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Large reversible magnetocaloric effect in the ferromagnetic pyrochlores $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Yb}$)

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ARTICLE INFO

Keywords:

$R_2\text{Mn}_2\text{O}_7$ pyrochlore oxides

Magnetocaloric effect

Ferromagnetic order

ABSTRACT

We report the large reversible magnetocaloric effect (MCE) in the cubic pyrochlores $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Yb}$) near their second-order ferromagnetic (FM) transition at $T_C \approx 39$ K due to a simultaneous FM ordering of rare-earth R^{3+} and transition-metal Mn^{4+} localized moments. Under the magnetic field change of 1 T (7 T), the maximum magnetic entropy change $-\Delta S_M^{\text{max}}$ is 5.7 (20.1), 4.3 (18.4), 3.9 (13.9) $\text{J kg}^{-1} \text{K}^{-1}$, and the estimated magnetic refrigerant capacity RC reaches 20.0 (564), 18.4 (503.7), 13.1 (371.4) J kg^{-1} for $\text{Dy}_2\text{Mn}_2\text{O}_7$, $\text{Ho}_2\text{Mn}_2\text{O}_7$, and $\text{Yb}_2\text{Mn}_2\text{O}_7$, respectively. We have discussed their magnetic properties and its correlation with MCE in terms of the intrinsic single-ion anisotropy of R^{3+} ions. Our results demonstrate that $R_2\text{Mn}_2\text{O}_7$ cubic pyrochlores constitute a promising material platform for magnetic refrigeration applications in the intermediate temperature range.

1. Introduction

Recently, magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted great attention as a promising replacement for conventional gas compression–expansion technique [1–3]. The MCE in various magnetic materials has been extensively studied for better understanding of the fundamental physics of these materials [4–6]. After decades of research, some promising magnetocaloric materials have been discovered to operate in different temperature regions, such as RAl_2 [7] and RNi_2 ($R = \text{rare earth}$) [8–11] in the low temperature range (< 20 K), RCO_2 [12,13] in the intermediate temperature range (20–77 K), Dy [14,15] and GdSiGe [6,16] in the high-temperature region (> 77 K). In recent years, several alloy systems including La-Fe-Si [17,18], Mn-Fe-P-As [19], Fe-Rh [20], Mn-Co-Ge [21], and Ni-Mn-X ($X = \text{Sn}, \text{In}, \text{Sb}, \text{Ga}$) based magnetic shape memory alloys [22–26] have been identified as giant MCE materials near room temperature associated with a first-order ferromagnetic (FM) transition (for a recent review see Ref. [27]).

From the viewpoint of practical applications, magnetic materials with a second-order FM transition are attractive for potential magnetic refrigeration with fully reversible entropy change. Recently, we found

that pyrochlore oxide $\text{Er}_2\text{Mn}_2\text{O}_7$ synthesized under high-pressure condition exhibits a large and reversible MCE near its second-order FM transition at $T_C = 35$ K [28]. Under a magnetic field change of 5 T, the maximum magnetic entropy change $-\Delta S_M^{\text{max}}$ is $16.1 \text{ J kg}^{-1} \text{K}^{-1}$, and the estimated magnetic refrigerant capacity reaches 522 J kg^{-1} , which is among the largest values of MCE materials in the intermediate temperature range. Such an excellent MCE performance of $\text{Er}_2\text{Mn}_2\text{O}_7$ is mainly attributed to the large saturation moment of $18.9 \mu_B$ per formula unit (f.u.) owing to a simultaneous FM ordering of Er^{3+} and Mn^{4+} localized moments. Since $\text{Er}_2\text{Mn}_2\text{O}_7$ is a representative example of the FM pyrochlore oxides $R_2\text{Mn}_2\text{O}_7$, it is necessary to evaluate MCE of other members, in particular $R = \text{Ho}^{3+}$ and Dy^{3+} with a larger magnetic moment than Er^{3+} .

In this work, we have thus synthesized all the other members of cubic pyrochlores $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Yb}$) under high-pressure and high-temperature conditions and evaluated their MCE via detailed isothermal magnetization measurements. Similar as $\text{Er}_2\text{Mn}_2\text{O}_7$, they all exhibit large and reversible MCE near their second-order FM transition around $T_C \approx 39$ K. Under a magnetic field change of 7 T, the maximum magnetic entropy change $-\Delta S_M^{\text{max}}$ is 20.1, 18.4, $13.9 \text{ J kg}^{-1} \text{K}^{-1}$, and the estimated magnetic refrigerant capacity RC reaches 564, 503.7,

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<https://doi.org/10.1016/j.jmmm.2019.165494>

Received 22 April 2019; Received in revised form 25 June 2019; Accepted 26 June 2019

Available online 28 June 2019

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371.4 J kg⁻¹ for Dy₂Mn₂O₇, Ho₂Mn₂O₇, and Yb₂Mn₂O₇, respectively. These values are slightly lower than expected and we have rationalized their MCE performances and magnetic properties in terms of their intrinsic single-ion anisotropy of R³⁺ ions. Nonetheless, their MEC performance remains superior in comparison with known MCE materials in the similar temperature region. In addition, the insulating nature of these oxides can avoid the magnetic eddy current loss in the process of magnetic circulation to a large extent. Our results thus demonstrate that R₂Mn₂O₇ cubic pyrochlores constitute a promising material platform for magnetic refrigeration applications in the intermediate temperature range.

