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Phase transition-induced magnetocaloric effects in $R_2Mo_2O_7$ (R = Er, Dy, Gd and Y) molybdates

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ABSTRACT

We have investigated the magnetic properties and magnetocaloric effects (MCEs) of $R_2Mo_2O_7$ (R = Er, Dy, Gd and Y). Magnetic ground states of $R_2Mo_2O_7$ largely depend on the radius of rare earth ion. $Er_2Mo_2O_7$, $Dy_2Mo_2O_7$ and $Y_2Mo_2O_7$ with small rare earth radius exhibit spin-glass state around 20 K, while $Gd_2Mo_2O_7$ with larger rare earth radius undergoes a ferromagnetic state below 78 K and a reentrant spin-glass behavior below 34 K. Magnetic phase transition leads to magnetocaloric effect. In particular, a natural table-like $-\Delta S_M$ and a very large refrigerant capacity (RC) value of 94.4 J/kg was observed in a field change of 0–10.5 kOe for $Gd_2Mo_2O_7$ due to two successive magnetic transitions at ~78 and ~10 K. These notable magnetocaloric properties make the $Gd_2Mo_2O_7$ a potential candidate for low-field Ericsson-cycle magnetic refrigeration in the low temperature range.

1. Introduction

Magnetic refrigeration based on magnetocaloric effect (MCE) 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 [1,2]. 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 [1,2]. The total entropy of a magnetic system mainly contains magnetic entropy and lattice entropy. Lattice entropy is given by a function of Debye temperature (θ_D) and temperature (T) according to Debye approximation and rises rapidly as T or T/θ_D increases. For the temperature range above 15 K, lattice entropy grows comparable to or larger than the magnetic entropy and consequently reduces the efficiency of adiabatic demagnetization cooling process in the Carnot magnetic refrigeration cycle since the large heat capacity of lattice functions as a heat load [3]. Whereas an ideal magnetic Ericsson-cycle is composed of four processes with perfect regeneration as described in detail in Ref. [4] in which two kinds of isomagnetic field processes (varying temperature) in strong and weak magnetic fields replace the two adiabatic processes in the magnetic Carnot cycle. The effect of lattice entropy is perfectly removed since the lattice entropy change can be fully counteracted by two kinds of isomagnetic field processes which are performed within the same temperature range [4]. Therefore, ideal magnetic Ericsson-cycle is highly efficient for magnetic refrigeration above 15 K [3,4]. Actually, a real magnetic Ericsson cycle does not possess perfect regeneration, which consequently lower its efficiency [5]. The more a real magnetic Ericsson cycle accesses to ideal magnetic Ericsson-cycle, the higher its efficiency is. This requires magnetic refrigerant with a constant magnetic entropy change (ΔS_M) between two kinds of isomagnetic field processes of the material in the temperature range of the operation of the thermodynamic Ericsson magnetic refrigeration cycle (known as table-like MCE) [6,7]. Only two kinds of materials can meet this requirement: (1) the material with the successive magnetic phase transition; (2) manufacturing composite materials undergoing adjacent phase transitions. The typical examples are $Gd_{0.54}Er_{0.46}NiAl$ compound [8] and the mixture of $ErAl_2$, $HoAl_2$, and $(Ho_{0.5}Dy_{0.5})Al_2$ [4], respectively.

Cubic pyrochlore molybdates $R_2Mo_2O_7$ (R = rare earth or Y ion) consist of R (so-called A sites) sublattice and Mo (so-called B sites) sublattice, and the two sublattices are displaced by a half unit cell [9]. Recently, pyrochlore molybdates $R_2Mo_2O_7$ have been greatly focused on due to their multiple magnetic, electronic ground states

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and other physical properties varied with the rare earth ion radius. One of the attractive characters in $R_2Mo_2O_7$ is the transition from ferromagnetic metallic (FMM) state (for R = Gd, Sm and Nd) to spin-glass insulating (SGI) state (for R = Yb-Tb and Y) by decreasing radius of the rare earth ions, R sites substituting or imposing the external pressure [10–15]. In this paper we investigated the magnetic properties and phase transition-induced magnetocaloric effects of cubic $R_2Mo_2O_7$ (R = Er, Dy, Gd and Y) polycrystalline.

