Structural, magnetic, magnetocaloric and specific heat investigations on Mn doped PrCrO$_3$ orthochromites

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Structural, magnetic, magnetocaloric and specific heat investigations on Mn doped PrCrO$_3$ orthochromomites

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Abstract
We have synthesized PrCr$_{0.85}$Mn$_{0.15}$O$_3$ (PCMO) chromite and investigated the influence of manganese (Mn) doping at Cr-sites on the structural, magnetic, magnetocaloric and thermal properties of PrCrO$_3$ compound. No structural transition was observed with Mn substitution and the doped compound crystallized into distorted orthorhombic structure with $Pnma$ space group which was confirmed by Rietveld refinement of x-ray powder diffraction patterns. Neel temperature, noticed at 168 K from the temperature variation of magnetization, smaller than that reported for PrCrO$_3$, indicated the influence of Mn$^{3+}$ substitution in decreasing the antiferromagnetic ordering. Magnetization was almost eight times higher than that reported for undoped sample. Magnetocaloric effect measured via the magnetic entropy change and relative cooling power demonstrated significant values in the temperature range 10–20 K. The values of magnetic entropy change are much superior to that reported for other polycrystalline orthochromites and even at smaller applied field strength. The material exhibited second order magnetic phase transition. The Debye temperature and the density of states at Fermi level were also calculated. The overall results make PrCr$_{0.85}$Mn$_{0.15}$O$_3$ chromite a potential candidate to replace the existing materials for low temperature magnetic refrigeration.

Keywords: orthochromites, magnetic refrigeration, specific heat

(Some figures may appear in colour only in the online journal)
orthorhombic perovskite (CAFM) behaviour. Further, the Cr$^{3+}$ ions produce the internal field at the rare-earth site [3, 6, 11]. Therefore, depending upon whether a magnetic ion, or non-magnetic ion is present at the rare-earth site, the internal field will (or will not) rotate the magnetic moment of the rare-earth ion in the opposite direction to that of Cr$^{3+}$ ions. This way, the difference of the two magnetic moments will decide whether the particular orthochromite will demonstrate the magnetization reversal under low value of applied magnetic field. Whenever the applied magnetic field becomes greater than the internal field produced by chromium ions, the magnetization flipping along the field direction takes place resulting in the positive magnetization over the measurement range of temperature [4]. So far, many orthochromites like YCrO$_3$ [12–14], LaCrO$_3$ [15], CeCrO$_3$ [3, 16], PrCrO$_3$ [17–19], NdCrO$_3$ [20, 21], SmCrO$_3$ [22–24], GdCrO$_3$ [25, 26], DyCrO$_3$ [27, 28], YbCrO$_3$ [4, 29] and HoCrO$_3$ [30, 31] have been investigated for their complex magnetic properties and interesting results have been reported on them. As far as the PrCrO$_3$ (PCO) orthochromite is concerned, only a very few studies exist on it [17–19]. For example, Gordon et al. measured its magnetic properties from liquid helium temperature to Neel temperature and obtained the latter ~237 K [17]. Similar studies have been reported by Venugopal Rao et al. on polycrystalline powder prepared by citric acid route [19]. Liu et al. have studied the effect of Ca$^{2+}$ ion doping on the electrical properties of PrCrO$_3$ and proved the applicability of the compound for a superior solid oxide fuel cell (SOFC) [32]. Prasad et al. reported the relaxor-like giant permittivity in PrCrO$_3$ and attributed it to the grain boundary effects [18]. From this, we conclude that only a few attempts have been made to tailor the structural and magnetic properties of PrCrO$_3$ chromite through site engineering which is commonly known as substitution or doping.

Recently, another interesting phenomenon called magneto-caloric effect (MCE) has been reported in chromites. Magnetic refrigeration (MR) measured through the indirect measurement of MCE in the cryogenic temperature range has been carried out systematically and carefully. In fact, giant MCE has been observed near the magnetic phase transitions in rare-earth chromites and multiferroic manganites [26, 31, 33, 34].

