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Observation of giant magnetocaloric effect in $EuTi_{1-x}Cr_xO_3$

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ABSTRACT

The magnetic properties and magnetocaloric effect in $EuTi_{1-x}Cr_xO_3$ ($x = 0, 0.02, 0.04, 0.1$) compounds are investigated. The magnetic ground state (AFM) of pure $EuTiO_3$ can be significantly changed to be FM with slight Cr-doping. A giant reversible MCE and large RC in $EuTi_{1-x}Cr_xO_3$ compounds were observed. The value of $-\Delta S_M{}^{max}$ reaches to 40.3 J/kg K for $EuTiO_3$ under the magnetic field change of 5 T. Especially, under the magnetic field changes of 1 and 2 T, the values of $-\Delta S_M{}^{max}$ are evaluated to be 12.5 and 22.5 J/Kg K and the maximum values of RC are 64 and 127 J/kg, without magnetic and thermal hysteresis for $EuTi_{1-x}Cr_xO_3$ system. Therefore, the giant reversible MCE and large RC make the $EuTi_{1-x}Cr_xO_3$ compounds could be considered as a good candidate material for low-temperature and low-field magnetic refrigerant.

1. Introduction

In recent years, magnetic refrigerator (MR) is becoming a promising cooling tool for both cryogenic and room temperature applications due to its high efficiency, compactness and environmental friendly compared to the conventional gas refrigeration [1–3]. Magnetocaloric (MCE) material is one of the critical parts for the development of MR since the efficiency scales directly with the magnetic entropy change ($-\Delta S_M$) for moderate magnetic fields. Numerous materials exhibiting giant $-\Delta S_M$ around their transition temperatures have been found. For application near room temperature, there are $Gd_5Si_2Ge_2$ [4], $LaFe_{13-x}Si_x$ [5], $MnAs_{1-x}Sb_x$ [6] and $MnFeP_{0.45}As_{0.55}$ [7] et al. On the other hand, at low temperature, mainly to be applied to gas liquefaction as helium, hydrogen and natural gas and potential applications in space science [8], such as, TmGa [9], TmCuAl [10], $ErMn_2Si_2$ [11], HoCuSi [12], $ErCr_2Si_2$ [13] and HoCoSi [14] et al. Additionally, if a sufficient MCE of material can be achieved upon application of low magnetic fields (e.g., less than 2 T), it is feasible to design a refrigeration cycle using permanent magnets. Therefore, it is desirable to search for materials that have giant MCE with zero or inappreciable thermal and field hysteresis loss under low field ($\Delta H \leq 2$ T).

Cubic perovskite $EuTiO_3$, which exhibits G-type AFM order and quantum paraelectric (PE) behavior, has attracted considerable attention since the discovery of its large magnetoelectric (ME) effect [15,16]. In $EuTiO_3$, the nearest–neighbor interaction between Eu spins has two possible exchange mechanisms. A superexchange mechanism between Eu^{2+} 4f spins via the 3d states of nonmagnetic Ti^{4+} ions which leads to AFM exchange, and an indirect exchange via the Eu 5d states, which results in FM exchange [17,18]. The competition between the AFM superexchange and an indirect ferromagnetic exchange leads to a delicate balance between AFM and FM phases, which explain by Akamatsu et al. through first-principles calculations based on a hybrid Hartree-Fock density functional approach [17]. What's more, the $EuTiO_3$ has strong spin-lattice coupling, the magnetic ground state can be switched from AFM to FM, when the lattice constant changed [19]. Additionally, in oxides, oxygen vacancies have been approved to be intrinsic defects and are believed to have a critical impact on their properties [20]. Coey et al. reported that oxygen vacancies play a key role in obtaining room temperature FM in non-magnetic oxide systems [21,22]. Alho et al. [23] theoretically predicted an anisotropic magnetocaloric effect of the same order of magnitude of the usual

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magnetocaloric effect for antiferromagnetic systems using Hamiltonian model. The anisotropic magnetic properties come from the anti-parallel alignment of the magnetic sites and can be optimized depending on the magnetic field change. Km Rubi report the magnetic entropy change in magnetoelectric $Eu_{1-x}Ba_xTiO_3$ for $0.1 < x < 0.9$ [24].

