Enhancement of magnetoelectric coupling in Cr doped Mn$_2$O$_3$

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Abstract

The effect of Cr doping has been undertaken to investigate its effect on the structural, magnetic, dielectric and magnetoelectric properties of newly discovered multiferroics material $\alpha$-Mn$_2$O$_3$. The Cr doping modifies the room temperature crystal symmetry i.e. transforms from orthorhombic to cubic symmetry. Similar to $\alpha$-Mn$_2$O$_3$, two magnetic transitions have been observed in all Cr doped samples. The effect of Cr doping manifested on the low temperature transition. The lower magnetic transition shifted toward higher temperature (25 K for pristine to 40 K for Cr $= 10\%$) whereas the high temperature transition decreases slightly with increasing Cr content. A clear frequency independent transition is observed in temperature dependent complex dielectric measurements for Mn$_{2-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.10$) samples around high temperature magnetic ordering $\sim$80 K which corroborate the magnetoelectric coupling in these samples. Interestingly, the magnetodielectric value enhanced significantly with Cr doping and a maximum increase of $\sim$21$\%$ is observed for 10$\%$ Cr doped sample at 5 K around 70 kOe magnetic field.

Keywords: magnetoelectric coupling, multiferroics, magnetism, transition metal oxide

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
multiferroics materials and understanding their microscopic origin. The ABO₃ type compound are one of the most studied class of oxide materials for their multiferroicity and ME coupling [7, 9–12]. Stoichiometrically, the Mn₂O₃ is same as the first ME material Cr₂O₃ [24, 25]. The Mn₂O₃ has different phases depending upon the synthesis conditions. Recently, we have evidence of the multiferroicity and ME coupling in α-Mn₂O₃ [26]. Magnetically, it shows two antiferromagnetic (AFM) transitions one at 25 K and the other at 80 K. Corresponding to the AFM ordering around 80 K, a clear frequency independent transition is observed in the dielectric permittivity and the transition temperature is magnetic field independent even at 80 kOe magnetic field. We have also showed that the emergence of electric polarization near the AFM regime and its modulation with magnetic field. Around the same time, Cong et al also observed spin induced multiferroicity in the high temperature and high pressure phase ζ-Mn₂O₃ [27]. The pristine α-Mn₂O₃ is orthorhombic at room temperature [26, 28] and undergoes cubic to orthorhombic transition at 308 K [29, 30]. The effect of substitution has interesting effects on ME properties [31–34]. In this system, Mn formed octahedral surrounding and having Jahn–Teller (J–T) active cation due to the 3+ oxidation state. The substitution of Cr³⁺ at Mn site which is a non-active J–T cation can influence its different properties like structural, magnetic, dielectric, magnetodielectric etc because of the empty eg orbital in case of Cr³⁺ than one electron in eg level in case of Mn³⁺. Here, we present the effect of Cr doping on the structural, magnetic, dielectric and magnetodielectric properties of α-Mn₂O₃. Our results illustrates that the Cr doping modifies the crystal structure from orthorhombic to cubic structure. The incorporation of non J–T cation i.e. Cr at Mn site influences the magnetic interactions and leads to the modification of magnetic ordering temperature and ME properties. The maximum value of magnetodielectric is observed for 10% Cr doped sample at 5 K which is around 21% higher than the pristine α-Mn₂O₃.

2. Experimental details

The polycrystalline samples of Mn₂₋ₓCrₓO₃ (0 ≤ x ≤ 0.10) have been prepared through the standard solid state reaction method. The high purity MnO₂ and Cr₂O₃ (99.99%) have been mixed in stoichiometric ratio and sintered at 800 °C for 12 h. The room temperature (RT) synchrotron x-ray diffraction (SXRD) measurements were performed at beamline-12 at Indus-2, RRCAT, Indore (λ = 0.7986 Å) [35]. The dc magnetization measurements were done on a 7 T Quantum Design SQUID-VSM. The temperature and magnetic field dependent complex dielectric measurements were performed using a home-made insert coupled with a 9 T superconducting magnet from American Magnetics and a Keysight E4980A LCR meter [26]. The temperature dependent remnant electric polarization is performed using Keithley 6517B electrometer in Columbic mode in different magnetic fields during warming at a rate of 2 K min⁻¹. Before measuring the charge vs temperature behavior the sample was short circuited for 30 min and then charge vs time measurements were done for 2 h to remove the stray charges if any were present. The direction of electric and magnetic fields was parallel to each other. In case of dielectric and electric polarization under magnetic field, the magnetic field was applied at the lowest temperature.

