Observation of giant magnetocaloric effect under low magnetic fields in $EuTi_{1-x}Co_xO_3$*

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The magnetic properties and magnetocaloric effect (MCE) in $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) compounds have been investigated. When the Ti^{4+} ions were substituted by Co^{2+} ions, the delicate balance was changed between antiferromagnetic (AFM) and ferromagnetic (FM) phases in the $EuTiO_3$ compound. In $EuTi_{1-x}Co_xO_3$ system, a giant reversible MCE and large refrigerant capacity (RC) were observed without hysteresis. The values of $-\Delta S_M^{\max}$ were evaluated to be around 10 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ for $EuTi_{0.95}Co_{0.05}O_3$ under a magnetic field change of 10 kOe. The giant reversible MCE and large RC suggests that $EuTi_{1-x}Co_xO_3$ series could be considered as good candidate materials for low-temperature and low-field magnetic refrigerant.

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

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1. Introduction

In recent years, the development of magnetic refrigeration technology based on the magnetocaloric effect (MCE) has provided a new choice for traditional gas refrigeration with great significance in saving energy and environment protection.[1] In varying magnetic fields, the MCE is the magneto–thermodynamic phenomenon of a magnetic material evaluated from the isothermal magnetic entropy change ($-\Delta S_M$) and the adiabatic temperature change (ΔT). A number of materials exhibiting giant $-\Delta S_{\rm M}$ have been found near transition temperatures, such as $LaCaMnO_3$,[2] $MnAs_{1-x}Sb_x$,[3] MnFeX (X = P, As, Si, Ge),[4] La (Fe, M)$_{13}$ (M = Si, Al), Ni–Mn–Ga alloy new materials,[5,6] and so on. In addition, it is also valuable to study at low temperatures in the fields of hydrogen liquefaction and air science.

In the past few years, the research of large MCE materials at low temperatures mainly focused on the rare earth intermetallic compounds and the classical materials: $R{\rm Al}_2$,[7–10] RNi (R = Gd, Ho, Er),[11] RMAl (M = Ni, Co, Cu),[12,13] etc. Currently, oxide has become a new research hotspot. The spin degree of freedom, the orbital degree of freedom, and the coupling and interaction between lattice degrees of freedom in the perovskite $R{\rm TiO}_3$ (R = rare earth) system, make the $R{\rm TiO}_3$ system show many peculiar physical phenomena. In $EuTiO_3$, Ti is tetravalent ($3d^0$) and Eu is divalent with a large spin moment ($S = 7/2$) due to the stable $4f^7$ electronic configuration. The cubic perovskite $EuTiO_3$ has aroused widespread concern with the G-type AFM order, large magneto–electric (ME) effect and the quantum paraelectric (PE) behavior.[14,15] In $EuTiO_3$, there may be two exchange mechanisms based on the first-principles calculation of the nearest neighbor Eu interaction. One is the super-exchange mechanism that leads to antiferromagnetic (AFM) exchange, which is between Eu^{2+} 4f spins via the 3d states of nonmagnetic Ti^{4+} ions. The other is the indirect exchange mechanism, which leads to ferromagnetic (FM) exchange via the Eu 5d states.[16,17] The competition of AFM and FM phases is a delicate balance. The magnetic ground state can be switched from AFM to FM due to its strong spin lattice coupling in the $EuTiO_3$, when the lattice constants were changed such as a increased with the lattice constant relaxed or c increased with a fixed.[18] The delicate change may cause an important effect on the magnetic entropy. It has been shown that a small amount of (Ba and Sr) substitution at the Eusite or (Cr and Nb) substitution at the Ti site drives the system into a FM metallic state. For example, Rubi reported the magnetic entropy change in magnetoelectric $Eu_{1-x}Ba_xTiO_3$ for $0.1 < x < 0.9$.[19] Mo *et al.* reported the giant magnetocaloric effect in $Eu_{1-x}Sr_xTiO_3$ and $EuTi_{1-x}Cr_xO_3$.[20,21] Roy *et al.* reported the $-\Delta S_M$ in magnetoelectric $EuTi_{0.85}Nb_{0.15}O_3$ compound.[22]

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In this paper, with Ti to be substituted by Co, $EuTi_{1-x}Co_xO_3$ compounds exhibit a giant reversible MCE. At the same time, it is possible that Co with a certain magnetic moment will impact the nature of the sample. The results show that $EuTi_{1-x}Co_xO_3$ processes an effective application prospect at low temperature magnetic refrigeration.

2. Experiments

The samples of $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) were synthesized by the sol–gel method. In the first step, a stoichiometric amount of europium oxide (Eu_2O_3), butyl phthalate ($Ti(OC_4H_9)_4$) and cobalt nitrate ($Co(NO_3)_2$), were dissolved into 25 mL of nitric acid (HNO_3 8 mol/L). Then, the ethylene glycol was added as a dispersant and then continually stirred for about 1 h to make it completely dissolved. In the second step, the solution was heated at 90 °C until a dry gel was obtained. In the third step, the samples were pretreated at 400 °C for 30 min, then cooled down and ground into powder. In the fourth step, the samples were heated 900 °C for 2 h in air to remove carbon. Finally, the samples were annealed at 1100 °C in 10% H_2 and 90% Ar atmosphere for 3 h to obtain $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) materials.