In this paper, we have investigated the influence of Mn ion doping on the structural magnetic, magnetocaloric and specific heat properties of PrCrO$_3$ compound. To the best of our knowledge, this is for the first time that such studies are being reported on Mn doped PrCrO$_3$ orthochromites.

2. Experimental details

Polycrystalline samples of PrCr$_{0.85}$Mn$_{0.15}$O$_3$ (PCMO) were prepared by the solid state reaction method in ambient conditions by taking high purity Pr$_6$O$_{11}$, MnO$_2$ and Cr$_2$O$_3$ as starting materials (all chemicals from Sigma Aldrich). The mixture was ground thoroughly and first calcined for 24 h at 600 °C followed by crushing and second calcination at 900 °C for 12 h. After second calcination the powder was pulverized and pelletized in the form of uniform and compact pellets, which were sintered at 1350 °C for 24 h in air. The phase identification was carried out by x-ray diffractometer (PANalytical-Empyrean) using Cu K$_\alpha$ radiation with wavelength 1.540 Å at a scanning rate of 0.02° from 20° ≤ θ ≤ 80°. The magnetic measurements were observed by vibrating sample magnetometer (VSM) between 4 K–300 K. The isotherms $M(H)$ measurements were measured between 0 and 90 kOe from 2 K to 102 K.

3. Result and discussions

3.1. Structural analysis

Figure 1(a) shows the x-ray diffraction patterns of sintered PCMO sample powder along with the Rietveld refinement using Fullprof Suite software [35]. The material is G-type (a > b > c) orthorhombic perovskite (Pnma space group) single phase in nature with lattice parameters $a = 5.491 \pm 0.002$ Å, $b = 7.7167 \pm 0.004$ Å. In place of this symbol please use the symbol like after 1.540 in the 11th line in the Experimental details. Please use that symbol everywhere in this paper in place this symbol and $c = 5.4525 \pm 0.003$ Å. The lattice volume of PCMO unit cell is larger than that reported for pristine PrCrO$_3$ sample [36] which can be attributed to the larger size of Mn$^{3+}$ (0.645 Å) ion when compared with Cr$^{3+}$ (0.615 Å) ion. The results of the refinement are summarized in table 1.
Table 1. Structural parameters and atomic positions for PCMO powder at room temperature.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr: 4c(x, 0.25, z)</td>
<td>0.03664</td>
<td>0.25</td>
<td>-0.00536</td>
<td>1.0128</td>
</tr>
<tr>
<td>Cr: 4b(0, 0, 0.5)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.8461</td>
</tr>
<tr>
<td>Mn: 4b(0, 0, 0.5)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.1516</td>
</tr>
<tr>
<td>O1: 4c(x, 0.25, z)</td>
<td>0.48616</td>
<td>0.25</td>
<td>0.07783</td>
<td>0.9984</td>
</tr>
<tr>
<td>O2: 8d(x, y, z)</td>
<td>0.29633</td>
<td>0.04511</td>
<td>-0.27708</td>
<td>2.8443</td>
</tr>
</tbody>
</table>

