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Influences of La and Ce doping on giant magnetocaloric effect of EuTiO*

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Giant reversible magnetocaloric effects and magnetic properties in $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) are investigated. The antiferromagnetic ordering of pure $EuTiO_3$ can significantly change to be ferromagnetic as substitution of La ($x = 0.1$) and Ce ($x = 0.1$) ions for Eu^{2+} ions. The values of $-\Delta S_M$ and RC are evaluated to be 10.8 J/(kg·K) and 51.8 J/kg for $Eu_{0.9}Ce_{0.1}TiO_3$ and 11 J/(kg·K) and 39.3 J/kg for $Eu_{0.9}La_{0.1}TiO_3$ at a magnetic field change of 10 kOe, respectively. The large low-field enhancements of $-\Delta S_M$ and RC can be attributed to magnetic phase transition. The giant reversible MCE and large RC suggest that $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) compounds could be promising materials in low temperature and low magnetic field refrigerants.

Keywords: magnetocaloric effect, magnetic entropy change, magnetic phase transformation

PACS: 75.30.Sg, 65.40.gd, 75.30.Kz **DOI:** 10.1088/1674-1056/27/1/017501

1. Introduction

Compared with the traditional gas compression/expansion refrigeration technology, the magnetic refrigeration (MR) technology based on the magnetocaloric effect (MCE) possesses advantages, such as high efficiency and energy saving, being green, stable, and reliable. The basic mechanism of the MCE is magneto-thermodynamic phenomenon of a magnetic material, which is evaluated from the isothermal magnetic entropy change ($-\Delta S_M$) and the adiabatic temperature change (ΔT) in a changing magnetic field.[1] The researches of magnetic refrigeration materials mainly concentrate in the areas of room temperature and low temperature, such as $LaCaMnO_3$,[2] $Gd_5Si_2Ge_2$,[3] $MnFeX$ (X = P, As, Si, Ge),[4] and Ni–Mn–Ga,[5,6] RCo_2,[7,8] RNi_2 (R = Gd, Dy, Ho, Er),[9–11] $RCoAl$ (R = Tb, Dy, Ho),[12,13] etc.

The low-temperature magnetocaloric materials are very important in the field of hydrogen liquefaction and air science. In the past few years, the rare earth intermetallic compounds have become a main research subject. Recently, in the rare earth oxides, the intermetallic oxide has become a new research hotspot such as $DyMnO_3$,[14] Gd_2NiMnO_6,[15] $HoMn_2O_5$,[16] etc. The perovskite oxide RMO_3 (R = rare earth; M = transition metal) system has a strong coupling between spin, lattice, orbital and charge degrees of freedom. It shows unique optical, electrical, magnetic and excellent magnetoresistance effect, catalytic performance, and magnetocaloric effect.

The $EuTiO_3$ exhibits G-type AFM order, and the modulated magnetic ground state with antiferromagnetic (AFM) and ferromagnetic (FM) phase co-existence has been reported in $EuTiO_3$, based on the first-principles calculation.[17,18] There are two corresponding mechanisms here. One is the super-exchange mechanism that leads to antiferromagnetic (AFM) exchange, and the other is the indirect exchange mechanism that leads to ferromagnetic (FM) exchange. What is more, the $EuTiO_3$ has strong spin lattice coupling. The competition between AFM and FM phases is a delicate balance, so the magnetic state can be easily switched from AFM to FM, such as a increasing with the lattice constant relaxed or c increasing, with a fixed.[19] The $EuTiO_3$ has taken the center stage of research due to the observations of the giant magnetocaloric (GMC) and giant magneto-electric (GME) effects around its AFM ordering temperature of Eu spins ($T_N \sim 6$ K).[20–24] It has been shown that a small number of (Ba and Sr) substituteions at the Eu site or (Cr and Nb) substitution at the Ti site drive the system into an FM metallic state. Rubi reported the magnetoelectric effect in $Eu_{1-x}Ba_xTiO_3$ for $0.1 < x < 0.9$.[20] Mo *et al.* reported the giant magnetocaloric effects in $Eu_{1-x}Sr_xTiO_3$ and $EuTi_{1-x}Cr_xO_3$.[21,22] Roy *et al.* reported the $-\Delta S_M$ in magnetoelectric $EuTi_{0.85}Nb_{0.15}O_3$