In the present paper, a giant reversible MCE and large RC in $EuTi_{1-x}Cr_xO_3$ compounds were observed. Our results suggest $EuTi_{1-x}Cr_xO_3$ could be expected to have effective applications in low temperature magnetic refrigeration.

2. Experiments

The samples of $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) were synthesized by a simple method. Details: Europia (Eu_2O_3) was dissolved in nitric acid (HNO_3 8 mol/L) and stirred for about half an hour. Next, tetra-butyl titanate ($Ti(OC_4H_9)_4$) and chromic nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) in stoichiometric proportions was added into the Europium nitrate solution and stirred for about an hour. Then, Glycol ($C_2H_6O_2$) in 1:1 M ratio with respect to the metal nitrates was added as a dispersant. Stirring was continued until a homogeneous solution. The solution was kept at 90 °C for 5 h to form the dried gel. Finally, samples were first pre-treated at 400 °C in air for about 4 h, and then the temperature was slowly increased to 800 °C and kept an hour to remove carbon. The final powders were annealed at 900 °C in 5% H_2 and 95% Ar atmosphere for 2 h to obtain $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) materials.

The structures of the $EuTi_{1-x}Cr_xO_3$ were investigated by X-ray diffraction (XRD) with Cu Kα radiation at room temperature. Magnetizations were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) obtained by thermal treatment at 900 °C for 2 h in 5% H_2 and 95% Ar. The x-ray powder diffraction pattern confirmed the single-phase nature of the compound (no XRD peaks arising from impurities such as $Eu_2Ti_2O_7$, Eu_2O_3, and TiO_2 were detected), and crystallizing in the cubic perovskite structure (space group 221). The lattice parameters were determined to be a = 3.908 (2) Å, with Rwp = 14.6% and $CHI^2 = 2.42$ for $EuTiO_3$ by the Rietveld technique using GSAS program shown in Fig. 1. With increasing the Cr concentration the lattice parameters were decreased as shown in the inset of Fig. 1. The diffraction peaks just slightly move to the right, because the size Cr^{3+} ion (~0.52 Å) is smaller than Ti^{4+} (~0.61 Å), associated with the doping of Cr at Ti site.

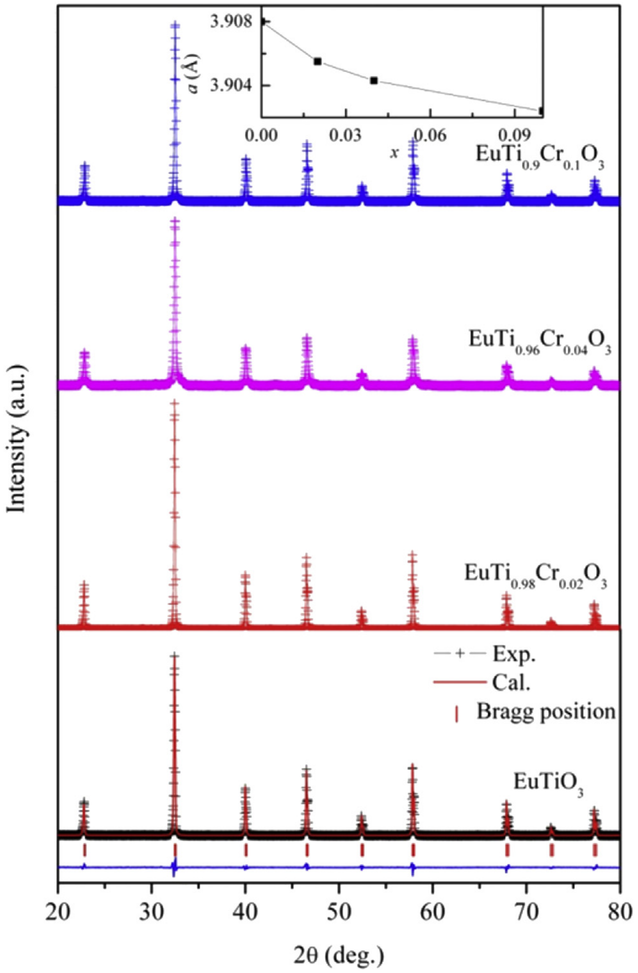

Fig. 1. XRD patterns of the $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1). The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The short vertical lines indicate the angular positions of the Bragg peaks of $EuTiO_3$. The lower curve shows the difference between the observed and calculated intensity. Inset: the lattice parameters change with the Cr concentration.

