Ericsson-like giant magnetocaloric effect in GdCrO₄–ErCrO₄ composite oxides near liquid hydrogen temperature

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In this paper, magnetic and magnetocaloric properties of RCrO₄ (R=Gd and Er) oxides have been investigated. It is found that GdCrO₄ and ErCrO₄ exhibit a second-order magnetic transition from ferromagnetic to paramagnetic states at their Curie temperatures of 22.0 K and 14.9 K, respectively. The maximal magnetic entropy change (ΔSM) for a field variation of 0–5 T have reached 22.8 J kg⁻¹ K⁻¹ for GdCrO₄ and 20.5 J kg⁻¹ K⁻¹ for ErCrO₄. The collective magnetic contributions from R³⁺ and Cr⁵⁺ ions lead to the large ΔSM. For the same field variation, table-like ΔSM of ~19.5 J kg⁻¹ K⁻¹ and a large refrigerant capacity (RC) of 117 J kg⁻¹ have been achieved for the composite material formed by GdCrO₄ and ErCrO₄ with the mass ratio of 1:1 from 16.0 K to 22.0 K. Since the liquid hydrogen temperature (20.3 K) locates within this range, large reversible magnetocaloric effect, high RC as well as the low cost make GdCrO₄–ErCrO₄ composite material a potential candidate for magnetic refrigerant for the storage of liquid hydrogen.

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1. Introduction

Magnetic refrigeration based on magnetocaloric effect (MCE) of solid-state working substances has been widely employed in ultra-low temperature [1,2]. Recently, it has been anticipated to be a promising alternative technology available to high temperature and even room temperature, due to its higher energy-efficient and environment-friendly features as compared with the common gas-compression refrigeration technology that is used currently [3,4]. In fact, systems exhibiting large MCE in low temperature are also important for basic research as well as special technological applications such as space science and liquefaction of hydrogen in fuel industry [3,4]. Above 15 K, the influence of the lattice entropy must be considered. As we all know, lattice entropy is only affected by temperature and it rises rapidly as the temperature rises. Magnetic Ericsson-cycle is composed of four processes, i.e., isothermal magnetization, isomagnetic field process in strong magnetic field, isothermal demagnetization, and isomagnetic field process in weak magnetic field. The lattice entropy change are fully counteracted by two kinds of isomagnetic field processes. Therefore, magnetic Ericsson-cycle is ideal for refrigerating effectively above 15 K [5,6]. However, Ericsson-type magnetic refrigerators require the magnetic entropy change (ΔSM) of the material to be a constant value in the temperature range of the operation of the thermodynamic cycle (known as table-like MCE) [7,8]. This is usually achieved either in the material with the successive magnetic phase transition or in manufacturing composite materials undergoing neighboring phase transitions. The typical examples are Gd₀.₅₄Er₀.₄₆NiAl compound [5] and the mixture of ErAl₂, HoAl₂, and (Ho₀.₅Dy₀.₅)Al₂ [6]. Rare-earth intermetallic compounds usually exhibit large MCE [4]. However, many disadvantages such as high cost and poor corrosion resistance are accompanied. Therefore, the MCE of rare-earth intermetallic oxides without such shortcomings, especially manganites, are widely studied [4,9]. As a matter of fact, perovskite manganites show MCE at high temperature and even room temperature but the MCE values for most of them are smaller [4,9–12]. But multiferroic manganites such as RMnO₃ [13,14] show large MCE at low temperature due to their large rare-earth moment. Recently, giant MCE have also been successively observed in rare-earth transition metal oxides such as RMO₃ (R=heavy rare earth, M=Fe, Cr, and Ti) [15–17] and zircon-type RCrO₄ (R=Gd, Dy, and Ho) [18,19], which again motivates the interest for exploring of excellent magnetic refrigerants in this kind of materials. Zircon-type RCrO₄ compounds exhibit complicated magnetic properties due to the strong competition between ferromagnetic and antiferromagnetic superexchange interactions of 3d and 4f spins [20–
25]. Magnetic measurement, neutron diffraction, and 3D neutron depolarization data have been used to determine the magnetic phase of ErCrO₄ at low temperature [21–23]. ErCrO₄ oxide with the zircon-type structure was originally reported by Sáez-Puche et al. [21] to exhibit antiferromagnetic phase below the Néel temperature of 15 K. After which, it was found that zircon-type ErCrO₄ underwent a magnetic transition from ferromagnetic (FM) to paramagnetic (PM) states at Curie temperature of ~15 K [22,23]. Furthermore, a large saturation magnetization value of 6.0 μ_B at 2 K has also been reported [22]. Therefore, large MCE could be expected in zircon-type ErCrO₄ oxide. In this letter, we report the large MCE within zircon-type ErCrO₄, as well as the table-like MCE within GdCrO₄–ErCrO₄ composite material.