3. Results and discussion

3.1. Crystal structure

The RT Rietveld refinement of SXRD patterns for α-Mn₂O₃ and Mn₂₋ₓCrₓO₃ (0.01 ≤ x ≤ 0.10) are shown in figure 1. The refinement is performed using Fullprof software [36]. Our structural analysis infers that for Cr doped samples the crystal structure is cubic at RT with space group Ia-3 instead of orthorhombic Pcab as for pristine α-Mn₂O₃. The insets in figures 1(a)–(d) show the zoomed view of diffraction pattern for 2θ = 23°–26°. It is interesting to note that in Cr doped samples, there is no additional peak at 2θ = 24.30° corresponding to hkl ~ (034) as observed for α-Mn₂O₃ within the instrument resolution. The details of the RT crystal structure are given in our earlier work [14]. These results suggest that the crystal structure of Cr doped samples is cubic at RT. Earlier Geller and Espinosa also showed that Cr doping leads to the formation of cubic structure at RT [30]. The α-Mn₂O₃ undergoes cubic to orthorhombic transition at 308 K. These results corroborate that Cr doping lower the cubic to orthorhombic transition. The change of crystal structure from orthorhombic to cubic can be explained on the basis of replacement of J–T active cation (Mn³⁺) with non J–T active cation (Cr³⁺) which reduces the structural distortion. Even 1% Cr doping shows cubic structure at RT. The arrow in the insets of figures 1(b)–(d) show the 2θ value where the peak related to orthorhombic structure is observed in pure Mn₂O₃, see the inset of figure 1(a). The details of unit cell for Mn₂₋ₓCrₓO₃ (0.01 ≤ x ≤ 0.10) are given in table 1. Table 1 suggests that the lattice parameters as well as the unit cell volume decreases with increasing Cr-content. The lattice parameters change systematically with increasing x, which imply that Cr-ions do replace the Mn-ions. The schematic representation of the crystalline structure of Mn₁₋ₓCrₓO₃ on the basis of SXRD results is presented in figure 1(e).

3.2. Magnetic properties

The temperature dependent dc magnetic susceptibility (χ = M/H) of Mn₂₋ₓCrₓO₃ (0.01 ≤ x ≤ 0.10) at 500 Oe during zero field cooled warming (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) conditions is presented in figures 2(a), (d) and (g). These plots show that for x = 0.01, 0.05 and 0.10; χ exhibit two AFM transitions (TN₁) ~79, 78, 77 K and other transition (TN₂) around 35, 37 and 40 K, respectively. For x = 0.10, an additional clear feature is observed around 94 K, see figure 2(g). All these transitions are clearly seen in the dχ/dT vs T plots and presented in the figures 2(c), (f) and (i) (left y-axis). As compared to pure α-Mn₂O₃, TN₁ decreases slightly whereas the TN₂ shifts toward higher temperature which is consistent with earlier reports [26]. In addition all χ vs T plots show that the χ increase rapidly after TN₂ which is different from pristine
From table 2, it is clear that the value of \( \alpha \) is very high as compared to the pristine sample, which further suggests the modifications in magnetic interactions with Cr doping. The observed results are summarized in table 2.

Table 1. Lattice parameters and unit cell volume of Mn\(_2\)-xCr\(_x\)O\(_3\) (0.01 \( \leq x \leq 0.10 \)) at room temperature.

| \( x \)  | Lattice parameters (Å) | Volume (Å\(^3\)) |
|---------|------------------------|------------------|
| 0.01    | 9.4173(3)              | 835.17(4)        |
| 0.05    | 9.4036(4)              | 831.54(7)        |
| 0.10    | 9.3968(3)              | 829.73(5)        |

Mn\(_2\)O\(_3\) [26]. These observations suggest the modifications in the magnetic interactions with Cr doping.

The fcc and fcw curves for all the compositions show a thermal hysteresis around lower magnetic transition as seen for pure Mn\(_2\)O\(_3\), which suggest the first order nature of this transition. The effective magnetic moment (\( \mu_{\text{eff}} \)) and the Curie–Weiss paramagnetic temperature (\( \theta_P \)) are determined by Curie–Weiss law \( \chi = \frac{C}{T - \theta_P} \) (where C is Curie-Weiss constant) from the linear part of the inverse dc susceptibility data at high temperature (160–300 K), not shown here (see supplementary information figure S1). The observed results are summarized in table 2. From table 2 it is clear that the value of \( \mu_{\text{eff}} \) decreases slightly with increasing Cr content. For \( \alpha\)-Mn\(_2\)O\(_3\) sample, \( \mu_{\text{eff}} = 4.87 \) \( \mu_B \) which is approximately equal to the theoretical value of 4.90 \( \mu_B \) for Mn\(^{3+}\). The valence state of Cr should be +3, the spin only value is calculated using equation \( \mu_{\text{eff}} = \sqrt{(1 - x)\mu_{\text{Mn}}^2 + x\mu_{\text{Cr}}^2} \) where \( x \) is the Cr ion content.

