Metamagnetic phase transition induced large magnetocaloric effect in a Dy$_{0.5}$Ho$_{0.5}$MnO$_3$ single crystal

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Magnetic refrigeration based on the magnetocaloric effect is gaining interest in orthogonal or hexagonal rare-earth manganite. However, a more comprehensive understanding of the underlying mechanism is still required. We grew a high-quality single crystal of Dy$_{0.5}$Ho$_{0.5}$MnO$_3$ using the optical floating zone method, since the parent crystals DyMnO$_3$ and HoMnO$_3$ have orthogonal and hexagonal structures, respectively. The magnetic and magnetocaloric properties and refrigeration mechanisms are thoroughly investigated. Doping modifies the magnetism according to the results obtained from the investigation of magnetic and dielectric properties and heat capacity. The spin reorientation transition shifts towards low temperature in comparison to HoMnO$_3$. Near the Néel temperature of rare-earth sublattices (5 K), the highest changes in negative magnetic entropy under 0–70 kOe are 18 J kg$^{-1}$ K$^{-1}$ and 13 J kg$^{-1}$ K$^{-1}$ along the a- and c-axes, respectively. The low-temperature metamagnetic phase transition caused by the alterations in the magnetic symmetry of Ho$^{3+}$ contributes to an increased magnetocaloric effect in comparison to the parent crystals, rendering it a promising choice for magnetic refrigeration applications. Dy$_{0.5}$Ho$_{0.5}$MnO$_3$ exhibits a clear magnetocrystalline anisotropy with enhanced refrigeration capacity and negative magnetic entropy change along the a-axis. The adiabatic temperature change of Dy$_{0.5}$Ho$_{0.5}$MnO$_3$ is 8.5 K, larger than that of HoMnO$_3$, rendering it a promising choice for low-temperature magnetic refrigeration applications.

Introduction

Rare-earth manganite RMnO$_3$ (RMO, R = Y, La–Lu) shows considerable potential for application in future spintronic devices owing to its multifunctional properties including multiferroicity, magnetoelastic, and magnetocaloric characteristics. However, research on the mechanism of magnetocaloric properties and refrigeration remains uncomprehensive. Recently developed refrigeration technology, known as magnetic refrigeration, is more effective, sustainable, and energy-efficient compared to the conventional gas compression refrigeration system. Magnetic refrigeration can be achieved in two ways: one involves exploiting the magnetocaloric effect (MCE) by manipulating the magnetic field, which is accompanied by a large change in magnetic entropy ($\Delta S_m$) and eventually leads to a large adiabatic temperature change ($\Delta T_{ad}$); another technique relies on the rotation of the crystal or magnetic field based on the “rotating MCE” (RMCE), which necessitates high anisotropic energy in the crystal. Due to its enhanced efficiency, ease of use, and reduced energy loss, the RMCE has garnered significant attention.

The anisotropic energies of heavy RMO single crystals with small rare-earth ion radii are significant, implying potential applications in RMCE. When the radius of the rare-earth ion is bigger than that of Dy$^{3+}$, RMO generally forms an orthogonal structure, and when it is lower than that of Ho$^{3+}$, it forms a hexagonal crystal structure. Since Mn$^{3+}$ forms a triangular lattice in the $ab$ plane, the magnetic order of the spins becomes geometrically frustrated. HoMnO$_3$ (HMO) and DyMnO$_3$ (DMO) are two typical examples of the RMO family with different...
ground states. HMO exhibits an antiferromagnetic transition of Mn$^{3+}$ at $T^{N}_{S}=76 \text{ K}$, followed by a spin reorientation transition (SRT) at 39 K. Dielectric anomalies accompany the phase change, peaking sharply at $T_{SR}$. Furthermore, Ho$^{3+}$ exhibits antiferromagnetic order at $T^{N}_{Ho}=5.2 \text{ K}$. The hexagonal HMO exhibits a significant MCE, with a maximum negative magnetic entropy change ($\Delta S_{m}$) of 13 J kg$^{-1}$ K$^{-1}$ under 0–70 kOe with a refrigeration capacity (RC) of 320 J kg$^{-1}$. HMO exhibits a significant MCE, with a maximum negative magnetic entropy change ($\Delta S_{m}$) of 13 J kg$^{-1}$ K$^{-1}$ under 0–70 kOe with a refrigeration capacity (RC) of 320 J kg$^{-1}$. The large magnetocaloric effect has not been reported and the magnetocaloric characteristics of DMO are unimpressive in comparison to HMO.$^{13}$