2. Experimental process

The polycrystalline samples of zircon-type RCrO₄ (R = Gd and Er) have been prepared by standard solid-state reaction method by intensively mixing the stoichiometric amounts of R(NO₃)₃·6H₂O and Cr(NO₃)₃·9H₂O (Alfa Aesar, purity higher than 99.99%). In order to stabilize the unusual Cr⁵⁺ oxidation state, constant oxygen flow was employed during the following annealing process: 50 min to 160 °C for 2 h, 20 min to 200 °C for 2 h, 100 min to 600 °C for 6 h, and then 150 min to 150 °C. Finally, the samples were left to cool down to room temperature in the furnace naturally. Powder X-ray diffractometer was performed to characterize the crystal structure of the samples. Magnetic measurements were carried out on a commercial superconducting quantum interference device–vibrating sample magnetometer (SQUID-VSM) from Quantum Design.

3. Results and discussion

Fig. 1 shows the Rietveld refined powder X-ray diffraction patterns of RCrO₄ (R = Gd and Er) oxides. All the diffraction peaks can be indexed to a zircon-type structure (space group I₄₁/amd). The lattice parameters obtained from the refinement are a = 7.210 (3) Å and c = 6.322(8) Å for GdCrO₄ oxide, a = 7.095(3) Å and c = 6.240(8) Å for ErCrO₄ oxide, which are almost consistent with the previous reports [20,22].

The low-field temperature (T)-dependence of magnetization (M) has been measured in order to determine magnetic state, phase transition temperature and the nature of the transition. Fig. 2(a) displays the zero-field cooling (ZFC) and field-cooling (FC) magnetization curves of RCrO₄ (R = Gd and Er) oxides under a field of 0.01 T. As shown in the curves, both compounds exhibit FM–PM transitions. The Curie temperature T_C, corresponding to the maximum slope of FC M–T curve, is determined to be 22.0 K for GdCrO₄ and 14.9 K for ErCrO₄, respectively. They are in agreement with the result reported in the literatures [19,22,23]. It can also be seen from Fig. 2(a) that the ZFC and FC curves are completely reversible near T_C, which is rather common in magnetic materials with a second-order magnetic transition. However, a significant thermal irreversibility between the ZFC and FC branches is clearly observed below T_C. Neutron diffraction investigations for GdCrO₄ indicated that the ordered magnetic moments of the Cr⁵⁺ ions were located along the crystallographic c-axis, forming an angle of
24° with the ordered moments of the Gd$^{3+}$ ions [24]. Therefore, the thermomagnetic irreversibility is likely to be attributed to the small anisotropic contribution in the Gd–Cr magnetic exchange interactions since the ordered moments of both sublattices are not fully collinear. For ErCrO$_4$, a collinear ferromagnetic structure between Cr$^{5+}$ sublattice and Er$^{3+}$ sublattice was confirmed by neutron diffraction data [22]. Crystal field effect may cause the high anisotropy of ErCrO$_4$, which leads to the irreversibility of ZFC and FC branches below $T_c$.

The reciprocal magnetic susceptibilities $\chi^{-1}$ versus temperature for ErCrO$_4$ and GdCrO$_4$ under a field of 0.01 T are shown in Fig. 2(b). The magnetic susceptibility above 50 K obeys the Curie–Weiss (CW) law. The effective magnetic moments per molecule for ErCrO$_4$ and GdCrO$_4$ are calculated to be 9.8 $\mu_B$ and 7.7 $\mu_B$, respectively. Both are larger than the values of their free R ion counterparts (9.5 $\mu_B$ for Er ion and 7.0 $\mu_B$ for Gd ion), respectively. This result confirms the magnetic contribution from Cr$^{5+}$, which agrees well with the conclusion yielded by the neutron diffraction study. Meanwhile, positive PM Weiss temperatures ($\theta_w$) for ErCrO$_4$ and GdCrO$_4$ are obtained to be 2.4 K and 17.2 K, which reassures that a FM–PM phase transition takes place near $T_c$. However, the very small value of $\theta_w$ for ErCrO$_4$ indicates the strong competition between FM and AFM interactions, similar to the case of DyCrO$_4$ and HoCrO$_4$ [18,19]. Moreover, closer inspection for the ZFC susceptibility results that the anomaly derives from a spin-glass like phase emerges due to the strong competition between FM and AFM interactions [18,19]. We believe that the anomaly in the ZFC $d\chi/dT$–$T$ curve of ErCrO$_4$ is due to the same reason.