2. Experimental

Polycrystalline samples R₂Mn₂O₇ (R = Dy, Ho, Yb) with the cubic pyrochlore structure were synthesized under high-pressure conditions in the presence of an oxygen-releasing agent. We first prepared fine powders of the starting precursors with the wet-chemistry method by dissolving the mixture of Dy₂O₃, Ho₂O₃, Yb₂O₃ and MnCO₃ in citric acid saturated solution with some drops of nitric acid. Evaporation of the solution led to an organic resin, which was dried at 120 °C and decomposed at 600 °C for 12 h. The organic materials and the nitrates were eliminated in a subsequent treatment at 800 °C in air for 2 h. The resultant precursor powders were mixed with KClO₄ (30 wt%), placed in a gold capsule, sealed and placed in a cylindrical graphite heater, and then subjected to heat treatment at 2 GPa at 1000 °C for 60 min in a piston-cylinder apparatus. After releasing pressure, the resultant product was washed in water to dissolve KCl and then dried in air at 150 °C for 1 h. In order to obtain dense pellets of R₂Mn₂O₇ for magnetic measurements, the phase-pure powders were retreated at 6 GPa and 1000 °C for 30 min by packing the powders in a gold capsule with separated KClO₄ at both ends.

Phase purity of the obtained R₂Mn₂O₇ (R = Dy, Ho, Yb) polycrystalline samples was examined by powder x-ray diffraction (XRD) at room temperature. Rietveld refinements on the XRD patterns were performed with the FullProf program. The magnetic properties of these samples were measured with a commercial Magnetic Property Measurements System (MPMS-III, Quantum Design) in the temperature range 2 K to 300 K and in the field range +7 T to -7 T.

3. Results

3.1. Structural characterization

Fig. 1 displays the powder XRD patterns of R₂Mn₂O₇ (R = Dy, Ho, Yb) after Rietveld refinement. The refinements converged well and confirm that all the obtained samples are single phases with the cubic pyrochlore structure in space group *Fd-3m* (No. 227). The obtained lattice parameters, *a* = 9.9419(3) Å for Dy₂Mn₂O₇, 9.9211(1) Å for Ho₂Mn₂O₇, and 9.8357(1) Å for Yb₂Mn₂O₇, all agree well with those reported in literature [29,30]. The selected bond lengths and angles after refinements are listed in Table 1. Both the unit-cell dimension, bond lengths and angles show systematic changes upon reduction of the R³⁺ size.

3.2. Magnetic properties

The left panel of Fig. 2 displays the temperature dependence of magnetic susceptibility $\chi(T)$ for (a) Dy₂Mn₂O₇, (c) Ho₂Mn₂O₇, and (e) Yb₂Mn₂O₇, respectively. They are measured under an external field of $\mu_0 H = 0.1$ T by three different procedures: the ZFCW and FCW curves were recorded upon warming up after zero-field-cooled and field-cooled from room temperature, respectively, while FCC data were collected upon cooling down from room temperature under field. For each sample, the sharp increase of $\chi(T)$ around 40 K corresponds to the paramagnetic to FM transition at *T*_C, which can be defined as the peak