3.2. Magnetic properties

Figure 2(a) demonstrates the magnetization versus temperature variation under 200 Oe applied field in the field cooled (FC) mode. One can notice that magnetization is positive throughout the measurement range and increases with decreasing temperature. The maximum value of magnetization for the present compound is almost eight times higher when compared with that of the undoped PrCrO$_3$ material’s magnetization even when it was measured under 1 T magnetic field [19]. This comparison attests the influence of Mn doping in enhancing the magnetic properties of chromites at low temperatures. In order to identify any magnetic transition, the derivative of magnetization with temperature i.e. $dM/dT$ was plotted against temperature and the results are shown in figure 2(b) wherefrom two transitions at $T_{N1} \sim 197$ K (from paramagnetic to antiferromagnetic state and usually defined as Neel temperature) and $T_{N2} \sim 17$ K can be discerned. It is worth mentioning here that the Neel temperature of the undoped PCO sample is $\sim 237$ K [17], whereas in the present case it decreases to 197 K with 15% of Mn doping. This can be understood in terms of the appearance of double exchange interaction between Mn$^{3+}$ and Cr$^{3+}$ ions via O$^{2-}$ leading to decrease in antiferromagnetic superexchange interaction. Thereby, $T_{N1}$ can be expected to decrease with Mn-doping. Further, $T_{N2}$ in figure 2(b) is assigned as a spin reorientation temperature due to ordering of Pr$^{3+}$–Pr$^{3+}$ ions spins (4$^2$f; effective paramagnetic moment $\mu_{\text{eff}} = 3.58$ $\mu_B$). It is also argued that there is a spin structure change from the high temperature canting $\Gamma_2$ to collinear $\Gamma_2$ at $T_{N2}$. Figure 2(b) also depicts the inverse of susceptibility against temperature and it indicates that the high temperature paramagnetic region satisfies the Curie–Weiss behaviour ($\chi^{-1} = \frac{C}{T - \theta_C}$). The calculated effective magnetic moment was 7.45 $\mu_B$ (from the Curie constant $C$) along with Curie temperature ($\theta_C$) of $-184$ K, which is indicative for antiferromagnetic interactions. However, orthochromites like the present one possess distorted orthorhombic structure and the Cr–O–Cr bond angle $\theta$ deviates from 180°. Consequently, it results in the imperfect superexchange interaction and the ensuing CAFM (ferromagnetic + antiferromagnetic) behaviour below the Neel temperature. On comparing effective magnetic moment and Curie temperature values for the present PCMO compound with undoped PCO one [19] ($4.87$ $\mu_B$ and $-158$ K), we can clearly distinguish the contribution of manganese ions in magnetic behavior.

In order to confirm the coexistence of ferromagnetic and antiferromagnetic phases below the Neel temperature, the isothermal magnetization $M(H)$ loops at several characteristic temperatures 2, 50, 100, 150, 200 and 300 K were acquired in zero field mode (ZFC) and the graphs are shown in figure 2(c). The loops which are symmetric about the field axis exhibit hysteresis but without any saturation. The magnetization increases linearly for all the isothermal loops in the region of larger applied magnetic field. Such loops are also attributed to the coexistence of AFM (high field) and weak FM (low field) states. Several factors contribute to the observation of combined ferromagnetic and antiferromagnetic behaviors below the Neel temperature for the present compound.
For example, below $T_{N1}$, due to Dzialoshinski–Moriya type antisymmetric exchange interaction, Cr$^{3+}$ ions are in the canted state resulting in the presence of ferromagnetic and antiferromagnetic states [41, 42]. Moreover, the interaction between Mn$^{3+}$ ($t_{2g}^{3} e_{g}^{0}$) and Cr$^{3+}$ ($t_{2g}^{3} e_{g}^{0}$) ions via O$^{2−}$ would be ferromagnetic as Mn doping results in the decrease of Néel temperature [43–46]. As the temperature decreases further, $f$-orbitals in Pr$^{3+}$ ions and $p$-orbitals of oxygen also start interacting and well below the Néel temperature, the Pr$^{3+}$–O$^{2−}$ superexchange interaction also increases, resulting into the onset of Cr$^{3+}$–O$^{2−}$–Pr$^{3+}$ interaction. This interaction is ferromagnetic as here the empty $e_g$ orbital of Cr$^{3+}$ ions overlaps with one end of oxygen $p$-orbital and the other end of the same overlaps with a partially filled $f$-orbital of Pr$^{3+}$ ion. This weak ferromagnetic superexchange coupling gives rise to opening up of hysteresis loop below 197 K (shown in figure 2(a)) with decreasing temperature and the remnant magnetization also increases [25]. The net magnetization is thus given by the relation $M(H) = \chi_{AF} H + M_s$, where $\chi_{AF} H$ is the antiferromagnetic contribution and $M_s$ is the saturation magnetization of the weak ferromagnetism [47]. The value of $M_s$ can be obtained by subtracting the antiferromagnetic