In this study, we substituted Dy$^{3+}$ for the Ho site in HMO and grew a single crystal of Dy$_{0.5}$Ho$_{0.5}$MnO$_3$ (DHMO). It has the same crystal structure as HMO and comparable magnetic properties, indicating that the interaction between Ho$^{3+}$ and Mn$^{3+}$ is stronger than that between Dy$^{3+}$ and Mn$^{3+}$ in the co-doped crystal. The spin reorientation transition temperature ($T_{SR}$) is, however, shifted by 4 K to a lower temperature due to the Dy doping effect. Remarkably, doping enhances the MCE's performance over the parent single crystals and improves its adaptability for magnetic refrigeration devices. The RC is 329 J kg$^{-1}$ and $\Delta S_{m}$ reaches 18 J kg$^{-1}$ at 0–70 kOe and 5 K (close to $T^{N}_{S}$). The large MCE, which is reflected in both the $a$- and $c$-axes, is caused by the low-temperature metamagnetic phase transition. DHMO is also a candidate for RMCE because both $\Delta S_{m}$ and RC exhibit substantial anisotropy, and the RC along the $a$-axis is greater than that of the $c$-axis by 172 J kg$^{-1}$ under 0–70 kOe. Large $\Delta T_{ad}$ calculated using the heat capacity and magnetic entropy change data proves its excellent refrigeration performance.

Experimental methods

A DHMO single crystal was grown using the optical floating zone furnace (FZ-T-10 000-H-VI-P-SH, Crystal System Inc.) to avoid the impurities induced by a crucible. The seed and feed rods are polycrystalline rods synthesized by a solid-state reaction with the raw materials Dy$_2$O$_3$, Ho$_2$O$_3$, and Mn$_3$O$_4$ (purity 99.99%). In the growth process, seed and feed rods were counter-rotated at a rate of 30 rpm. DHMO crystallizes during a slow cooling process under an air atmosphere. A powder X-ray diffractometer (Bruker D2 PHASER) featuring a copper target was used for X-ray diffraction (XRD). The wavelengths of the characteristic X-rays are $\lambda_{Cu}=1.54056$ Å and $\lambda_{K}_{\alpha2}=1.54433$ Å. A back reflection Laue X-ray camera (Try-SE. Co., Ltd) was used to identify the crystallographic orientations. An X-ray with continuous wavelength is used to incident on the fixed DHMO single crystal, which produces diffraction spots in the range of diffraction angles. Magnetic measurements were achieved utilizing a vibrating sample magnetometer (VSM) equipped with a Physical Property Measurement System (PPMS-14T, Quantum Design Inc.). The magnetization–temperature ($M$–$T$) curves were obtained by dropping down the temperature from room temperature to 2 K without applying a magnetic field followed by heating under a 50 Oe field and measuring (zero-field-cooled warming, ZFC), cooling the crystal to 2 K while measuring (field-cooled cooling, FCC), and lastly heating to 300 K while measuring (field-cooled warming, FCW). Dielectric measurements were conducted by using an LCR meter (Agilent E4980A). The relaxation method was used to determine the heat capacity utilizing the specific heat measurement option in the PPMS.