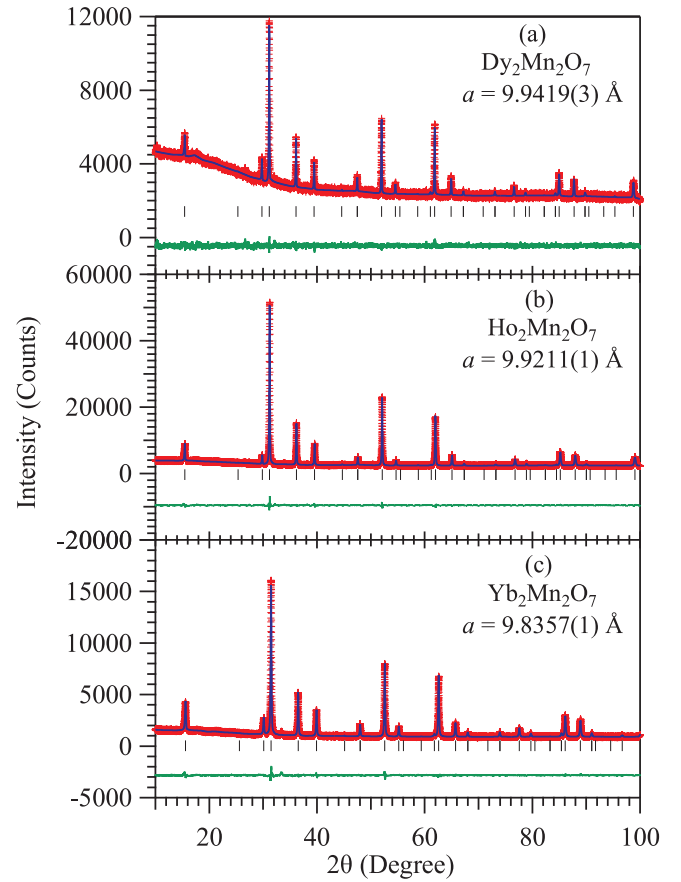


Fig. 1. Observed (cross), calculated (solid line) and difference (bottom line) XRD profiles for (a) Dy₂Mn₂O₇, (b) Ho₂Mn₂O₇, and (c) Yb₂Mn₂O₇ after Rietveld refinements. The Bragg positions are shown as the tick marks.

Table 1

Summary of the structural information and magnetic properties of the ferromagnetic pyrochlores R₂Mn₂O₇ (R = Dy, Ho, Er, Yb).

Materials	Dy ₂ Mn ₂ O ₇	Ho ₂ Mn ₂ O ₇	Er ₂ Mn ₂ O ₇	Yb ₂ Mn ₂ O ₇
<i>a</i> (Å)	9.9419(3)	9.9211(1)	9.8842(1)	9.8357(1)
<i>V</i> (Å ³)	982.69(4)	976.53(2)	965.66(2)	951.51(2)
R-O1(×6) (Å)	2.496(5)	2.450(2)	2.4430(11)	2.409(2)
R-O2(×2) (Å)	2.1525(1)	2.1480(1)	2.1417(5)	2.1295(1)
Mn-O1(×6) (Å)	1.897(4)	1.915(2)	1.9154(11)	1.911(3)
∠R-O1-R (°)	89.5(3)	91.44(7)	91.90(5)	92.41(9)
∠R-O2-R (°)	109.47(1)	109.47(1)	109.47(1)	109.47(1)
∠Mn-O1-Mn (°)	135.8(2)	132.60(5)	131.84(3)	131.03(7)
<i>R</i> _p (%)	2.23	2.25	2.83	2.70
<i>T</i> _C (K)	39	38	35	38
<i>θ</i> _{CW} (K)	41.5	39.8	37.4	43.5
μ_{eff} (μ_B /f.u.)	15.9	14.3	14.8	9.3
$\mu_{\text{eff}}^{\text{theo}}$ (μ_B /f.u.)	16.0	15.96	14.6	8.44
<i>M</i> _s ^{exp} (μ_B /f.u.)	17.3	15.1	18.9	10.4
<i>M</i> _s ^{theo} (μ_B /f.u.)	26	26	24	14
<i>M</i> _s ^{exp} / <i>M</i> _s ^{theo}	0.66	0.58	0.79	0.74

position of $d\chi/dT$. The determined *T*_C values are very close to each other, i.e. *T*_C = 39 K for Dy₂Mn₂O₇, *T*_C = 38 K for Ho₂Mn₂O₇ and Yb₂Mn₂O₇, respectively. These values agree well with those reported previously [31]. A splitting between ZFC and FC curves below 30 K was evidenced for Dy₂Mn₂O₇ and Ho₂Mn₂O₇, while these curves are perfectly overlapped with each other for Yb₂Mn₂O₇. As will be discussed below, the bifurcation of ZFC/FC curves in the former two samples might originate from the stronger magnetocrystalline anisotropy with a dominant Ising character for Dy³⁺ and Ho³⁺ moments.