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compound.[23]

In the present paper, we show the great enhancements of both $-\Delta S_{\rm M}$ and RC upon applying moderate field changes (1 T) to $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) compounds with respect to $EuTiO_3$. The values of $-\Delta S_{\rm M}$ and RC are calculated to be 10.8 J/kg·K and 51.8 J/kg for $Eu_{0.9}Ce_{0.1}TiO_3$ and 11 J/kg Kand 39.3 J/kg for $Eu_{0.9}La_{0.1}TiO_3$ at magnetic field change of 10 kOe, respectively The reversible giant low-field MCE and RC make them an excellent candidate for the applications in a cooling device

2. Experiments

The $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) samples were prepared by the sol-gel method. Stoichiometric mixtures of europium oxide (Eu_2O_3), butyl phthalate (Ti $(OC_4H_9)_4$) and ceria (CeO_2) or lanthanum oxide (La_2O_3), were dissolved in 25 mL of nitric acid (HNO_3 8 mol/L). Then ethylene glycol ($C_2H_6O_2$) was added as a dispersant, and stirred for an hour. Next, the solution was heated at 90 °C until a dry gel was obtained. Finally, the samples were pretreated at 900 °C for two hours in air to obtain $Eu_2Ti_2O_7$ and $Eu_{1-x}R_xTiO_3$ (R = La, Ce), and these materials were annealed at 1100 °C in 10% H_2 and 90% Ar atmosphere for 3 h.

The structures of the $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) were determined by x-ray diffraction (XRD) with Cu Kα radiation. The magnetic properties of the samples were measured by physical property measurement system (PPMS).

3. Results and discussion

Figure 1(a) shows the XRD patterns of $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$(R = La, Ce) single crystal at 295 K. They crystallize into the cubic perovskite structure with $Pm3m$ space group. The lattice parameters are determined respectively to be $a = 3.908(2)$ Å for $EuTiO_3$, $a = 3.910(4)$ Å for $Eu_{0.9}Ce_{0.1}TiO_3$ and $a = 3.911(5)$ Å for $Eu_{0.9}La_{0.1}TiO_3$ with $R_{\rm wp} < 15\%$ and $\rm CHI^2 < 10\%$ by the Rietveld technique using GSAS program shown in Table 1. In oxides, oxygen defects are almost inevitable, which approve to be intrinsic defects, and believed to have a critical influence on their properties.[25] The oxygen content in $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) samples is determined by the thermogravimetric analysis (TGA). The perovskite $EuTiO_3$ is obtained by pyrochlore $Eu_2Ti_2O_7$ under the hydrogen reduction reaction: the reduction of Eu^{3+} to Eu^{2+}. Hence, the $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) can oxidize $Eu_2Ti_2O_7$ and $R_2Ti_2O_7$(R = La, Ce) through the following reaction:

$$2Eu_{0.9}R_{0.1}TiO_{3+\delta} + (0.5-\delta)O_2 \rightarrow 0.9Eu_2Ti_2O_7 + 0.1R_2Ti_2O_7. \quad (1)$$

The oxygen nonstoichiometric parameter δ of perovskite phase can be calculated from the weight gain of the sample during oxidation on heating in air from the following formula:

$$\frac{0.9\mathrm{M}(Eu_2Ti_2O_7) + 0.1\mathrm{M}(R_2Ti_2O_7)}{2\mathrm{M}(EuTiO_3) + \delta\mathrm{M}O_2} = 100\% + \Delta m\%. \quad (2)$$