Results and discussion

Structure characterization

Fig. 1(a) and (b) show the XRD patterns obtained for the orientated DHMO single crystal. The peaks can be indexed with (h00) ($h=3$) and (00l) ($l=2, 4$) without any impure peaks, confirming that the measurement directions are $a$- and $c$-axes. Also, Laue diffraction patterns along the crystalline axes are shown in Fig. 1(c) and (d). Sharp and clear diffraction spots indicate the good orientation and high quality of the crystal. The powder XRD spectrum and Rietveld refinement results are shown in Fig. 1(e). All the peaks can be indexed, indicating the monophasic nature. Using the pseudo-Voigt method fits the peak shape with the calculation method of the structural model (Rietveld method). $R_{wp}$ is 11.3, showing that experimental data are well-fitted with the calculation data. The crystal structure is hexagonal with the space group $P6_{3}cm$ and is composed of layered corner-sharing trigonal MnO$_5$ bipyramids split by R$^{3+}$ layers.$^{12}$ Doping leads to the buckling change of MnO$_3$, with the lattice parameters $a=b=6.1677(4)$ Å, $c=11.4385(2)$ Å. As reported for Dy$_{1-x}$Ho$_x$MnO$_3$ (0.1 $\leq x \leq$ 1.0) polycrystals, the
Curie–Weiss fitting in ZFC mode shows that the \(1/m\) magnetism progressively transforms into paramagnetism. The zation diminishes as temperature increases, and its antiferromagnetic moment is negligible within the temperature range of the measurement. 29 The magnetization along the \(a\)-axis at 50 Oe. Different from the HMO single crystal, there is no obvious spin–flip and thermal hysteresis over the whole temperature range of the measurement. 29 The magnetization diminishes as temperature increases, and its antiferromagnetism progressively transforms into paramagnetism. The Curie–Weiss fitting in ZFC mode shows that the \(1/T\) curve in the \(a\)-axis is in good accordance with the Curie–Weiss law and the Curie–Weiss temperature \(T_{cw} = -12.20\) K. Fitting factor \(R^2\) is greater than 0.999, and the effective magnetic moment \(\mu_{eff}\) is 11.34\(\mu_B\). The presence of antiferromagnetic exchange interaction is indicated by the negative paramagnetic temperature. The \(M-T\) curves in Fig. 2(b) reveal that the magnetization variation trend in the \(c\)-axis appears to be identical with the \(a\)-axis. However, the Curie–Weiss law can only be confirmed by the \(1/T\) curve between 100 K and 300 K, which indicates that DFMO is not a strictly antiferromagnetic structure at low temperatures but the short-range ferromagnetic interactions exist in the \(c\)-axis. The Curie–Weiss temperature \(T_{cw} = -68.07\) K and effective moment \(\mu_{eff} = 11.53\mu_B\). A higher Curie temperature shows a stronger interaction in the \(c\)-axis than in the \(a\)-axis and reflects the anisotropic nature of the exchange interaction. Utilizing the theoretical moments of 4.9\(\mu_B\) (Mn\(^{3+}\), spin-only \(S = 2\)), 10.4\(\mu_B\) (Ho\(^{3+}\)) and 10.6\(\mu_B\) (Dy\(^{3+}\)), 13,29 as well as assuming that the total effective moment can be calculated using

\[
\mu_{total} = \mu_{eff}(\text{Mn}) + \mu_{eff}(\text{Ho})/2 + \mu_{eff}(\text{Dy})/2, \quad (1)
\]

where \(\mu_{total} = 11.60\mu_B\) is expected. The experimental value is quite comparable with the theoretical value and previously reported results, 23 implying that both ions are free in the ground states.

The AC susceptibility was measured to determine the phase transition. The oscillating component of the magnetic field \(H(t)\) can be expressed as eqn (2), and the oscillating component of the magnetization \(M(t)\) can be expressed as eqn (3).

\[
\begin{align*}
H(t) &= H_{AC}\cos(\omega t), \\
M(t) &= M_{AC}\cos(\omega t + \varphi).
\end{align*}
\]