The experimentally extracted and theoretical value of \( \mu_{\text{eff}} \) for different Cr content is given in table 2. The magnitude of \( \theta_P \) is very high as compared to the pristine sample, which further suggests the modifications in magnetic interactions with Cr doping. There is no significant change in the \( MH \) behavior of all these samples and show almost linear behavior without any hysteresis which again confirm the AFM ground state of the studied samples (see supplementary information figure S2). We have not observed any magnetic field induced transition at least up to 70 kOe magnetic field. This modification in magnetic properties is due to the replacement of J–T active cation Mn\(^{3+}\) with non J–T active cation Cr\(^{3+}\). In case of Mn\(^{3+}\) there is one electron in \( \varepsilon_g \) level whereas it is empty in case of Cr\(^{3+}\). The Cr doping leads to complex magnetic interactions with different combinations [37]. The possible magnetic interactions are Mn–O–Mn, Mn–O–Cr and Cr–O–Cr.

### 3.3. Magnetodielectric properties

The temperature dependent dielectric constant of Mn\(_{2-x}\)Cr\(_x\)O\(_3\) (0.01 \( \leq x \leq 0.10 \)) at 100 kHz at 0 and 80 kOe magnetic fields during warming (1 K min\(^{-1}\)) is shown in figures 2(b), (e) and (h). The dielectric constant decreases with decreasing temperature and exhibit a frequency independent transition around 79, 78 and 77 K for 0.01, 0.05 and 0.10, respectively. The transition in dielectric results is frequency independent as in case of pristine Mn\(_2\)O\(_3\) [26]. The dielectric behavior at different frequencies for \( x = 0.01 \) and 0.10 is presented in the inset of the figures 2(b) and (h), respectively. The decrease in the transition temperature in dielectric results with Cr content is in accordance with the magnetic transition. The occurrence of dielectric anomaly at magnetic ordering illustrates the coupling between magnetic and dielectric properties. Moreover, the dielectric anomalies at \( T_N1 \) for all compositions are magnetic field independent as in case of pure Mn\(_2\)O\(_3\). In addition, below 20 K the dielectric constant increases with decreasing temperature in both the 0 and 80 kOe fields. The change in the dielectric value vs temperature is very small and we could not detect any clear change in dielectric around \( T_N2 \). To see the changes across the magnetic transitions, we have shown \( d\varepsilon/dT \) vs \( T \) for all compositions in figures 2(c), (f) and (i); right y-axis). These figures show that there is small change in the slope of \( d\varepsilon/dT \) around 20 K. The temperature dependent \( d\varepsilon/dT \) and \( d\varepsilon/\delta H \) has one to one correspondence. Figures 2(c), (f) and (i) corroborate that like pristine Mn\(_2\)O\(_3\), there is a tail like feature above \( T_N1 \) for all the studied compositions and this feature is more prominent in case of \( x = 0.10 \). The value of \( \delta \) for \( x = 0.01, 0.05 \) and 0.10 are also very small, see supplementary information figure S3.

Further, to investigate the effect of magnetic field on the dielectric behavior, we have performed isothermal magnetodielectric (MD) measurements at different temperatures and frequencies for different Cr content. The MD is calculated using relation MD = \( (\varepsilon' - \varepsilon_{H=0})/\varepsilon_{H=0} \). The MD% for different Cr content at 5 K is shown in figure 3(a). The observed MD is negative and it decreases with increasing magnetic field up to 80 kOe at lower temperature. Above magnetic ordering the value of MD is nearly zero. For \( \alpha\)-Mn\(_2\)O\(_3\), maximum MD value at 5 K is 0.015% and positive in sign. In case of Cr doping, the sign of MD is negative and its magnitude increases with Cr-doping till \( x = 0.10 \). For \( x = 0.10 \), the maximum MD at 5 K is \( \sim 0.21\% \) which is around 21% higher than the pristine sample. The magnitude of MD is comparable with other multiferroics like spinel MCr\(_2\)O\(_4\) [38], FeV\(_2\)O\(_4\) [39], \( \alpha\)-CoV\(_2\)O\(_6\)
Figure 2. Temperature variation of magnetic susceptibility (a), (d) and (g); dielectric permittivity (b), (e) and (h) at 100 kHz at 0 and 80 kOe magnetic fields and inset in (e) and (h) shows the dielectric permittivity at different frequencies at 0 Oe. The panels (c), (f) and (i) show temperature variation of $\chi'/dT$ and $\varepsilon'/dT$ for different compositions.