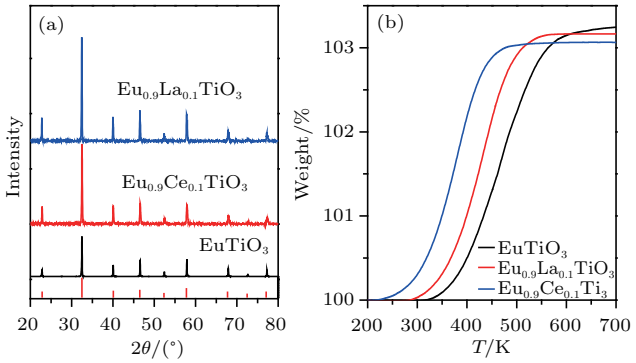


Fig. 1. (color online) (a) XRD patterns of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce). (b) Thermogravimetry (TGA) trace of $Eu_{0.9}Ce_{0.1}TiO_3$ and $Eu_{0.9}La_{0.1}TiO_3$.

Table 1. Values of $-\Delta S_{\rm M}$ and RC under the field changes of 10 kOe and 20 kOe for $EuTiO_3$, $Eu_{0.9}Ce_{0.1}TiO_3$, and $Eu_{0.9}La_{0.1}TiO_3$.

Samples	Lattice parameters	$\Delta H = 1$ T		$\Delta H = 2$ T	
		$-\Delta S_{\rm M}^{\rm max}$ /J·kg^{-1}·K^{-1}	RC /J·kg^{-1}	$-\Delta S_{\rm M}^{\rm max}$ /J·kg^{-1}·K^{-1}	RC /J·kg^{-1}
$EuTiO_3$	3.908	9.8	27	21.1	98
$Eu_{0.9}Ce_{0.1}TiO_3$	3.910	10.8	51.8	18.8	114.6
$Eu_{0.9}La_{0.1}TiO_3$	3.911	11.0	39.3	19.6	103.4

Figure 1(b) shows the TGA results of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) samples, obtained by measuring the weight gain in a temperature range from room temperature to 700 K in air at a rate of 5 K/min. The δ values for $EuTiO_3$, $Eu_{0.9}La_{0.1}TiO_3$, and $Eu_{0.9}Ce_{0.1}TiO_3$ are calculated to be -0.006, 0.012, and 0.027, from the weight gain of $\Delta m = 3.245\%$, $\Delta m = 3.162\%$ and $\Delta m = 3.062\%$, respectively. The negative sign suggests a slight vacancy of oxygen in $EuTiO_3$ and the positive sign refers to a slight excess of oxygen in the $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce), so the compositions can be written as $Eu_{0.9}La_{0.1}TiO_{3.012}$ and $Eu_{0.9}Ce_{0.1}TiO_{3.027}$. The small oxygen excess may be caused by cationic deficiency at the Eu sites according to valence state compensation, but they are smaller than the theoretical values ($Eu_{0.9}La_{0.1}TiO_{3.05}$ and $Eu_{0.9}Ce_{0.1}TiO_{3.05}$). It indicates that there are oxygen defects in the $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce).

Figure 2(a) shows the zero-field cooling (ZFC) and field cooling (FC) of the $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) compounds under an applied magnetic field of 0.1 kOe. The $EuTiO_3$ exhibits a significant AFM order, and phase transition from AFM to PM at $T_{\rm N} = 5.7$ K with no thermal hysteresis. However, the M–T curves for $Eu_{0.9}La_{0.1}TiO_3$ and $Eu_{0.9}Ce_{0.1}TiO_3$ exhibit FM order and the ferromagnetic Curie temperature increases from $T_{\rm C} = 5$ K and 5.5 K, respectively. They may be because