For all three samples, no thermal hysteresis was observed between

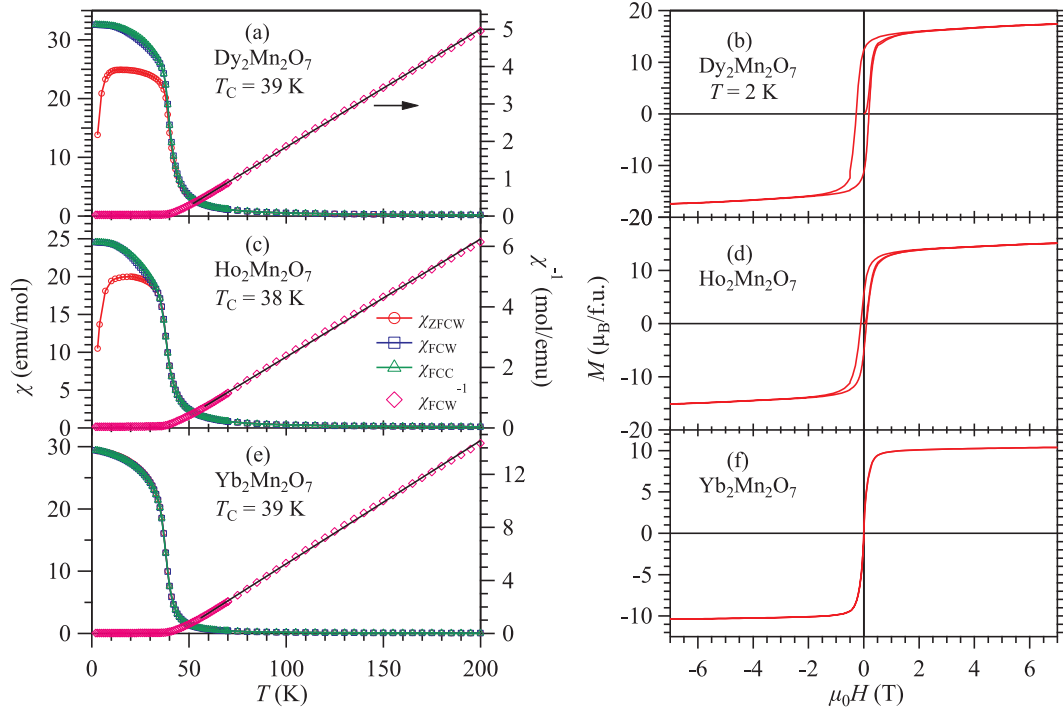


Fig. 2. Temperature dependence of dc magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ for (a) $\text{Dy}_2\text{Mn}_2\text{O}_7$, (c) $\text{Ho}_2\text{Mn}_2\text{O}_7$, and (e) $\text{Yb}_2\text{Mn}_2\text{O}_7$ measured under $\mu_0 H = 0.1$ T in three different procedures: ZFCW (red circle) and FCW (blue square) recorded upon warming up after zero-field-cooled and field-cooled from room temperature, FCC (green triangle) recorded during cooling down under field. The T_C value was determined from the minimum of $d\chi_{\text{FCW}}/dT$. The solid line represents the Curie-Weiss fitting to $\chi^{-1}(T)$ in the paramagnetic region. Magnetization loop $M(H)$ at 2 K for (b) $\text{Dy}_2\text{Mn}_2\text{O}_7$, (d) $\text{Ho}_2\text{Mn}_2\text{O}_7$, and (f) $\text{Yb}_2\text{Mn}_2\text{O}_7$ in the field range 7 T to -7 T.

FCW and FCC curves, in accordance with the second-order nature of the FM transition. The inverse magnetic susceptibility $\chi_{\text{FCW}}^{-1}(T)$ for these samples follows nicely the Curie-Weiss (CW) behavior in the paramagnetic region. We have applied the CW fitting to these $\chi^{-1}(T)$ curves in the paramagnetic region 50–200 K and obtained the effective moment μ_{eff} and the CW temperature θ_{CW} , which are 15.9 μ_B and 41.5 K for $\text{Dy}_2\text{Mn}_2\text{O}_7$, 14.3 μ_B and 39.8 K for $\text{Ho}_2\text{Mn}_2\text{O}_7$, and 9.28 μ_B and 43.5 K for $\text{Yb}_2\text{Mn}_2\text{O}_7$, respectively. These values are also listed in Table 1. The obtained μ_{eff} s are close to those expected theoretical values of $\mu_{\text{eff}}^{\text{theo}} = \{[2\mu_{\text{eff}}(R^{3+})]^2 + [2\mu_{\text{eff}}(\text{Mn}^{4+})]^2\}^{1/2}$ by considering both localized R^{3+} and Mn^{4+} moments, as shown in Table 1. The positive $\theta_{\text{CW}} \sim T_C$ s are consistent with the dominant FM interaction in these samples.

The right panel of Fig. 2 depicts the isothermal magnetization $M(H)$ curves of these three samples measured at 2 K between -7 T and $+7$ T. A typical FM behavior is observed, and the saturation moment at 7 T reaches $M_s = 17.3$, 15.1, and 10.4 $\mu_B/\text{f.u.}$ for $\text{Dy}_2\text{Mn}_2\text{O}_7$, $\text{Ho}_2\text{Mn}_2\text{O}_7$, and $\text{Yb}_2\text{Mn}_2\text{O}_7$, respectively. Although these values are large, they are smaller than expected values of $M_s^{\text{theo}} = 26$ $\mu_B/\text{f.u.}$ for $\text{Dy}_2\text{Mn}_2\text{O}_7$ and $\text{Ho}_2\text{Mn}_2\text{O}_7$, and 14 $\mu_B/\text{f.u.}$ for $\text{Yb}_2\text{Mn}_2\text{O}_7$, assuming a perfect alignment of the full moments of R^{3+} ($=g_R\mu_B$) and Mn^{4+} ($3\mu_B$). Since the magnetic moment of Mn^{4+} in $\text{Er}_2\text{Mn}_2\text{O}_7$ has been verified by neutron diffraction to be close to the expected value [28], the difference between observed M_s and expected M_s^{theo} should originate mainly from the R^{3+} ions. If we assume that Mn^{4+} ions attain the full moment of 3 μ_B , the magnetic moment of R^{3+} ions, i.e. 5.6 μ_B/Dy^{3+} , 4.5 μ_B/Ho^{3+} , and 2.2 μ_B/Yb^{3+} , respectively, reach about half of their full moments. As discussed below, the reduction of saturation moments in these ferromagnetic pyrochlores is caused by the strong single-ion anisotropy of R^{3+} ions, i.e. an Ising character for Dy^{3+} and Ho^{3+} , and XY anisotropy for Er^{3+} and Yb^{3+} , which prevent the full alignment of R^{3+} moments even under 7 T. It is also noteworthy that a clear magnetic hysteresis was observed in $\text{Dy}_2\text{Mn}_2\text{O}_7$ and $\text{Ho}_2\text{Mn}_2\text{O}_7$ with a coercive force H_c about 0.2 T and 0.1 T, respectively, whereas an H_c as small as 20 Oe was

