Giant magnetocaloric effect in Gd$_2$NiMnO$_6$ and Gd$_2$CoMnO$_6$ ferromagnetic insulators

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Abstract

We have investigated the magnetocaloric effect in double perovskite Gd$_2$NiMnO$_6$ (GNMO) and Gd$_2$CoMnO$_6$ (GCMO) samples by magnetic and heat capacity measurements. Ferromagnetic ordering is observed at ~ 130 K (~ 112 K) in GNMO (GCMO), while the Gd exchange interactions seem to dominate for $T < 20$ K. In GCMO, below 50 K, antiferromagnetic behaviour due to the 3d–4f negative exchange interaction is observed. A maximum entropy ($-\Delta S_M$) and adiabatic temperature change of ~ 35.5 J Kg$^{-1}$ K$^{-1}$ (~ 24 J Kg$^{-1}$ K$^{-1}$) and 10.5 K (6.5 K) is observed in GNMO (GCMO) for a magnetic field change of 7 T at low temperatures. Absence of magnetic and thermal hysteresis and their insulating nature make them promising for low temperature magnetic refrigeration.

Keywords: magnetocaloric, double perovskites, magnetic oxides

(Some figures may appear in colour only in the online journal)
2. Experimental details

Polycrystalline Gd₂B₄MnO₉ (B = Ni and Co) samples were prepared by solid-state reaction method using high purity precursor materials of Gd₂O₃, NiO, Co₃O₄ and MnO₂. Stoichiometric proportion of the powders were thoroughly mixed and heated at temperatures from 1000 °C to 1350 °C with an intermediate grindings until the desired phase was obtained. The structural analysis was done using a Phillips powder x-ray diffractometer with Cu-Kα radiation. Rietveld refinement has revealed monoclinic crystal structure of P2₁/n space group for both the samples similar to other double perovskite compounds [13–15, 19]. Magnetic measurements were done with an EverCool Quantum Design SQUID-VSM magnetometer. The heat capacity at different constant magnetic fields was measured using relaxation method in a Quantum design-physical property measurement system (PPMS).

3. Results and discussion

Figures 1(a) and (b) shows the temperature dependent magnetization, \( M(T) \) in zero-field cooled (ZFC) and field-cooled (FC) modes with 0.01 T dc field for both the samples. In GNMO, a paramagnetic (PM) to ferromagnetic (FM) ordering is observed at \( T_C \sim 132 \text{ K} \) and a rise in \( M_{FC} \) at low temperatures (\( T < 20 \text{ K} \)) can be attributed to the polarization of Gd spins with \( \text{Gd}^{3+} - \text{O} - \text{Gd}^{3+} \) exchange interactions. In case of GCMO, PM to FM phase transition is noticed at \( T_C \sim 112 \text{ K} \) and it is followed by a broad peak around \( \sim 47 \text{ K} \) suggesting the polarization of magnetic moments with an antiferromagnetic (AFM) like behaviour. At low temperatures, an increasing magnetization due to Gd can be found similar to GNMO. The FM ordering can be attributed to the super exchange interaction of \( \text{Ni}^{2+} - \text{O} - \text{Mn}^{4+} \) \((\text{Co}^{2+} - \text{O} - \text{Mn}^{4+})\) magnetic species in GNMO (GCMO). The AFM arrangement of magnetic moments at \( \sim 47 \text{ K} \) in GCMO can be ascribed to the negative 3d–4f exchange interactions in between FM network of Co/Mn sublattice and Gd spins, like in R₂MnO₃ and RCrO₃ (R = Gd, Ho, and Dy) systems [20–23]. We have observed no bifurcation in between field-cooled cooling and field-cooled warming modes of magnetization (not shown here) that suggests the absence of thermal hysteresis in both the samples.

Temperature dependent magnetic susceptibility (\( \chi \)) in PM state is fitted to Curie–Weiss (CW) law with an additional susceptibility contribution of Gd magnetic moments and effective \( \chi \) given as,

\[
\chi = \frac{C_{\text{Ni/Co}-\text{Mn}}}{T - \theta} + \frac{C_{\text{Gd}}}{T}
\]

where, \( C_\theta \) is the Curie constant and \( T_\theta \) is the Curie temperature.

From the fitting, in GNMO sample, the obtained CW temperature (\( \theta \)) is \( 145 \text{ K} \) and the effective PM moments (\( \mu_{\text{eff}} \)) are \( 6.37 \mu_B \) and \( 13.2 \mu_B \) respectively. In GCMO, \( \theta \sim 111.2 \text{ K} \) and \( \mu_{\text{eff}} \) are \( 5.81 \mu_B \) and \( 14.9 \mu_B \). In both the samples, the effective PM moment values are close to the theoretically calculated spin-only contribution of \((\text{Ni/Co}) - \text{O} - \text{Mn}\) network and rare-earth Gd spins.