Fig. 2 shows the zero-field-cooling (ZFC) and field-cooling (FC) temperature dependence of magnetization for $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) compounds under an applied magnetic field of 0.01 T. The values of M are enormous difference as doping Cr, it refers to the fact that the dominant magnetic order in the x = 0.0 sample is AFM type, while it is not the case for the $x = 0.02$, $x = 0.04$ and $x = 0.1$. The peak feature of these M–T curves for $EuTiO_3$ results from the antiferromagnetic (AFM) to paramagnetic (PM) magnetic transition at $T_N = 5.7$ K, induced by Eu^{2+} spins ordering below T_N, which is identical with the G-AFM transition point of previous reported [15,25,26]. For $EuTi_{1-x}Cr_xO_3$ ($x = 0.02$, 0.04, 0.1) compounds, the M–T curves exhibit a ferromagnetic (FM)-PM transition and the Curie point $T_C = 5.2$ K for $x = 0.02$, $T_C = 6.2$ K $x = 0.04$ and $T_C = 9.7$ K for $x = 0.1$ respectively. Furthermore, the ZFC and FC curves for $EuTiO_3$ are well reversible, indicating no thermal hysteresis as shown in Fig. 2. However, for $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) samples, there is an obvious bifurcation between the ZFC curve and FC curve at the low temperature region, indicates the nature of spin-glass-like behaviors. Owing to this magnetic frustration behavior, the spin-glass-like surface layer would contribute to the difference between the ZFC and FC curves as well as the cusp-like peak for the ZFC case [18].

On the other hand, we notice that the reciprocal magnetic susceptibility (χ_m^{-1}) of these compounds follow the Curie–Weiss law $\chi_m^{-1} = (T-\theta_p)/C_m$ above 10 K. Here θ_p is the PM Curie temperature and C_m is the Curie–Weiss constant. The effective magnetic moments (μ_{eff}) are obtained based on the value of C_m. With increasing the content of Cr, the values of μ_{eff} are decreased as shown in the inset of Fig. 2. But the values of μ_{eff} also belong to a reasonable region ($\mu = 7 \pm 1\ \mu_B$), which are found to be consistent to the free ion as previously reported [27]. The localized 4f moments on the Eu^{2+} ($S = 7/2$, $L = 0$) sites order, and the Eu^{2+} $4f^7$ band is a reason for narrowing of the optical band gap in the title compounds [28]. The slightly decrease may be attributed to generate some Eu^{3+} ions, for the $EuTi_{1-x}Cr_xO_3$ ($x = 0.02$, 0.04, 0.1) samples, in order to compensate the heterovalent, the oxygen vacancies and some Eu^{3+} ions are necessarily produced as substitution of Cr^{3+} ions for Ti^{4+}ions.

Fig. 3 shows the isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T under

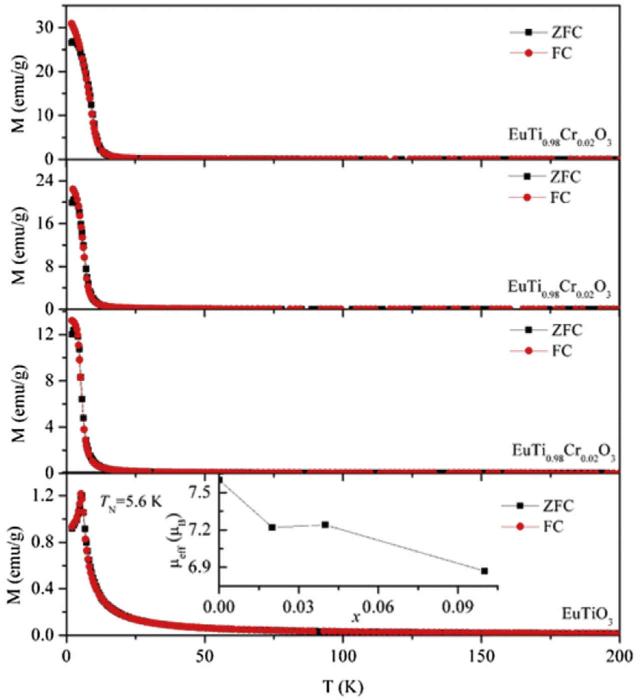

Fig. 2. Temperature dependences of ZFC and FC magnetizations of $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) under the magnetic field of 0.01 T.