The susceptibility can be expressed as:

\[
\chi_{AC} = M_{AC}/H_{AC} = \chi' - i\chi'', \quad (4)
\]

where \(\chi'\) and \(\chi''\) refer to the real and imaginary components, respectively. \(\chi'\) correlates with the fluctuation in magnetization, while \(\chi''\) reflects the absorption of the applied alternate energy of the magnetic field. The dependences of \(d\chi'/dT\) and \(\chi''\) on temperature are illustrated in Fig. 3.(a) and (b). The slope of the curve changes at \(T_{MI} = 70.2\) K, corresponding to the antiferromagnetic transition of Mn\(^{3+}\). Neighbouring Mn\(^{3+}\) spins form a 120° angle due to a particular alignment of their magnetic moments. SRT of Mn\(^{3+}\) occurs at \(T_{SR} = 34.8\) K. The superexchange...
interaction rotates the Mn$^{3+}$ spin 90° in the basal plane.$^{37}$ The magnetic symmetry shifts from $P6_3cm$ to $P6_3cm$ according to the neutron scattering and optical experiments.$^{27,38}$ $T_{SR}$ is lower than that of HMO (39 K).$^{29}$ It should be noted that DMO has a lower SRT temperature (17.1 K),$^{21}$ and the inter-doping of Dy and Ho ions at the R-site alters the system’s superexchange interaction and shifts the $T_{SR}$. When the temperature is $T_{N2} = 4.9$ K, the slopes of the $d\chi'/dT-T$ and $\chi'-T$ curves shift due to the antiferromagnetic transition of R$^{3+}$ from antiferromagnetic ordering to paramagnetic ordering at low temperature.

Magnetic transitions regularly coincide with dielectric anomalies. As a result, we studied the magnetodielectric effect to determine the correlation between the magnetic order and dielectric features, as shown in Fig. 3(c). The anomalous peak at $T_{SR}$ results from the asymmetric Dzyaloshinskii–Moriya exchange interactions between R and Mn sublattices.$^{32}$ The microscopic mechanism is the direct coupling of $P6_3cm$ and $P6_3cm$ symmetries.$^{28}$ The distinctive anomaly might be associated with spin–lattice coupling.$^{20}$ Thus, the heat capacity ($C_p$) is measured to determine the thermodynamic properties. There exists a kink at $T_{SR}$ (Fig. 3(d)), which shows the thermodynamic consistency of the magnetic and magnetodielectric properties. Also, a peak arises at $T_{N2} = 4.9$ K, corresponding to the magnetic measurement.

**Magnetocaloric characterization**

Shao et al. discovered that the magnetic configuration transition induced $-\Delta S_m^{\max}$ of the DHMO polycrystal reaches $7$ J kg$^{-1}$ K$^{-1}$.$^{34}$ The magnetic properties of different crystal axes exhibit variations, yet the magnetic symmetry change along two different directions cannot be determined by isothermal magnetization curves due to the average impact of polycrystals. To explore the magnetic symmetry changes, we investigated magnetic changes in the DHMO single crystals by analyzing isothermal magnetization curves along the $a$- and $c$-axes, as depicted in Fig. 4. At 70 kOe and 2 K, magnetization reaches 146 emu g$^{-1}$ and 93 emu g$^{-1}$ along the $a$- and $c$-axes, respectively. There are also visible kinks with a strong magnetic field in the $c$-axis, which transfer to a lower field as the temperature increases. The magnetic configuration of R$^{3+}$ altered while Mn$^{3+}$ remained unchanged during the phase transition, so the change in magnetization is not very drastic. Maxwell’s relation (eqn (5)) was utilized to estimate the $\Delta S_m$ in the magnetic field range of 0–70 kOe (Fig. 5), and the data are obtained from the isothermal magnetization curves,

$$\Delta S_m = \int_0^T \partial M/\partial TDH.$$  \hspace{1cm} (5)

Because the magnetization measurements are performed under separate field and temperature conditions, $\Delta S_m$ is determined numerically using the expression:

$$\Delta S_m = \sum_{i} (M_{i+1} - M_i)/(T_{i+1} - T_i)\Delta H_i.$$  \hspace{1cm} (6)

**Fig. 3** (a) $d\chi'/dT-T$ curve and (b) $\chi'-T$ curve along the $a$-axis. The AC magnetic field is 1 Oe without an applied DC magnetic field. (c) Temperature dependence of the dielectric constant along the $a$-axis. $\varepsilon = Cd/A$, where $C$, $A$, and $d$ are the electric capacity, the area of the electrode, and distance between the electrodes. (d) Temperature dependence of heat capacity without applied magnetic field. 1 Oe (CGS) = 1/4$\pi$ x 10$^8$ A m$^{-1}$ (SI).