evidenced in $\text{Yb}_2\text{Mn}_2\text{O}_7$, in accordance with the perfect overlap of ZFC and FC curves in Fig. 2(e).

3.3. Magnetocaloric effect

To evaluate the MCE, we measured a series of isothermal magnetization $M(H)$ curves between 2 K and 100 K for each sample. The data are shown in Fig. 3(a, c, e) for these three samples. Then, the magnetic entropy change $-\Delta S_M$ associated with the FM transition can be calculated from the $M(H)$ data according to the Maxwell relation:

$$\Delta S_M \left(\frac{T_1 + T_2}{2} \right) = \frac{1}{T_1 - T_2} \left[\int_0^{\mu_0 H} M(T_2, \mu_0 H) d(\mu_0 H) - \int_0^{\mu_0 H} M(T_1, \mu_0 H) d(\mu_0 H) \right] \quad (1)$$

The obtained $-\Delta S_M$ as a function of temperature under various magnetic fields are displayed in Fig. 3(b, d, f) for these three samples. As can be seen, the $-\Delta S_M(T)$ curves cover a relatively broad temperature range centered around T_C , which moves slightly to higher temperatures with increasing magnetic field. Under a field change of 0.5, 1, 3, 5, 7 T, the maximum values of $-\Delta S_M$ reach 3.15, 5.65, 12, 16.4, and 20.1 $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ for $\text{Dy}_2\text{Mn}_2\text{O}_7$, 2.11, 4.3, 10.3, 14.7, and 18.3 $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ for $\text{Ho}_2\text{Mn}_2\text{O}_7$, and 2.17, 3.85, 8.2, 11.3, and 13.9 $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ for $\text{Yb}_2\text{Mn}_2\text{O}_7$, respectively.

The field dependences of $-\Delta S_M^{\text{max}}$ for the series of $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) are also displayed in Fig. 4(a). The results of $\text{Er}_2\text{Mn}_2\text{O}_7$ were taken from our previous report for comparison [28]. As can be seen, under a given field change $-\Delta S_M^{\text{max}}$ decreases in the sequence of $\text{Dy} > \text{Er} > \text{Ho} > \text{Yb}$, roughly following the same trend of saturation moment attained for each compound, as seen in Table 1. But the difference between $\text{Dy}_2\text{Mn}_2\text{O}_7$ and $\text{Er}_2\text{Mn}_2\text{O}_7$ is marginal, and the $-\Delta S_M^{\text{max}}$ of $\text{Er}_2\text{Mn}_2\text{O}_7$ at 7 T is even slightly larger than that of $\text{Dy}_2\text{Mn}_2\text{O}_7$.