Thermal evolution of heat capacity \( (C_P) \) of GNMO and GCMO samples under different magnetic fields (i.e. 0, 1, 3, 5 and 7 T) are depicted in figures 1(c) and (d) respectively. The \( C_P \) versus \( T \) displays distinct transitions in both the samples. A \( \lambda \)-type anomaly under zero field at \( \sim 130 \text{ K} \) in GNMO and \( \sim 112 \text{ K} \) in GCMO samples correspond to the second-order magnetic phase transition. In both the samples, with the increase of magnetic field, magnitude of the peak decreases and shifts to high-temperature side which is the characteristic feature of FM ordering. The broadening of \( C_P \) (\( T \)) peak under external field is due to the randomization of magnetic moments in wide temperature region. Above \( 20 \text{ K} \), \( C_P \) (\( T \)) increases with increasing temperature and follows the \( T^3 \) dependence due to the lattice contribution [24], and all \( C_P \) versus \( T \) curves gets merged for different magnetic fields as shown in the inset of figures 1(c) and (d). The increasing trend in heat capacity below \( \sim 20 \text{ K} \) can be noticed in both GNMO and GCMO samples and can be attributed to the Gd magnetic contribution. With the application of magnetic field, \( C_P \) (\( T \)) value increases and broadens the dip at \( \sim 20 \text{ K} \) and shifts to higher temperature; this anomalous behaviour can be attributed to the schottkey contribution that arises from the splitting of degenerate ground state energy levels at \( \text{Gd}^{3+} \) state in crystal fields [25, 26]. In contrast to GNMO sample, a peak in \( C_P \) (\( T \)) can be noticed at \( \sim 5 \text{ K} \) in GCMO corresponding to the onset of AFM ordering of Gd magnetic moments. In GNMO, this peak can be noticed only with the Gd magnetic field and this suggests the Gd ordering occurs at temperatures lower than \( 2 \text{ K} \).

Isothermal field-dependent magnetization i.e. \( M(H) \) of GNMO and GCMO samples at 2 K is shown in the figure 2(a). Both the samples show no hysteresis and such kind of magnetic reversibility in \( M(H) \) is beneficial for the solid-state magnetic refrigeration. GNMO shows S-shaped \( M(H) \) behaviour with significant changes in magnetization at low fields and saturation like behaviour for \( H \gtrsim 6 \text{ T} \). The observed saturation magnetization (\( M_S \)) value of \( \sim 18.9 \mu_B/\text{f.u.} \) matches well with the theoretically estimated value of \( 19 \mu_B/\text{f.u.} (5 \mu_B/\text{f.u.} \text{ for Ni}^{2+} - \text{O} - \text{Mn}^{4+} \text{ pair and } 14 \mu_B/\text{f.u.} \text{ for Gd}) \). While GCMO exhibits a linear variation of magnetization from low fields to \( 4 \text{ T} \) (see inset of figure 2(a)) and shows no saturation even for \( H \gtrsim 6 \text{ T} \). Further, in GCMO, the magnetization value at high field (\( 7 \text{ T} \) in our set up) is \( \sim 16.5 \mu_B/\text{f.u.} \), which is smaller than theoretically estimated sum of the fully polarized \( \text{Co}^{2+} - \text{O} - \text{Mn}^{4+} \) interaction \((6 \mu_B/\text{f.u.}) \) and magnetic moment of Gd spins \((14 \mu_B/\text{Gd}) \). Incomplete saturation of magnetization in GCMO can be related to the presence of significant 3d–4f interactions.
negative AFM exchange correlations. Figures 2(b) and (c) shows the representative isothermal $M(H)$ plots of GNMO and GCMO samples taken in the temperature range of 2–40 K. With this data, we have calculated MCE using Maxwell’s relation [27],

$$\Delta S_m(T, H) = \int_0^H \frac{\partial M}{\partial T} \, dH$$

Since, isothermal $M(H)$ curves are measured by discrete field changes, the following expression is used,

$$-\Delta S_M = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i,$$  \hspace{1cm} (2)