The isothermal magnetization curves as a function of magnetic field for RCrO$_4$ (R=Er and Gd) compounds were measured in applied fields of up to 5 T or 7 T in a wide temperature range from 5 to 50 K near $T_c$, as shown in Fig. 3(a) and (b). One can find that both oxides exhibit FM behavior below $T_c$. However, GdCrO$_4$ shows a more obvious saturation-like behavior than ErCrO$_4$ up to the highest applied field, which can still be interpreted by its weaker crystal field effect. The Arrott plots [26] of the RCrO$_4$ (R=Er and Gd) oxides are shown in Fig. 3(c) and (d). According to the Banerjee criterion [27], a magnetic transition is expected to be of the first order when the slope of $M^2$ vs $H/M$ plot is negative, whereas it would be of the second order when the slope is positive. It is very clear that the Arrott plots for ErCrO$_4$ and GdCrO$_4$ indicate a character of second-order magnetic transition.

The magnetic entropy change $\Delta S_m$ for RCrO$_4$ (R=Er and Gd) is calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$. The values of $\Delta S_m$ of GdCrO$_4$ and ErCrO$_4$ for different magnetic field variations as a function of temperature are shown in Fig. 4(a) and (b). One can see that the temperature dependence of $\Delta S_m$ shows a maximum value near $T_c$. The maximum value of $\Delta S_m$ is found to increase monotonically as the applied magnetic field increases. For a magnetic field variation from 0 to 5 T, it reaches 22.8 J kg$^{-1}$ K$^{-1}$ at 22.0 K for GdCrO$_4$ and 20.5 J kg$^{-1}$ K$^{-1}$ at 16.0 K for ErCrO$_4$. They are comparable with or much larger than those of some rare-earth intermetallic magnetocaloric compounds with a magnetic ordering temperature around 20 K under the same field change, such as Er$_3$Ni$_2$ (19.5 J kg$^{-1}$ K$^{-1}$ at 16 K) [28], DyNi$_2$ (21.3 J kg$^{-1}$ K$^{-1}$ at 20 K) [29], ErFeSi (23.1 J kg$^{-1}$ K$^{-1}$ at 24 K) [30], PrNi (6.1 J kg$^{-1}$ K$^{-1}$ at 20 K) [31], GdPd$_2$Si (15 J kg$^{-1}$ K$^{-1}$ at 17 K) [32]. Furthermore, comparing

![Fig. 3. Magnetic isothermals of ErCrO$_4$ (a) and GdCrO$_4$ (b) measured under increasing field and Arrott-plots of ErCrO$_4$ (c) and GdCrO$_4$ (d) near $T_c$.](image)
to the above compounds, a remarkable virtue of the studied oxides in this paper is the low cost of fabrications.

Based on the molecular field theory (MFT), the magnetic entropy change $\Delta S_M$ is written as:

$$
\Delta S_M(T, H) = N k_B \ln(2J + 1) - \ln \left( \frac{\sinh^{2J+1}(\frac{\mu_B H}{k_B T})}{\sinh^2(\frac{\mu_B H}{k_B T})} \right) + x \sigma,
$$

where $\sigma = B_2(\chi)$ is the Brillouin function with $\chi = g \mu_B H / k_B T$, where $\mu_B$, $k_B$, and $g$ have the conventional meanings, $J$ is the total angular quantum number, $N$ is the number of spins per unit mass, $\chi$ is the molecular field coefficient. The solid lines shown in Fig. 4 (a) and (b) are the corresponding theoretical $\Delta S_M$ values calculated from the MFT in which $J=4$ and $g=2$ for GdCrO$_4$ and $J=6$, $g=15/14$ for ErCrO$_4$ are used. It can be seen that the experimental and theoretical curves coincide sufficiently well at high temperatures ($T \approx T_C$). However, as expected, at low temperatures ($T < T_C$) and in the vicinity of $T_C$, pronounced deviation of the theoretical curves from the experimental ones can be seen. This is because at these temperature ranges, the MFT is incapable of modeling the magnetization accurately.

Hydrogen is considered as one of the most promising candidates for clean energy sources because of its high energy density and being environmental-friendly. Generally, hydrogen gas needs to be cooled down to liquid form for its storage and transportation. The liquefying temperature of hydrogen is 20.3 K. It has been reported that above 15 K magnetic Ericsson refrigeration cycle is necessary for magnetic refrigerator in order to remove the effect of the lattice entropy for ferromagnet as a magnetic refrigerant. That is, temperature invariability for the magnetic entropy change is required for the Ericsson cycle. One can find from Fig. 4(a) and (b) that the peak values of $\Delta S_M$ near $T_C$ for GdCrO$_4$ and ErCrO$_4$ oxides are equal to each other approximately. The corresponding temperatures of the peak are 22.0 K and 16.0 K for GdCrO$_4$ and ErCrO$_4$, respectively. Since the liquefying temperature of hydrogen

Fig. 4. Magnetic entropy change as a function of temperature for GdCrO$_4$ (a) and ErCrO$_4$ (b) for typical magnetic field variations (closed shapes). The solid lines are calculated by MFT.