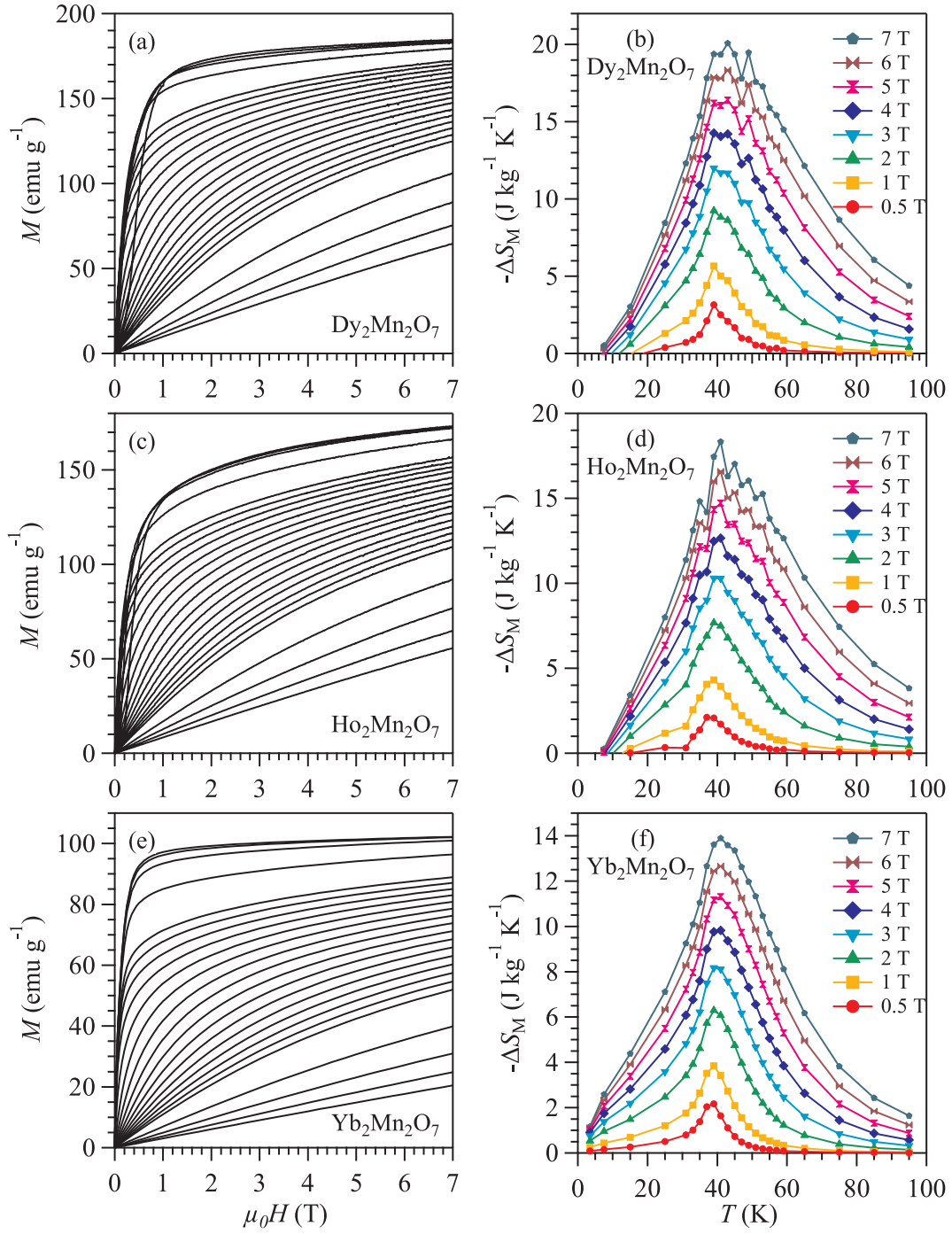


Fig. 3. Isothermal magnetization $M(H)$ curves for (a) $\text{Dy}_2\text{Mn}_2\text{O}_7$, (c) $\text{Ho}_2\text{Mn}_2\text{O}_7$, and (e) $\text{Yb}_2\text{Mn}_2\text{O}_7$ in the temperature range from 2 K to 100 K. The $M(H)$ curves from top to bottom are taken at 2, 5, 10, 20, 30 to 60 K with $\Delta T = 2$ K, 70, 80, 90, and 100 K. Temperature dependences of magnetic entropy change $-\Delta S_M$ under various magnetic-field changes up to 7 T for (b) $\text{Dy}_2\text{Mn}_2\text{O}_7$, (d) $\text{Ho}_2\text{Mn}_2\text{O}_7$, and (f) $\text{Yb}_2\text{Mn}_2\text{O}_7$.

Another important parameter characterizing the practical significance of MCE materials is the refrigerant capacity (RC), which represents the amount of heat that can be transferred between cold and hot sinks in one refrigeration cycle. The RC can be calculated via

$$RC = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_M dT \quad (2)$$

where T_{cold} and T_{hot} represent the corresponding temperatures at the full width at the half maximum (FWHM) of the $-\Delta S_M$ peak. Thus, a broader $-\Delta S_M$ curve gives a larger RC. Similar as $\text{Er}_2\text{Mn}_2\text{O}_7$ [28], the relatively broad $-\Delta S_M(T)$ curves in Fig. 3(b, d, f) should produce a considerable large RC for these three samples. Then, we determined the

RC under each field change by integrating the corresponding $-\Delta S_M(T)$ curves within the FWHM region.