![Figure 2](image2.png)

Figure 2. (a) $M(T)$ measured at $H = 200$ Oe in FC mode, (b) $\chi^{-1}(T)$ calculated at $H = 200$ Oe, along with $dM/dT$ graph, (c) Isothermal $M(H)$ curves at temperatures 2, 50, 100, 150, 200 and 300 K (the inset is weak FM component versus magnetic field at 2 K), (d) the temperature dependence of the saturation magnetization and the coercivity $H_c$ of the weak FM component.

![Figure 3](image3.png)

Figure 3. (a) Isothermal magnetization curves, (b) magnetic entropy change versus temperature at different applied magnetic field values.
contribution from the total magnetization. Inset of figure 2(c) shows the FM contribution for PCMO with the coercive field $H_c = 5.5$ kOe, and saturation magnetization of weak FM component is $M_s = 9.06$ emu g$^{-1}$ at $T = 2$ K. The values of the $M_s$ and $H_c$ decrease with increasing temperature up to the Neel temperature (figure 2(d)), and thereafter the hysteresis loops apparently disappears, indicating the phase transition to paramagnetic state.

3.3. Magnetocaloric measurements

In order to further examine the performance of PCMO compound for MR, $M(H)$ data was acquired by varying the magnetic field from 0 to 90 kOe. The data were acquired between 2 to 106 K temperature range with an interval of $\Delta T = 4$ K. The results are plotted in figure 3(a) where the data has been shown from 2 to 106 K at a temperature difference of 8 K for the sake of clarity. The change of magnetic entropy ($\Delta S$) caused by MCE is given by [48]:

$$\Delta S(T)_{\Delta H} = \int_{H_1}^{H_2} \left( \frac{\partial M(T, H)}{\partial T} \right) dH$$

(2)

Generally, for $\Delta S$ calculation from a series of $M$--$H$ curves, numerical integration of the above Equation by trapezoidal rule results [49]:

$$\Delta S(T_{av})_{\Delta H} = \frac{\delta H}{2 \delta T} \left( \delta M_1 + 2 \sum_{i=2}^{n-1} \delta M_i + \delta M_n \right)$$

(3)