here, $M_i$ and $M_{i+1}$ are initial magnetization values at $T_i$ and $T_{i+1}$ respectively for a field change of $\Delta H_i$. We have calculated magnetic entropy change ($-\Delta S_M$) using equation (2) and is plotted with temperature for different magnetic fields as shown in the figures 3(a) and (b) for GNMO and GCMO samples respectively. The value of $-\Delta S_M$ is positive in the entire temperature region and increases with the magnetic field; this indicates that the magnetic field favors FM ordering. In GNMO, $-\Delta S_M$ increases with the decrease of temperature and a maximum change of entropy of $\sim 35.5 \text{ J kg}^{-1} \text{K}^{-1}$ is observed at 2 K. In GCMO, a peak in $-\Delta S_M$ can be noticed at $\sim 5$ K that corresponds to the AFM ordering of Gd and it is consistent with the heat capacity data in figure 1(d). The maximum change of entropy $-\Delta S_M^\text{max}$ (peak maximum at 4 K) is $\sim 24 \text{ J kg}^{-1} \text{K}^{-1}$ for field change $\Delta H$ of 7 T. Theoretically, entropy is associated with the magnetic degrees of freedom and can be calculated using $\Delta S_M = R \ln (2S + 1)$, where $R$ is the universal gas constant and $S$ is the total spin quantum number and they are $40.68 \text{ J kg}^{-1} \text{K}^{-1}$ and $41.84 \text{ J kg}^{-1} \text{K}^{-1}$ for GNMO and GCMO respectively. Since the lattice contribution to the total entropy is negligible at low temperature, the maximum value of MCE calculated at 2 K is 82% in GNMO and 56% in GCMO with respect to the theoretically estimated magnetic entropy. Low value of $-\Delta S_M^{\text{max}}$ in GCMO is attributed to the incomplete saturation and low value of magnetization as noticed from $M(H)$ (figure 2(a)). Moreover, the negative exchange coupling between (Co–O–Mn) and Gd sublattices can also be an effective cause for the low value of MCE. The MCE values of GNMO are larger than the paramagnetic salts [28, 29] and HoMn$_2$O$_5$ single
crystal [30], while it is comparable to the Gadolinium Gallium Garnets Gd₃(Ga₁₋ₓFeₓ)₅O₁₂ [24], Gd and 3d-transition metal based small molecular magnetic systems [31], rare-earth manganese (RMnO₃, R = Ho, Tb, Gd, Dy and Yb) [32, 33], and magnetically frustrated EuHo₂O₄, EuDy₂O₄ compounds [34]. Interestingly all these systems have similar magnetic ordering below the liquid hydrogen temperatures (~ 20 K). MCE has also been calculated from the heat capacity measurements using the following thermodynamic relation,

\[
\Delta S_M(T, H) = \int_0^T \frac{C_p(H) - C_p(0)}{T} \, dT
\]

\[
\Delta S_M(T, H) = \int_0^T \frac{C_p(0)}{T} \, dT
\]

and magnetic field induced total entropy, \( S(H, T) \) is calculated by subtracting the corresponding \( -\Delta S_M \) from \( S(0, T) \). Then, \( \Delta T_{ad} \) value is estimated from the isentropic difference in between the entropy curves \( S(0, T) \) and \( S(H, T) \). Figure 4 shows the temperature dependent \( \Delta T_{ad} \) under different magnetic fields for GNMO and GCMO (inset) samples. \( \Delta T_{ad} \) shows a peak near FM transition with a magnitude of ~ 1.8 K in GNMO and ~ 0.8 K in GCMO samples for a field change of 7 T. At low temperatures <20 K with the onset of Gd ordering \( \Delta T_{ad} \) shows a peak value of ~ 10.5 K in GNMO and ~ 6.5 K for GCMO samples. We have measured the electrical resistivity in these samples, and it is of the order of 10⁶Ωm at 150 K and it increases further with the decrease of temperature. Particularly, for low temperature refrigeration, high electric resistivity is desirable as the low resistivity of the materials can induce significant eddy current loss that limits the cooling efficiency of magnetic refrigeration process [9, 35].

4. Conclusions

In summary, we have prepared GNMO and GCMO double perovskites by simple solid-state reaction method and studied their magnetocaloric properties. Magnetic and heat capacity measurements on GNMO sample has revealed a superior magnetocaloric performance of \( -\Delta S_M \sim 35.5 \text{ Jg}^{-1}\text{K}^{-1} \) and \( \Delta T_{ad} \sim 10.5 \text{ K} \) at low temperatures compared to GCMO where \( -\Delta S_M \sim 24 \text{ Jg}^{-1}\text{K}^{-1} \) and \( \Delta T_{ad} \)
6.5 K. Presence of 3d–4f interactions reduce the resultant magnetocaloric effect in GCMO. Further, simple synthesis, high chemical stability, absence of magnetic and thermal hysteresis and insulating nature suggest them as potential magnetic refrigerants below the liquid hydrogen temperatures.

Acknowledgments

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