Fig. 5. Magnetic entropy change as a function of temperature for GdCrO$_4$ and ErCrO$_4$ as well as the calculated composite material formed by GdCrO$_4$ and ErCrO$_4$ with the mass ratio of 1:1 for a magnetic field variation of 0–5 T (a). Temperature dependence of magnetic entropy change for Gd$_{0.5}$Er$_{0.5}$CrO$_4$ compound as well as the calculated and experimental composite materials formed by GdCrO$_4$ and ErCrO$_4$ with the mass ratio of 1:1 for the same field variation (b). The shade area gives the RC of the experimental composite material around quasi-platform part. The inset of (b) shows the ZFC $M$-$T$ curves of Gd$_{0.3}$Er$_{0.7}$CrO$_4$ compound and the experimental composite material under 0.1 T.
lies between them, using the mixture of GdCrO₄ and ErCrO₄ as the refrigerant of magnetic Ericsson cycle to keep the temperature stability of liquid hydrogen is a suitable choice. Fig. 5 displays the temperature dependence of $\Delta S_{m}$ for GdCrO₄ and ErCrO₄ as well as the calculated composite material formed by GdCrO₄ and ErCrO₄ compounds with the mass ratio of 1:1 for a field variation of 0–5 T. The best quasi-platform of $\Delta S_{m}$ with ~19.5 J kg⁻¹ K⁻¹ is observed from 16.0 K to 22.0 K. For the sake of credibility of quasi-platform for the mixture, we compress GdCrO₄ and ErCrO₄ powder into flat pieces separately, and then cut them into small squares with the same mass of 1.0 mg, followed by sticking them together to perform magnetic measurements in order to obtain the MCE of the mixture. The inset of Fig. 5(b) shows the ZFC temperature dependence of magnetization under 0.1 T. One can find two successive phase transitions at 14.6 K and 21.6 K, completely corresponding to those of GdCrO₄ and ErCrO₄. The magnetic entropy change curve of the mixture displays a quasi-platform for a field variation of 0–5 T [see Fig. 5(b)], which agrees with the result of the calculated composite material. Meanwhile, we have also successfully prepared Gd₀.₅Er₀.₅CrO₄ compound with the same zircon type structure as GdCrO₄ and ErCrO₄. Gd₀.₅Er₀.₅CrO₄ compound is equivalent to the mixture of GdCrO₄ and ErCrO₄ with the mass ratio of 1:1.03. As shown in the inset of Fig. 5(b), Gd₀.₅Er₀.₅CrO₄ compound just undergoes one FM–PM phase transition at its Curie temperature of 20.6 K, which locate between the Curie temperatures of GdCrO₄ and ErCrO₄. This illustrates the existence of additional magnetic interaction between Gd³⁺ ions and Er³⁺ ions in Gd₀.₅Er₀.₅CrO₄ compound. Correspondingly, the magnetic entropy change of Gd₀.₅Er₀.₅CrO₄ shows a maximum value of 19.6 J/kg K at 20.0 K. Thus, the quasi-platform of magnetic entropy change can only be obtained from the composite material of GdCrO₄ and ErCrO₄. A large refrigerant capacity (RC) value of 117 J kg⁻¹ is then achieved for the composite material of GdCrO₄ and ErCrO₄ with the mass ratio of 1:1, which is calculated by numerically integrating the area under the $\Delta S_{m}$–$T$ curve between 16.0 K and 22.0 K (see the shaded part in Fig. 5(b)). The large RC attributes to the appreciably large values of $\Delta S_{m}$ near $T_{C}$ for GdCrO₄ and ErCrO₄ oxides.

4. Conclusions

In summary, from the magnetization measurements it is found that GdCrO₄ and ErCrO₄ oxides undergo a FM–PM phase transition around 20 K. Large $\Delta S_{m}$ of 22.8 J kg⁻¹ K⁻¹ for GdCrO₄ and 20.5 J kg⁻¹ K⁻¹ for ErCrO₄ are obtained for a field variation of 0–5 T. For the composite material formed by GdCrO₄ and ErCrO₄ with the mass ratio of 1:1, the best table-like $\Delta S_{m}$ with ~19.5 J kg⁻¹ K⁻¹ and a large RC of 117 J kg⁻¹ from 16.0 K to 22.0 K have been achieved for the same field variation. The excellent magnetocaloric properties as well as the low cost of fabrication indicate the applicability of GdCrO₄ and ErCrO₄ oxides as magnetic refrigerants for the storage of liquid hydrogen.

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References