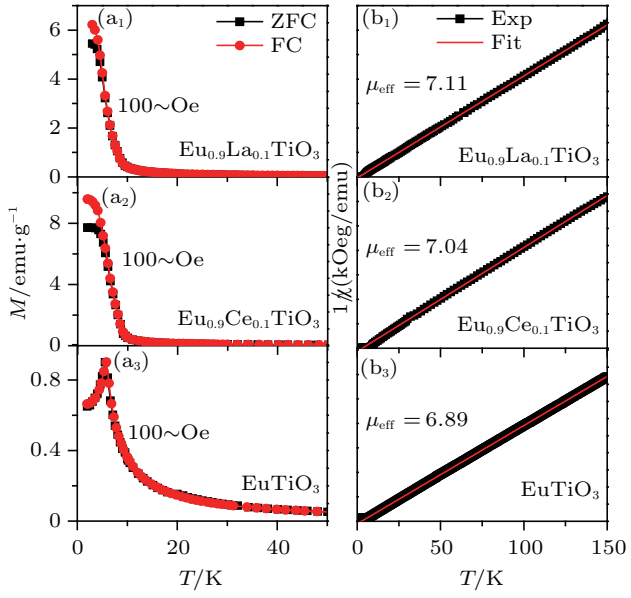


Fig. 2. (color online) (a) Temperature dependence of ZFC and FC magnetizations of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) under a magnetic field of 0.1 kOe; (b) the temperature dependence of inverse susceptibility fitting to the Curie–Weiss law.

the increase of the lattice constant leads to the magnetic transition from AFM to FM as Ce($x = 0.1$) and La($x = 0.1$) substitute for Eu. The microscopic origin of the strong spin-lattice coupling in $EuTiO_3$ is derived from the superexchange mechanism between Eu^{2+} 4f spins via the 3d states of nonmagnetic Ti^{4+} ions along the a, b-plane diagonal, and the AFM phase also comes from a superexchange mechanism.[26,27] Therefore, the change of lattice constant affects the superexchange mechanism, thereby changing the magnetic state. The ZFC and FC curves for $Eu_{0.9}La_{0.1}TiO_3$ and $Eu_{0.9}Ce_{0.1}TiO_3$ exhibit completely reversible behaviors as observed usually in the second-order phase transition, but an obvious bifurcation appears below the transition temperature. The spin-glass systems, ferromagnetic materials with high anisotropy, and materials with competing magnetic interactions all can lead to thermomagnetic irreversibility.[28] Figure 2(b) shows the temperature dependence of inverse susceptibility ($1/\chi$ vs. T) and the Curie–Weiss fitting of the $1/\chi$ (T). The values of effective magnetic moment ($\mu_{\rm eff}$) 6.89$\mu_{\rm B}$ for $EuTiO_3$ 7.04$\mu_{\rm B}$ for $Eu_{0.9}Ce_{0.1}TiO_3$, and 7.11$\mu_{\rm B}$ for $Eu_{0.9}La_{0.1}TiO_3$ can be obtain based on the $C_{\rm m}$, which belongs to a reasonable region ($\mu = (7 \pm 1)\mu_{\rm B}$).[29]

Figure 3 shows the isothermal magnetization curves at temperatures between $T = 2$ K and $T = 28$ K under the applied magnetic fields ranging from 0 to 50 kOe. For $EuTiO_3$, the isothermal magnetization curve increases linearly at low magnetic field and tends to be saturate with increasing magnetic field below Nair temperature ($T_{\rm N}$) as shown in Fig. 3(a). In the low fields, the magnetization value at low temperature is smaller than at the higher temperature as shown in Fig. 4(a_1). These are typical AFM natures. With the La^{3+} and Ce^{3+} ions instead of Eu^{2+} ions, the $M(H)$ data of magnetization isotherms increase rapidly at low magnetic fields and tend to be saturate under strong magnetic fields below $T_{\rm C}$ as shown in Figs. 3(b) and 3(c). The magnetization curves do not intersect