different temperature. The M (H) data show a linearly increase at considerably low fields and in strong magnetic fields the magnetization isotherm tends to saturate in $EuTiO_3$ below T_N, which exhibit typical AFM nature as shown in Fig. 3(a). For $EuTi_{1-x}Cr_xO_3$ (x = 0.02, 0.04, 0.1), the M (H) data show a rapid increase at considerably low fields and in strong magnetic fields the magnetization isotherm tends to saturate below T_C, which exhibit typical FM nature, as shown Fig. 3(b–d). Now, let us explain the phenomenon. In $EuTiO_3$, the localized nature of the 4f electrons, the nearest–neighbor interaction between Eu spins origins from two possible exchange mechanisms: a superexchange mechanism of AFM exchange and an indirect exchange of FM exchange [17,18]. The delicate balance between AFM and FM phases is decided by the competition between the AFM superexchange and indirect ferromagnetic exchange [17]. In $EuTi_{1-x}Cr_xO_3$ system, in order to compensate the heterovalent, the oxygen vacancies are necessarily produced at O^{2-} as substitution of Cr^{3+} ions for Ti^{4+}ions. The oxygen vacancies results in spin-polarized Ti^{4+} ions, which mediated an FM coupling between the local Eu 4f spins. Weiwei Li et al. demonstrated that the magnetic ordering of oxygen-deficient $EBTO_{3-\delta}$ thin films has been changed from AFM to FM, oxygen vacancies are effective to manipulating magnetic ordering in multiferroic materials [29]. Therefore, the FM behavior of $EuTi_{1-x}Cr_xO_3$ ($x = 0.02$, 0.04, 0.1) should be ascribed to the incorporation of Cr^{3+} ions.

No magnetic hysteresis can be observed from the field dependences of magnetization data collected during both increasing and decreasing field model at 2 K in the Fig. 4. Additionally, it is worth noting that with increasing the content of Cr^{3+} ions, the magnetization data is decreased as shown in the inset of Fig. 4. May be, when Cr^{3+} ions substitute Ti^{4+}ions, not only the oxygen vacancies are necessarily produced in order to compensate the heterovalent, but also some Eu^{2+} ions are inevitably changed to Eu^{3+} ions (no magnetic moments) with increasing the content of Cr^{3+} ions.

As is well known, the ΔS_M value can be calculated either from the magnetization isotherms by using the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H dH$ [30]. Fig. 5 shows the values of $-\Delta S_M$ for $EuTi_{1-x}Cr_xO_3$ (x = 0, 0.02, 0.04, 0.1) as a function of temperature under different magnetic field. The value of $-\Delta S_M$ is found to increase monotonically with applied magnetic field increasing. Under the magnetic field change from 0 to 5 T, the maximum values of $-\Delta S_M$ ($-\Delta S_M^{max}$) reach 40.3 J/kg K for $EuTiO_3$, 40 J/kg K for $EuTi_{0.98}Cr_{0.02}O_3$, 36.2 J/kg K for $EuTi_{0.96}Cr_{0.04}O_3$ at 5.5 K and 30 J/kg K for $EuTi_{0.9}Cr_{0.1}O_3$ around the liquid helium temperature. However, The value of $-\Delta S_M$ is increased under low magnetic