The obtained RC values of $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy, Ho, Yb}$) as a function of magnetic field are plotted in Fig. 4(b). The corresponding RC values for $\text{Er}_2\text{Mn}_2\text{O}_7$ are also included for comparison. As can be seen, RC of $R_2\text{Mn}_2\text{O}_7$ increase almost linearly with magnetic field, and RC values reach 746.8, 665, 566.8, 400.5 J kg^{-1} under a field change of 7 T for $R = \text{Er, Dy, Ho, and Yb}$, respectively. In comparison with $\text{Er}_2\text{Mn}_2\text{O}_7$, the RC values of $\text{Dy}_2\text{Mn}_2\text{O}_7$ become smaller, which should be ascribed to the relatively narrower $-\Delta S_M(T)$ curve shown in Fig. 3(b). Nonetheless, the RC values of the series of ferromagnetic $R_2\text{Mn}_2\text{O}_7$ remains quite

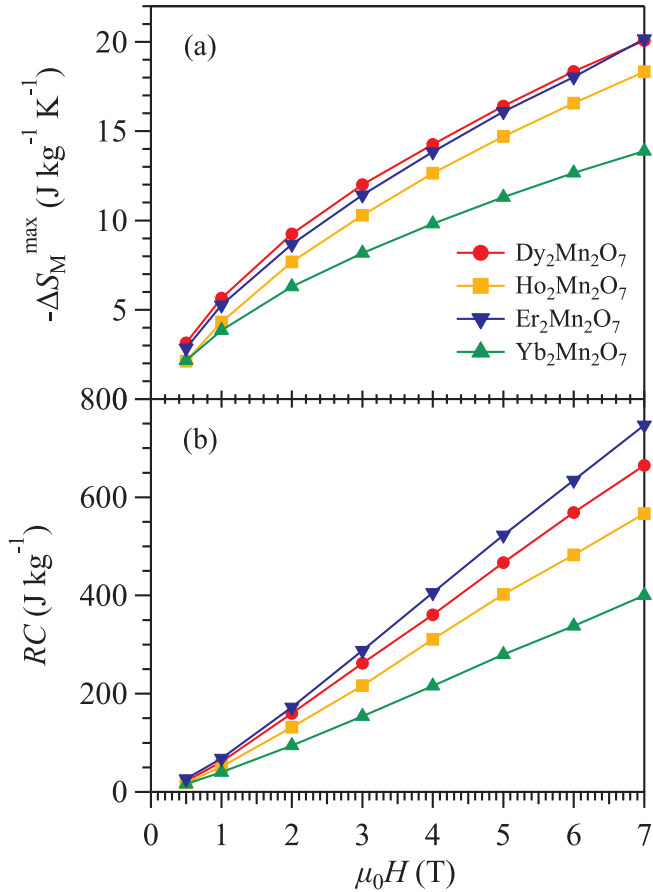


Fig. 4. Field dependences of (a) the maximum magnetic entropy change $-\Delta S_M^{\max}$ and (b) the refrigerant capacity RC for the series of $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) pyrochlore oxides. The data of $\text{Er}_2\text{Mn}_2\text{O}_7$ are taken from Ref. [28].

large among the known MCE oxide materials.

In Table 2, we have collected the $-\Delta S_M^{\max}$ and RC values of $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) under a field change of 1 T and 5 T, and compared with those typical large MCE materials in the similar temperature range. In comparison with the rare-earth manganese perovskite oxides, e.g. TbMnO_3 and HoMnO_3 , these ferromagnetic pyrochlore oxides exhibits comparable performance at high magnetic fields in terms of $-\Delta S_M^{\max}$ values, but their low-field (≤ 1 T) performances are much better. This should be attributed to the spontaneous order of R^{3+} moments rather than the gradual polarization by an external

magnetic field as in the perovskite manganese oxides. In addition, the RC values of $R_2\text{Mn}_2\text{O}_7$ are also much larger than those perovskite oxides with similar R^{3+} moment, e.g. ErTiO_3 (340 J kg^{-1}) and TbMnO_3 (250 J kg^{-1}). These comparison thus demonstrate that the cubic pyrochlores $R_2\text{Mn}_2\text{O}_7$ constitute a promising MCE material system that is featured by a cooperative two-sublattice FM order in the intermediate temperature range.

4. Discussions

In the cubic pyrochlore structure, both R and Tr cations in $R_2\text{Tr}_2\text{O}_7$ ($Tr = \text{transition metal}$) form three-dimensional networks of corner-shared tetrahedra, which is an archetype of geometrically frustrated lattice. Thus, long-range antiferromagnetic order between localized R^{3+} moments is usually suppressed to below ~ 1 K in $R_2\text{Ti}_2\text{O}_7$ with nonmagnetic Ti^{4+} ($3d^0$, $S = 0$). In contrast, in the cases of $R_2\text{Mn}_2\text{O}_7$, the presence of virtual charge transfer between partially filled t_{2g} orbitals and empty e_g orbitals due to a strong bending of Mn-O-Mn angle of $\sim 130^\circ$ results in a spontaneous FM order of the Mn^{4+} ($S = 3/2$) sublattices [28], which not only relieves the geometrical frustration but also produces a strong internal field to polarize the R^{3+} sublattice. As a result, a cooperative two-sublattice FM order is realized in $R_2\text{Mn}_2\text{O}_7$ and the resultant huge magnetization below T_C leads to large and reversible MCE as observed here.