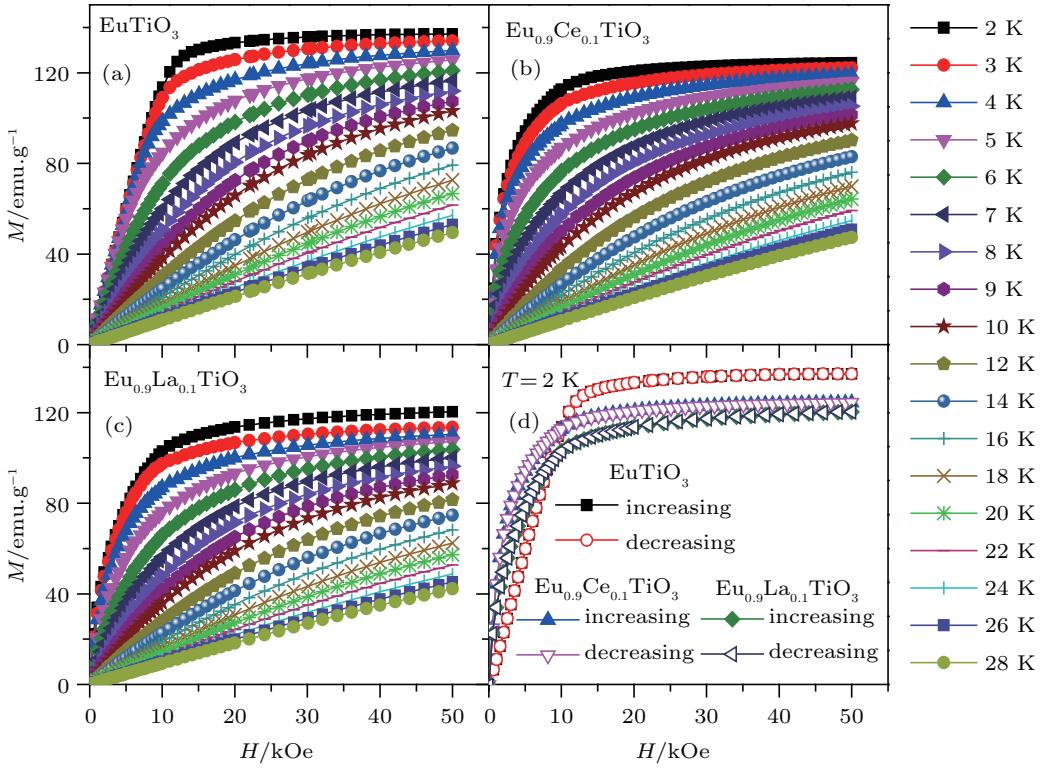


Fig. 3. (color online) (a)–(c) Magnetization isotherms of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) collected in a temperature range of 2–28 K; (d) field dependence of magnetization data for increasing and decreasing field model at 2 K.

in Figs. 4(a$_2$)–4(a$_3$). These are typical FM natures, which suggest magnetic transition from AFM to FM for the substitution of Eu for Ce and La. Figure 3(d) shows the increase and decrease model of isothermal magnetization curve at 2 K, indicating no magnetic hysteresis. The magnetic moments of per Eu atom, respectively, are 6.07μ_B for $EuTiO_3$, 6.12μ_B for $Eu_{0.9}Ce_{0.1}TiO_3$, and 5.92μ_B for $Eu_{0.9}La_{0.1}TiO_3$ at 5 T: these values are smaller than the expected values for Eu^{2+} ion, which is likely to be attributed to the crystalline electric field.

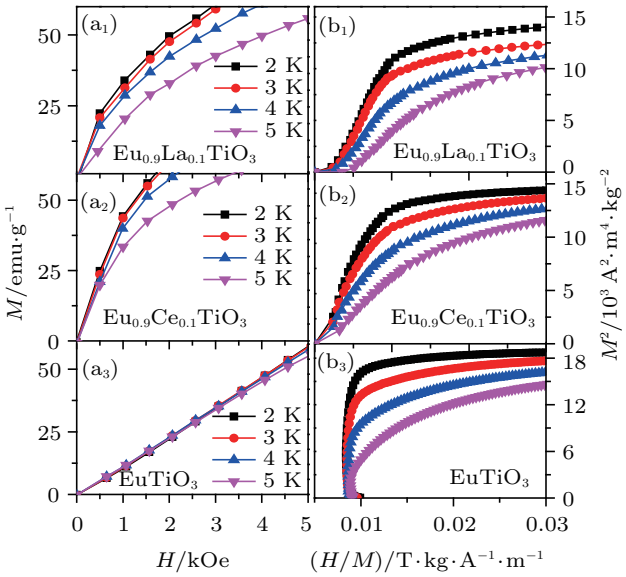


Fig. 4. (color online) (a) Magnetization isotherms of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) collected at 2, 3, 4, and 5 K under low field; (b) Arrott plot of the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) at 2, 3, 4, 5, and 6 K under low field.