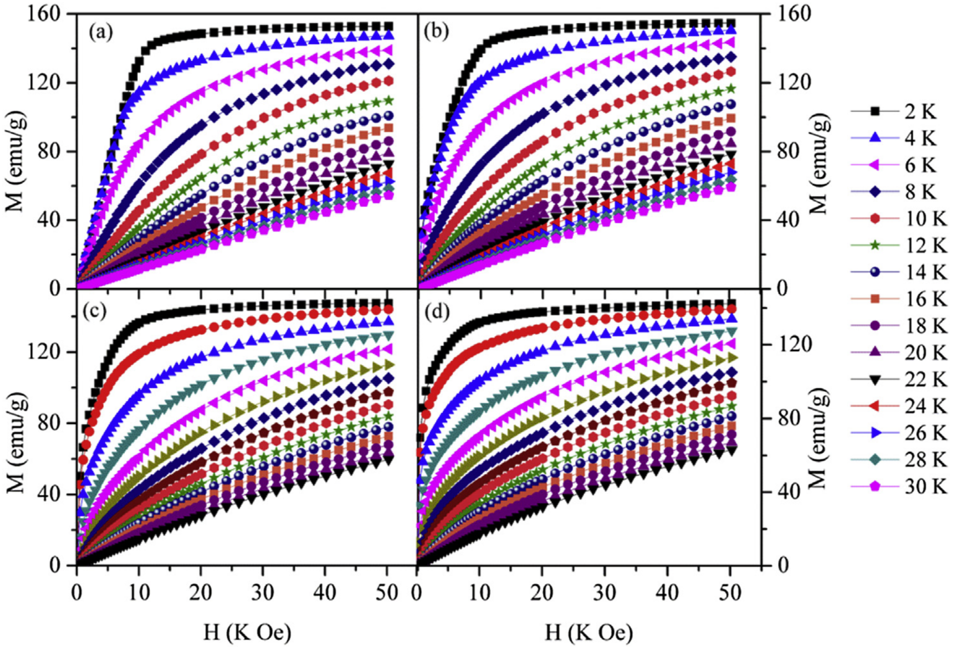

Fig. 3. Magnetization isotherms of $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) collected in the temperature range of 2–30 K (a: $x = 0$; b: $x = 0.02$; c: $x = 0.04$; d: $x = 0.1$).

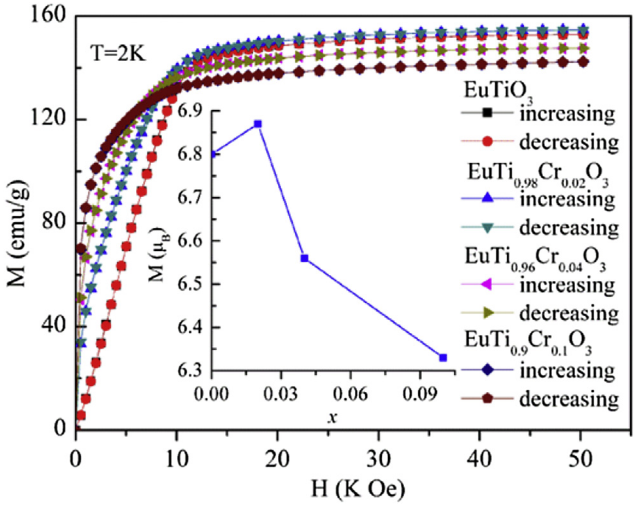

Fig. 4. The field dependences of magnetization data both increasing and decreasing field model at 2 K. Inset: The μ_B–x curve.

field, due to the magnetic ground state switched from AFM to FM as substitution of Cr^{3+} ions for Ti^{4+}ions. The value of $-\Delta S_M^{max}$ reaches 12.5 J/kg K at 5.5 K for $EuTi_{0.98}Cr_{0.02}O_3$ under a magnetic field change 0–1 T. Meanwhile, the Eu^{3+} also decreases the value of $-\Delta S_M$ in the $EuTi_{0.9}Cr_{0.1}O_3$ ($-\Delta S_M^{max} = 9.8$ J/kg) compounds due to some Eu^{2+} ions are changed to Eu^{3+} ions. Especially, Under the magnetic field changes of 2 T, the values of $-\Delta S_M^{max}$ are 22.3 J/kg K, 22.5 J/kg K, 20.3 J/kg K and 16.8 J/kg K for $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1), respectively. It is much larger than those of most potential magnetic refrigerant materials in a similar magnetic transition temperature under the same field change (2 T), such as TmCuAl (17.2 J/kg K) [10], $ErMn_2Si_2$ (20 J/kg K) [11] and $ErRu_2Si_2$ (11 J/kg K) [14] et al. Refrigerant capacity (RC) is another important parameter, which is a measure of how much heat can be transferred between the cold and the hot sinks in one ideal refrigeration cycle.