However, we should note that a complete alignment of the full R^{3+} moment in $R_2\text{Mn}_2\text{O}_7$ is hindered by the strong single-ion anisotropy dictated by the local site distortion featured by six long $R\text{-O}1$ and two $R\text{-O}2$ bonds, Table 1. It has been well established in the series of pyrochlores $R_2\text{Ti}_2\text{O}_7$ that Dy^{3+} and Ho^{3+} ions have a strong Ising anisotropy with the magnetic moment pointing along the local $\langle 111 \rangle$ axis of R^{3+} tetrahedron, while Er^{3+} and Yb^{3+} ions are featured by a strong XY anisotropy with the moment lying within the plane perpendicular to the local $\langle 111 \rangle$ axis [39]. As a result, the magnetization of R^{3+} sublattices always saturate to about half of the full free moment, e.g. $\sim 5 \mu_B$ for $\text{Dy}_2\text{Ti}_2\text{O}_7$ [40]. The single-ion anisotropy is so strong that a moderate field up to 7 T cannot fully polarize the R^{3+} moments. This can rationalize the fact that the observed saturation moment is reduced in comparison with the expected values as listed in Table 1. According to the $M_s^{\text{exp}}/M_s^{\text{theo}}$ ratio in Table 1, the XY-type Er^{3+} and Yb^{3+} ions contribute more to the magnetization than the Ising-type Dy^{3+} and Ho^{3+} ions. Thus, $\text{Er}_2\text{Mn}_2\text{O}_7$ exhibits comparable $-\Delta S_M^{\max}$ but larger RC in comparison with $\text{Dy}_2\text{Mn}_2\text{O}_7$.

5. Conclusion

In summary, we have performed a systematic study on the magnetic and MCE of the series of $R_2\text{Mn}_2\text{O}_7$ ($R = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) with cubic pyrochlore structure. These materials can be synthesized only under moderate high-pressure conditions, and display a cooperative, second-order FM transition around $T_C = 35\text{--}39$ K involving the simultaneous alignment of the rare-earth R^{3+} and transition-metal Mn^{4+} localized moments. As a result of large attainable saturation moments, these materials are found to display large and reversible MCE. In addition, the low-field performances are superior due to the cooperative nature of the FM transition. Under the magnetic field change of 1 T (7 T), the maximum magnetic entropy change $-\Delta S_M^{\max}$ is 5.7 (20.1), 4.3 (18.4), 3.9 (13.9) $\text{J kg}^{-1} \text{K}^{-1}$, and the estimated magnetic refrigerant capacity RC reaches 20.0 (56.4), 18.4 (503.7), 13.1 (371.4) J kg^{-1} for $\text{Dy}_2\text{Mn}_2\text{O}_7$, $\text{Ho}_2\text{Mn}_2\text{O}_7$, and $\text{Yb}_2\text{Mn}_2\text{O}_7$, respectively. We have discussed the magnetic properties and its correlation with MCE in terms of the intrinsic single-ion anisotropy of R^{3+} ions. Together with our previous work [28], our results demonstrate that cubic $R_2\text{Mn}_2\text{O}_7$ pyrochlores are promising candidate materials for magnetic refrigeration applications in the intermediate temperature range.

Table 2

Comparison of the maximum magnetic entropy change $-\Delta S_M^{\max}$ and refrigerant capacity RC under 1 T and 5 T for $R_2\text{Mn}_2\text{O}_7$ and various large MCE materials in the similar temperature range.

	$-\Delta S_M^{\max} (\text{J kg}^{-1} \text{K}^{-1})$		$RC (\text{J kg}^{-1})$		Refs.
	1 T	5 T	1 T	5 T	
$\text{Dy}_2\text{Mn}_2\text{O}_7$	5.7	16.1	61.4	467.0	This work
$\text{Ho}_2\text{Mn}_2\text{O}_7$	4.3	15.1	51.5	402.6	This work
$\text{Er}_2\text{Mn}_2\text{O}_7$	5.3	16.1	68.2	522.8	[28]
$\text{Yb}_2\text{Mn}_2\text{O}_7$	3.9	11.3	40.0	279.6	This work
TbMnO_3	1.2	15	26	250	[32]
HoMnO_3	–	12.5	–	312	[33]
ErTiO_3	2.8	10.5	50	340	[34]
TbNiAl	–	13.8	–	494	[35]
Dy_3Co	–	13.9	–	498	[36]
DyCoAl	–	16.3	–	487	[37]
ErGa	–	21.3	–	494	[38]

Acknowledgements

This work is supported by the National Key R&D Program of China (Grant Nos. 2018YFA0305700 and 2018YFA0305800), the National Natural Science Foundation of China (Grant Nos. 11574377, 11834016, 11874400), the Strategic Priority Research Program and Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (Grant No. XDB25000000, and QYZDB-SSW-SLH013). J.A.A. gratefully acknowledges the Spanish MINECO for granting the project MAT2017-84496-R. Q.C. and N.N.W. are grateful for the support of PRIUS project No. 2018-A44 to explore new ferromagnetic pyrochlores in Ehime University.

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