Based on the Banerjee criterion,[30] when the slope of the Arrott plot is negative, the magnetic transition is expected to be of the first order; on the contrary, it will be of the second order. Figure 4(b) shows the curves of M^2 for H/M. The negative slope of $EuTiO_3$ implies the first order below T_N. However, the Arrott plots of $Eu_{0.9}La_{0.1}TiO_3$ and $Eu_{0.9}Ce_{0.1}TiO_3$ suggest that the phase transition is of the second order for the positive slope.

The values of ΔS_M can be calculated by the magnetization isotherms data from the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$.[31] Figure 5(a) shows the temperature dependence of the ΔS_M for $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) under magnetic fields. The values of $-\Delta S_M$ increase with applied magnetic field increasing. The values of $-\Delta S_M^{max}$ are 40.7 J/(kg·K) for $EuTiO_3$ 33.8 and 34.4 J/(kg·K) for $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) under magnetic field change 0–50 kOe, respectively. The decrease of $-\Delta S_M^{max}$ is attributed to the decreasing of the Eu^{2+} with doping La ($x = 0.1$) and Ce ($x = 0.1$) respectively. In order to further confirm the magnetic transition after Eu has been substituted by La ($x = 0.1$) and Ce ($x = 0.1$), the values of $-\Delta S_M$ are calculated under low magnetic field change as shown in Fig. 5(b). The negative values of $-\Delta S_M$ for $EuTiO_3$ compound suggest the AFM order below T_N. However, when Eu is substituted by La ($x = 0.1$) and Ce ($x = 0.1$), the positive values of $-\Delta S_M$ below transition temperature indicate the AFM–FM magnetic transition.

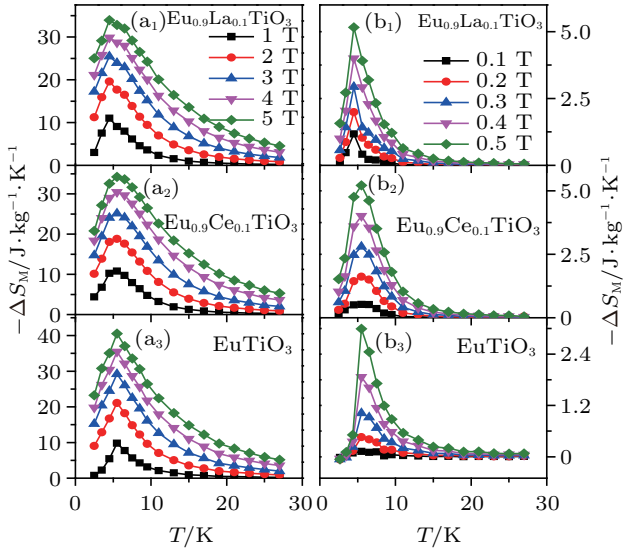


Fig. 5. (color online) (a) Temperature dependence of $-\Delta S_M$ for the $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) under different magnetic fields; (b) $-\Delta S_M$ under low magnetic field.

Figure 6 shows the values of $-\Delta S_M$ for $EuTiO_3$, $Eu_{0.9}La_{0.1}TiO_3$, and $Eu_{0.9}Ce_{0.1}TiO_3$ changing with temperature under magnetic field changes of 10 kOe and 20 kOe. Under the magnetic field change of 10 kOe, the values of $-\Delta S_M^{max}$ are 9.8 J/(kg·K), 10.8 J/(kg·K), and 11 J/(kg·K) for $EuTiO_3$, $Eu_{0.9}La_{0.1}TiO_3$ and $Eu_{0.9}Ce_{0.1}TiO_3$, respectively. The values of $-\Delta S_M$ increase below the transition temperature with doping La ($x = 0.1$) and Ce ($x = 0.1$), which may be caused