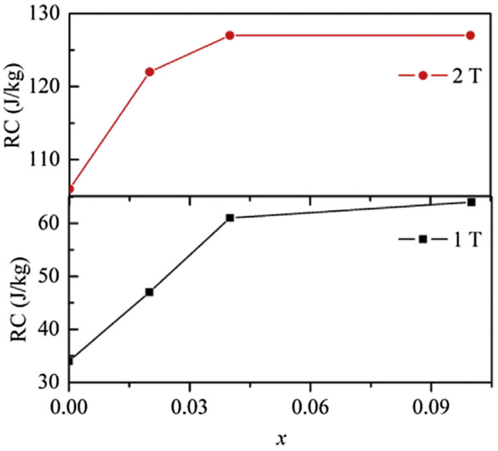

Fig. 6. The content of Cr^{3+} dependences of RC for $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) under magnetic field 1 and 2 T.

The RC, defined as a cooling capacity of $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures at half maximum of the peak taken as the integration limits [28]. By using this method, the RC values of the $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) are evaluated under the magnetic field changes of 1 and 2 T, the maximum values of RC are 64 and 127 J/kg as shown Fig. 6. The good results (giant $-\Delta S_M$ and large RC) and lower cost than intermetallic compounds make the $EuTi_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.04, 0.1) compounds be a very attractive candidate material for use in a magnetic refrigerator working in low temperature.

4. Conclusion

A giant low field reversible MCE has been observed in $EuTi_{1-x}Cr_xO_3$ compounds. Under the magnetic field changes of 2 T, the values of $-\Delta S_M^{max}$ and RC are evaluated to be 22.5 J/Kg K and 127 J/

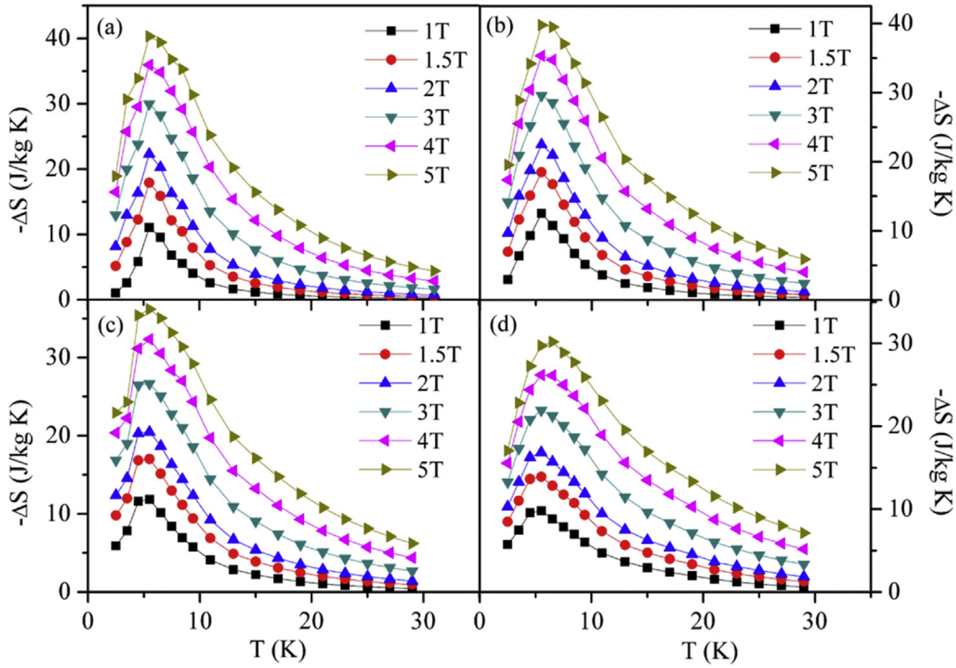

Fig. 5. Temperature dependences of magnetic entropy change for $EuTi_{1-x}Cr_xO_3$under different magnetic field (a: $x = 0$; b: $x = 0.02$; c: $x = 0.04$; d: $x = 0.1$).

kg, without magnetic and thermal hysteresis for $EuTi_{1-x}Cr_xO_3$ system. Especially, the giant values of $-\Delta S_M^{max}$ (more than 10 J/Kg K) is obtained for a relatively low field change of 0–1 T. The AFM ordering of pure $EuTiO_3$ can be significantly changed to be FM as slight substitution of Cr^{3+} ions for Ti^{4+}ions, which could increase the values of $-\Delta S_M$ and RC. But the Eu^{3+} ions lead to a negative impact for MCE. In a word, the results suggest the $EuTi_{1-x}Cr_xO_3$ compounds could be considered as a good candidate material for low-temperature and low-field magnetic refrigerant.

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