**Fig. 4** Isothermal magnetic curves along (a) $a$- and (b) $c$-axes from 2 to 46 K with the interval of 2 K (2–30 K) or 4 K (30–46 K). The arrows indicate the metamagnetic phase transition. 1 emu g$^{-1}$ (CGS) = 1 A m$^2$ kg$^{-1}$ (SI), 1 kOe (CGS) = 1/4$\pi$ x 10$^6$ A m$^{-1}$ (SI).
where $M_i$ and $M_{i+1}$ are magnetizations at $T_i$ and $T_{i+1}$, $\Delta H_i$ is the tiny magnetic field change. Magnetic entropy in the $a$- and $c$-axes exhibits the greatest change around the temperature of $R^{3+}$ antiferromagnetic ordering because the system undergoes a process from antiferromagnetic ordering to disorder. This differs from the test results of the DHMO polycrystals but is consistent with DMO, HMO, and most manganese oxides. The magnetocaloric effect in the system is contributed by $R$ and $Mn$ sublattices. The magnetic phase transition of $R$ ions results in the large $-\Delta S_m$ and $RC$, which is induced by the exchange interaction between $R$ and $Mn$ sublattices. The $-\Delta S_{m,max}$ of the $a$- and $c$-axes reaches $18$ J kg$^{-1}$ K$^{-1}$ and $13$ J kg$^{-1}$ K$^{-1}$ at $5$ K and $0$–$70$ kOe, respectively. As indicated in Table 2, $-\Delta S_{m,max}$ is more than double that of the DHMO polycrystal and greater than that of the parent crystal HMO single crystal, demonstrating that the doped single crystal has a considerable MCE. $RC$ is another essential physical metric in magnetocaloric research that intuitively reflects the refrigeration capacity of crystals from another perspective. $\Delta T_{ad}$ for low-temperature magnetic refrigeration can be calculated using $C_p$ combined with $-\Delta S_m$: firstly, $S(0, T)$ can be obtained from $C_p$:

$$S(0, T) = \int_{T_1}^{T_2} C_p(0, T) / T \, dT,$$

where $T_1$ and $T_2$ are the lower and higher temperatures. Then,

$$\Delta T_{ad}(S) = S(0, T) + \Delta S_m(H),$$

$\Delta T_{ad}(S)$ can be obtained from the inverse function $T(H, S)$ and $T(0, S)$, so

$$\Delta T_{ad}(S) = T(H, S) - T(0, S).$$

Thus, $\Delta T_{ad}(T)$ can be obtained from $\Delta T_{ad}(S)$ and $S(T)$. The peaks rise to $8.5$ K along the $a$-axis and $5.6$ K along the $c$-axis, as shown in Fig. 5(c) and (d). Compared with the parent single crystal HMO ($\Delta T_{ad} = 5$ K), $\Delta T_{ad}$ is largely improved, directly indicating that DHMO is promising in refrigeration.

The $d\delta/dH-H$ curves in the $a$- and $c$-axes are displayed in Fig. 6 to show the phase transition in isothermal magnetization curves clear. In the $a$-axis, the peak arises only when the temperature is less than $12$ K. As the temperature increases, the transition field $H_{c2}^{(a)}$ progressively expands, and the peak width expands until the peak vanishes. The metamagnetic phase transition occurs induced by the interaction between the Ho$^{3+}$ spin and Mn$^{3+}$ spin. The magnetic symmetry of Ho$^{3+}$ changes from $P6_3cm$ ($I_3$) to $P6_3cm$ ($I_3$), according to the results of HMO. However, the magnetic phase transition in the $c$-axis can be detected between $2$ and $30$ K, and the magnetic symmetry of Ho$^{3+}$ changes from $P6_3cm$ ($I_3$) to $P6_3cm$ ($I_3$). The peak (transition field $H_{c2}^{(a)}$) shifts to the low field as temperature increases, and the peak width increases.