Table 2. Experimentally determined and theoretically calculated effective paramagnetic moment ($\mu_{\text{eff}}$) and $\theta_P$ for Mn$_{2-x}$Cr$_x$O$_3$ (0 $\leq x \leq$ 0.10).

| $x$  | $\theta_P$ (K) | $\mu_{\text{eff}}$ (exp.) | $\mu_{\text{eff}}$ (theo.) |
|------|---------------|---------------------------|---------------------------|
| 0    | −25.59        | 4.87                      | 4.90                      |
| 0.01 | −117.37       | 4.81                      | 4.88                      |
| 0.05 | −142.38       | 4.78                      | 4.87                      |
| 0.10 | −105.73       | 4.58                      | 4.85                      |

40, spin chain system Ca$_3$Co$_2$O$_6$ [41], Fe$_2$TiO$_5$ [42] etc. The value of MD is less as compared to single crystal Cr$_2$O$_3$ [25]. These variation of dielectric with magnetic field endorse the enhancement of ME coupling in Cr doped Mn$_2$O$_3$ samples. The change in MD sign also suggests the change in magnetic interactions with Cr doping at Mn sites [43]. The MD for $x = 0.10$ is shown at two different temperatures in figure 3(b). The MD at 5 K infer that the dielectric behavior decreases almost quadratically until 60 kOe and then it decreases very slowly with further increase in magnetic field. This quadratic variation of MD suggests the contributions of higher order ME coupling [44] at lower magnetic field ($\sim$60 kOe for $x = 0.10$). The temperature dependent MD effect for $x = 0.10$ is extracted from temperature dependent dielectric at 0 and 80 kOe fields (from figure 2(h)). This also suggests the maximum MD at lowest temperature. We would also like to mention here that the Cr doping enhanced the dc resistivity and confirm that the studied samples are highly insulating. Therefore, the effect of any extrinsic contributions like magnetoresistance can be excluded.

3.4. Electric polarization

To evident the ferroelectricity in Cr doped samples, temperature dependent remnant electric polarization ($P$) is measured under different magnetic fields. The $P$ for $x = 0.10$ under different magnetic fields at electric field $\sim$217 kV m$^{-1}$ is presented in figure 4. The inset of figure 4 shows the $P$ for $x = 0.05$. This figure shows the emergence of $P$ around 105 K for both compositions. The variation of $P$ from low temperature to $\sim$80 K is very small. However, there is sharp decrease in $P$ across 80 K, which is near the magnetic ordering region. Moreover, the onset of $P$ is coinciding with the first derivative of magnetization and dielectric as presented in the insets of figures 2(c) and (i). This behavior is consisting with pristine Mn$_2$O$_3$ [14]. The $P$ at different magnetic fields is also presented for $x = 0.10$. The magnitude of $P$ is suppressed with the application of magnetic field. Similar to the small anomalies in dielectric behavior around 20 K, cusp like feature is also observed in $P$ around the same temperature. There is also a small change in $P$ around lower magnetic ordering. The one to one correspondence of $P$ and magnetization results infers the coupling between electric and magnetic ordering.
Figure 3. (a) Isothermal magnetodielectric of different compositions of Cr doped Mn$_2$O$_3$ at 5 K. (b) Magnetodielectric for $x = 0.10$ at 5 and 100 K. Inset shows the temperature dependent magnetodielectric for $x = 0.10$ at 50 kHz extracted from temperature dependent dielectric at 0 and 80 kOe.

Figure 4. Temperature dependent remnant polarization for $x = 0.10$ at different magnetic fields, inset shows remnant polarization for $x = 0.05$.

Our results give evidence of the significant enhancement of ME coupling after Cr doping in this system. More interestingly, multiferroicity and ME coupling occur above liquid nitrogen boiling temperature which is not common in many type II multiferroics.

4. Conclusion

In summary, we have studied the structural, magnetic and magnetoelectric properties of polycrystalline Mn$_{2-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.10$). Our structural analysis infers that the Cr doped samples crystallize in cubic symmetry with space group $Ia-3$ at RT. The change in crystal structure from orthorhombic to cubic with Cr doping may be due to the reduction in the octahedral distortion due to the non J–T active Cr at Mn site. The effect of Cr doping is also observed on the magnetic and dielectric properties. The low temperature magnetic ordering shifted toward the higher temperature whereas the high temperature transition decreases slightly with increasing Cr content. The existence of dielectric transition and emergence of electric polarization near magnetic ordering temperature corroborates the correlation between the magnetic and dielectric properties in the studied samples. The significant enhancement in MD ($\sim 0.21\%$) is observed for 10% Cr doped sample at 5 K.
which is ~21% higher than the pristine Mn$_2$O$_3$. Our results demonstrate the enhancement of magnetoelectric properties in Cr doped Mn$_2$O$_3$.

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