In summary, polycrystalline Mg-doped $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$) samples have been prepared to investigate the effect of A-site substitution on both FE and magnetic properties. It has been demonstrated that the polarization can be enhanced by the doping and the ferroelectricity of $\text{Ca}_{2-x}\text{Mg}_x\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($x \sim 0.3$, $y \sim 1.0$) becomes less sensitive to external magnetic field in comparison with $\text{Ca}_3\text{Co}_{2-y}\text{Mn}_y\text{O}_6$ ($y \sim 1.0$). We argue that the increased exchange constants as a result of reduced lattice unit volume may partially be responsible for these doping effects.

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