2. Experiment

Polycrystalline samples of $R_2Mo_2O_7$ (R = Er, Dy, Gd and Y) were prepared by standard solid-state reaction method by thoroughly mixing the stoichiometric reactants of Er_2O_3 (General Research Institute for Nonferrous Metals (GRINM), 99.95 wt%), Dy_2O_3 (GRINM, 99.99 wt%), Gd_2O_3 (GRINM, 99.99 wt%) and MoO_2 (Alfa Aesar, purity above 99 wt%). The mixtures were pressed into pellets and sintered at 1673 K for 24 h under the flowing argon atmosphere with one intermediate grinding. The powder X-ray diffractometer (Bruker AXS D2 PHASER diffraction system with combined Cu-Kα radiation, λ = 1.54184 Å) was employed to identify the phase purity and crystalline structure at room temperature in continuous PSD fast scan mode (θ–2θ scan type between 10° and 90°). The unit cell parameters were refined using Rietica software. The dc magnetic measurements were carried out for $R_2Mo_2O_7$ (R = Er, Dy, Gd and Y) powders (~3 mg for R = Er, Dy, Gd and ~ 40 mg for R = Y) in magnetic fields up to 70 kOe at the rate of 0.1 kOe/min and at temperatures between 2 K and 300 K on a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum design, MPMS-XL).

Table 1
Structural parameters after the Rietveld refinement of XRD data for $Er_2Mo_2O_7$, $Dy_2Mo_2O_7$, $Gd_2Mo_2O_7$ and $Y_2Mo_2O_7$ at room temperature.

R	$r(R^{3+})$ (Å)*	a(Å)	R_p	R_{wp}	χ^2	Ground state
Er	1.004	10.238(0)	15.30	7.525	0.823	SGI
Y	1.019	10.255(3)	7.421	6.357	0.483	SGI
Dy	1.027	10.287(1)	6.082	7.292	0.442	SGI
Gd	1.053	10.373(3)	5.525	6.806	0.336	FMM

* Taken from [17].

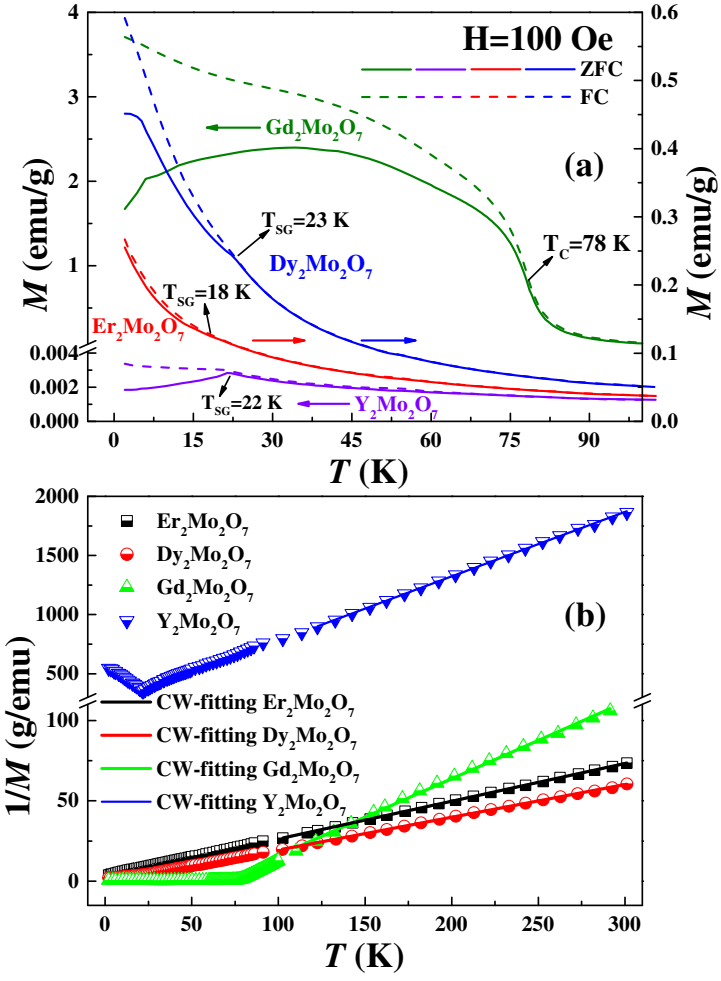

Fig. 1. Temperature dependence of ZFC and FC magnetizations (a) and the ZFC inverse magnetizations fitted to the Curie-Weiss law (b) of $Er_2Mo_2O_7$, $Dy_2Mo_2O_7$, $Gd_2Mo_2O_7$ and $Y_2Mo_2O_7$ under 0.1 kOe.