Table 2 | Comparison of the magnetic and magnetocaloric properties. DHMO and HMO represent Dy$_{0.5}$Ho$_{0.5}$MnO$_{3}$ and HoMnO$_{3}$, respectively. SC and PC stand for single crystal and polycrystal.

<table>
<thead>
<tr>
<th></th>
<th>DHMO SC</th>
<th>DHMO PC</th>
<th>HMO SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_N$ (K)</td>
<td>70</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td>35</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>$\Delta T_{ad}$ (K)</td>
<td>4.9</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>$-\Delta S_{m,max}$ (J kg$^{-1}$ K$^{-1}$)</td>
<td>18</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>RC (J kg$^{-1}$)</td>
<td>329</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>RCP (J kg$^{-1}$)</td>
<td>432</td>
<td>—</td>
<td>320</td>
</tr>
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</table>

at which $T_1$ and $T_2$ are the lower and higher temperatures at half of the $-\Delta S_{m,max}$. As illustrated in the inset of Fig. 5(b), the RC under 0–70 kOe along the $a$-axis is $329$ J kg$^{-1}$, which is higher than that of the polycrystalline sample (Table 2), as well as those of the overwhelming majority of manganese oxides in the RMO family, suggesting that DHMO is an ideal candidate material for cryogenic magnetic refrigeration. To comprehensively characterize the refrigeration efficiency and compare it with that of the parent crystal HMO, the relative cooling power (RCP) is calculated using eqn (8),

$$RCP = -\Delta S_{m,max} \cdot \text{FWHM},$$

where FWHM is the full width at half maximum of $-\Delta S_{m}-T$ curves. RCP under 0–70 kOe is $432$ J kg$^{-1}$, greater than that of the HMO single crystal ($320$ J kg$^{-1}$), proving the high refrigeration efficiency. Furthermore, RC and RCP along the $a$-axis are considerably greater than those along the $c$-axis ($157$ J kg$^{-1}$ and $205$ J kg$^{-1}$), showing a high magnetic anisotropy energy of the crystal. It can be applied in a new type of refrigeration material based on the RMCE that reduces loss by rotating the sample or magnetic field instead of the typical lifting of magnetic field.
indicating that the phase transition is also temperature dependent at low temperatures. After 12 K, the peak position remains essentially unaltered, and the phase transition is essentially stable and unaffected by the temperature field. The magnetic configuration transition is also reflected in the HMO single crystal, but due to the introduction of Dy 3+, the transition field of DHMO is relatively 10 kOe higher and has no obvious intermediate state. The change of Ho 3+ magnetic symmetry, which is sensitive to temperature, increases the disorder of the system, thus elevating the \( \Delta S_m \) of the system.

**Conclusions**

In conclusion, a hexagonal structured single crystal of half-doped DHMO was grown using an optical floating furnace. The doping-induced modulation of the superexchange interaction results in a shift of the \( T_{SR} \) of Mn 3+ to 35 K, which is proved from the results of the investigation of the magnetic, electrical, and thermal properties. DHMO shows a higher \( \Delta S_m \), RC, and RCP compared to those of the parent single crystal and polycrystalline samples, which makes it a more suitable magnetic refrigeration material. \( \Delta S_m \) in the \( a \)-axis reaches 18 J kg\(^{-1}\) K\(^{-1}\), and the RC becomes 329 J kg\(^{-1}\) at 0–70 kOe, which represents a considerably high value in the RMO system. On the other hand, \( \Delta S_m \) and RC are much larger than those in the \( c \)-axis. The prominent anisotropy makes it an innovative magnetic refrigeration technique based on the RMCE that includes rotating the sample or the magnetic field in place of the conventional change of magnetic field for magnetic refrigeration. Large \( \Delta T_{SR} \) calculated from \( C_p \) and \( \Delta S_m \) proves that DHMO is a promising candidate in refrigeration too. The metamagnetic phase transitions occurring at low temperatures with the magnetic configuration change of Ho 3+ induce an increase in system disorder and are responsible for the pronounced magnetocaloric effect observed in the DHMO single crystal.

**Author contributions**


**Data availability**

The data supporting this article are included in the figures and tables.

**Conflicts of interest**

There are no conflicts to declare.

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