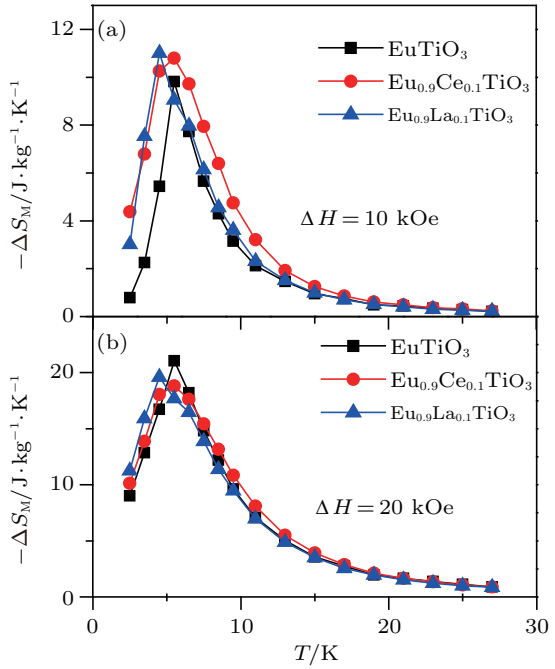


Fig. 6. (color online) Temperature dependence of $-\Delta S_M$ for $EuTiO_3$ and $Eu_{0.9}R_{0.1}TiO_3$ (R = La, Ce) under magnetic fields of (a) 10 kOe and (b) 20 kOe.

by the magnetic transition AFM–FM. Another key parameter is RC= $\int_{T_1}^{T_2} |\Delta S_M| dT$.[31] Table 1 shows the RC values of $EuTiO_3$, $Eu_{0.9}La_{0.1}TiO_3$, and $Eu_{0.9}Ce_{0.1}TiO_3$, which are calculated under 10 kOe and 20 kOe of the magnetic field. The values of RC are evaluated to be 51.8 J/kg and 114.6 J/kg for $Eu_{0.9}Ce_{0.1}TiO_3$ and 39.3 J/kg and 103.4 J/kg for $Eu_{0.9}La_{0.1}TiO_3$, respectively under 10 kOe and 20 kOe of the magnetic field. Compared with the RC value of $EuTiO_3$ the RC is significantly increased with La ($x = 0.1$) and Ce ($x = 0.1$). The MCE and RC values of the $Eu_{0.9}R_{0.1}TiO_3$ ($R =$ La, Ce) compounds are improved, which are an excellent candidate for cryogenic magnetic refrigeration. We hope that our study will further promote the research on magnetocaloric and relevant cooling devices.

4. Conclusions

Giant reversible magnetocaloric effects and magnetic properties in $Eu_{0.9}La_{0.1}TiO_3$ and $Eu_{0.9}Ce_{0.1}TiO_3$ are investigated. When part of Eu^{2+} ions are substituted by La^{3+} and Ce^{3+} ions, there is a slight excess of oxygen in the $Eu_{0.9}R_{0.1}TiO_3$ ($R =$ La, Ce), which could compensate for the mismatch of chemical valence and increase the lattice constant. It leads to the magnetic ground state switched from AFM to FM. The large low-field enhancements of $-\Delta S_M$ and RC are 10.8 J/(kg·K) and 51.8 J/kg for $Eu_{0.9}La_{0.1}TiO_3$ and 11 J/(kg·K), and 39.3 J/kg for $Eu_{0.9}Ce_{0.1}TiO_3$ for the case of magnetic field change of 10 kOe while pure $EuTiO_3$ counterpart has $-\Delta S_M = 9.8$ J/(kg·K) and RC = 27 J/kg. The increases of $-\Delta S_M$ and RC can be attributed to magnetic phase transition. The giant reversible MCE and large RC suggest that the compounds could be promising materials in low temperature and low magnetic field refrigerants. Our study shows that the MCE and RC are improved, which will promote further research on magnetocaloric and relevant cooling devices.

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