where the average temperature $T_{av} = (T_j + T_{j+1})/2$ from the two magnetization isotherms measured at $T_j$ and $T_{j+1}$ in a magnetic field changing by $\Delta H = H_H - H_1$ at a constant step $\delta H$. While $\delta T = T_{j+1} - T_j$ is the temperature difference between the two isotherms, $n$ is the number of points measured for each of the two isotherms with the magnetic field changing from $H_1$ to $H_n$ at $\delta H = \Delta H(n - 1)$. Further $\delta M_i = [M(T_{j+1}) - M(T_j)]$ is the difference in the magnetization at $T_{j+1}$ and $T_j$ for each magnetic-field step from 1 to $n$. It is worthwhile mentioning here that the sign of $-\Delta S$ provides information about the magnetic transition [50]. For a ferromagnetic (FM) transition, a positive value is obtained whereas an antiferromagnetic ordering displays a negative value due to an orientation disorder of the magnetic sublattices. Therefore, it is customary to plot values of $-\Delta S$ against $T$ for different $H$ values. The obtained results for the present PCMO compound are depicted in figure 3(b). It is clear that $-\Delta S$ is positive in the whole temperature measurement range with maximum value observed near $T_{N2}$. It suggests the peak due to FM ordering at $T_{N2}$. Further, $-\Delta S$ value is ~25.04 J kg$^{-1}$ K$^{-1}$ at 90 kOe. This value is two times higher than the one observed recently by our group in Mn doped SmCrO$_3$ compound [51]. The difference in the two values could be attributed to the higher magnetic moment associated with Pr$^{3+}$ ions (3.58 $\mu_B$) when compared with that of Sm$^{3+}$ ions (0.84 $\mu_B$). The magnetic entropy variation values for our PCMO compound are superior to (even at smaller applied magnetic field) the results reported on polycrystalline chromites and manganites in the temperature range 10--20 K [6, 31, 34]. For example, Yoshii [6] observed $-\Delta S$ value is ~4.6 J kg$^{-1}$ K$^{-1}$ in the 10-20 K temperature range under 5 T applied field whereas it is 11.44 J kg$^{-1}$ K$^{-1}$ for the compound investigated here (table 2). Yin et al [31] have reported $-\Delta S$ values 7.2 (at 20 K), 6.83 (at 20 K), 13.08 J kg$^{-1}$ K$^{-1}$ (at 5 K) for HoCrO$_3$, HoCr$_{0.7}$Fe$_{0.3}$O$_3$, and DyCr$_{0.7}$Fe$_{0.3}$O$_3$ samples, respectively under 7 T applied magnetic field. Again looking at the values shown in table 2 we notice better value even at 6 T magnetic field. Similarly, the present results are better than described by Shao et al on Ho doped DyMnO$_3$ manganites [34]. Further, our $-\Delta S$ values are slightly inferior to that obtained on GdCrO$_3$ single crystals, however, our sample is polycrystalline in nature: easy
to fabricate and cost effective when compared with single crystals.

In the present case, it is apparent that the rotation of Pr$^{3+}$ ions with applied field and ordering between them brings positive value corresponding to a FM state in the $T_{N2}$ region. It is also envisaged that the alignment of Mn$^{3+}$ ions along the applied field direction contributes in the enhancement of $-\Delta S$ values. The interaction among the 3$d$ electrons of Cr and Mn ions with 6$f$ electrons of Pr ion also leads to enhancement of magnetic entropy change values. We further calculated the relative cooling power (RCP) or refrigerant capacity by the following expression:

$$\text{RCP} = |\Delta S_{\text{max}}| \times \Delta T_{\text{FWHM}}.$$  \hspace{1cm} (4)

where $\Delta T_{\text{FWHM}}$ is the full width at half maximum of the temperature dependent magnetic entropy change. RCP value is $\approx 371$ J kg$^{-1}$ at the maximum field of 90 kOe. The RCP values at different fields (table 2) are quite high making the present compound one of the promising candidates for replacement of costlier, environment degrading, gas refrigerant materials in the liquid helium range.

Further the prediction about the order parameter of the magnetic transition could be made with the help of Arrott plot [52] between $H/M$ versus $M^2$. The first order phase transition yields negative slope whereas it is positive for second order. In case of PCMO compound, the slope of Arrott plot was found to be positive below $T_{N2}$, indicating the transition is of second order. The positive slope was observed above $T_{N2}$ signifying that the magnetic transition nature is of second order (figure 3(b) and its inset shows a zoomed view). Thus PCMO compound exhibits large magnetic entropy change and RCP values with second order phase transition near the spin reorientation temperature.

For the materials undergoing a second-order transition, $-\Delta S_{\text{max}}$ was predicted to develop as $H^{2/3}$ but later it was found that besides a term in $H^{2/3}$, $-\Delta S_{\text{max}}$ contains an extra term independent of $H$ [53]. This was explained on the basis of Landau’s theory of second order phase transitions. The obtained expression was [53]:

$$-\Delta S_{\text{max}} = \alpha \left( \frac{H}{4b} \right)^{2/3} - \frac{\alpha^2}{18b} \Delta T$$ \hspace{1cm} (5)

$\Delta T$ is the width of the distribution of transition temperatures around the mean point, $\alpha$ and $b$ are positive quantities independent of $T$ or $H$ that enter in the standard Landau expansion. Figure 5 shows as $-\Delta S_{\text{max}} \propto H^{2/3}$ signalling that an approach based on mean field theory only is sufficient to explain the magnetic behaviour for high fields for the present PCMO sample.

### 3.4. Heat capacity

Since specific heat capacity ($C_p$) measurement is sensitive to the phase transition, therefore, to get further insight into the transition nature at $T_{N2}$, we measured $C_p$ versus temperature without and with the application of 5 T magnetic field. The results are shown in figure 6. Though there is no anomaly apparent near $T_{N2}$, on plotting the derivative of specific heat with temperature i.e. $dC_p/dT$, a clear dip is observed at $T_{N2}$ (inset to figure 6) which is a signature of the second order phase transition in the present studied sample. The heat capacity or specific heat ($C_p$) of a magnetic material is given by the equation [54]:

$$C_p = \gamma T + \beta T^3 + \delta T^{3/2}$$ \hspace{1cm} (6)

where, $\gamma T$ describes the terms related to electronic contribution, $\beta T^3$ term gives the contribution from the lattice and $\delta T^{3/2}$ gives the magnetic contribution to $C_p$. Further, in the specific heat measurements large hyperfine interaction between the electronic and nuclear spins of magnetic rare-earth ion (in this case Pr$^{3+}$) commonly leads to a nuclear Schottky anomaly with a maximum at $\approx0.3$ K [55, 56]. Since, in the present study specific heat measurement ranges from 5 to 100 K, therefore, we excluded the hyperfine contribution to the specific heat. The fitting of equation (6) to the data is shown in figure 6(b) and the values of the parameters obtained from the fitting are: $\gamma = 0.186$ J K$^{-2}$ mole$^{-1}$, $\beta = 2.28 \times 10^{-5}$ J K$^{-4}$ mole$^{-1}$ and $\delta = 0.0034$ J mole$^{-1}$ K$^{-3/2}$. From this fit it is clear that magnetic contribution to the total heat capacity is very small as compared to the electronic contribution, therefore, magnetic contribution (which in fact is smaller as we proved above) is masked in figure 6(a). Further, the electronic contribution, $\gamma$ is related to the density of states (DOS) at the Fermi level: $\gamma = \pi^2 k_B^3 N(E_F)/3$, where $N(E_F)$ is the DOS.
Using $\gamma = 0.186 \, \text{J} \cdot \text{K}^{-2} \cdot \text{mole}^{-1}$ yielded $\alpha N(E_F) = 3.2 \times 10^{25} \, \text{eV}^{-1} \cdot \text{cm}^{-3}$ which is in agreement with the results reported on manganites [54, 57]. The lattice contribution, $\beta$, is related to the Debye temperature ($\Theta_D$) through the relation $\beta = \frac{3 \times N \Theta_D^3}{\pi^2}$. In the literature, therefore, it was not possible for us to bring out the difference caused by Mn doping in thermal parameters.

Finally, we could observe unprecedented high value of MCE in PMCO sample near the $T_N$ temperature along with the second order phase transition.

4. Conclusions

The impact of Mn doping on the structural, magnetic, magnetocaloric and specific heat properties of PCMO chromites has been investigated. Even with 15% Mn doping, the crystal structure of the compound remained orthorhombic with Pnma space group, however, the lattice volume was found to increase when compared to that of pristine (undoped) PrCrO$_3$ sample. Neel transition temperature decreased with doping of Mn and the magnetization was almost eight times higher than reported for undoped sample. MCE measured through the magnetic entropy change and RCP showed higher values than reported for other polycrystalline chromites and manganites. The Debye temperature and the DOS at Fermi level were also calculated. The material exhibited second order magnetic phase transition between 10–20 K.

Acknowledgments

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