The structures of the $EuTi_{1-x}Co_xO_3$ were determined by x-ray diffraction (XRD) with Cu $K\alpha$ radiation at room temperature, and then the magnetic properties of the samples were analyzed by a physical property measurement system (PPMS).

3. Results and discussion

Figure 1 shows the XRD patterns of the $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) samples. No other impurities can be found such as $Eu_2Ti_2O_7$, Eu_2O_3, and TiO_2 and crystallizing in the cubic perovskite structure (space group 221). With the increase of Co content, the diffraction peaks slightly move to the left due to the size of Co^{2+} (~ 0.745 Å) which is bigger than Ti^{4+} (~ 0.605 Å) as shown in the inset of Fig. 1. Eu^{3+} or oxygen vacancy is easliy formed due to mismatch of valence (Co^{2+} ion and Ti^{4+} ion). The oxygen vacancy is favorable for the magnetic transition.[23]

Figure 2 shows the function of magnetization versus temperature in the cases of zero-field cooling (ZFC) and field cooling (FC) of the $EuTi_{1-x}Co_xO_3$ compounds under an applied magnetic field of 0.1 kOe. The $EuTiO_3$ is clearly AFM type and has phase transition from AFM to PM at $T_N = 5.7$ K with no thermal hysteresis. The $T_N = 5.7$ K (AFM transition temperature) is similar to the previous results.[24,25] With the increase of Co doping content ($x = 0.025$, $x = 0.05$, $x = 0.075$, and $x = 0.1$), the ZFC and FC curves of the samples have an obvious bifurcation below the transition temperature, which may be the nature of spin-glass-like behaviors.

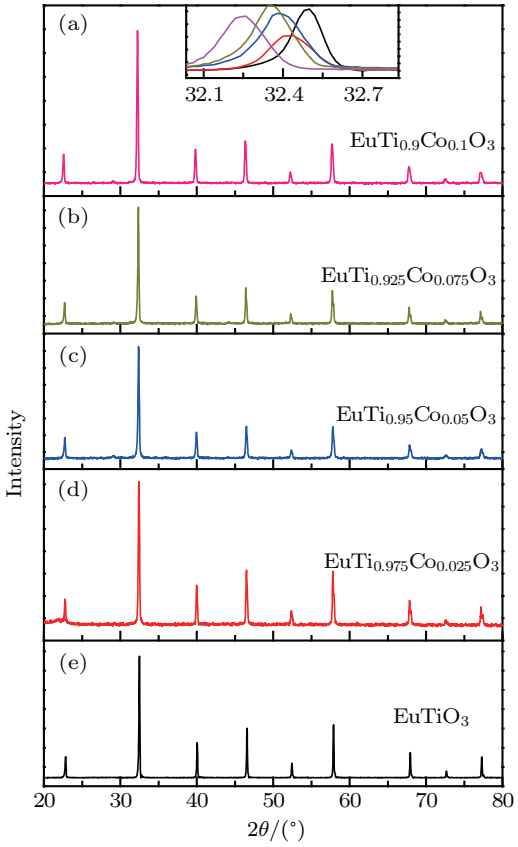


Fig. 1. (color online) The XRD patterns of the $EuTi_{1-x}Co_xO_3$ ($x =$ 0.1 (a), 0.075 (b), 0.05 (c), 0.025 (d), 0 (e)). Inset: the corresponding local amplification figure.

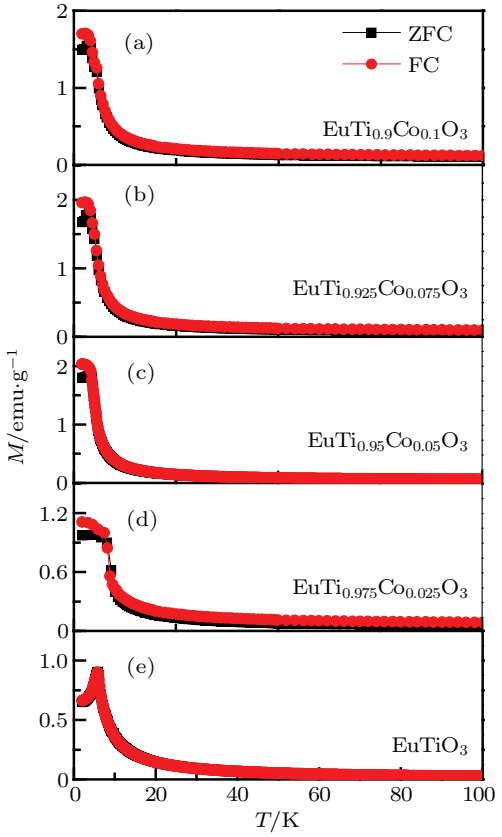


Fig. 2. (color online) Temperature dependences of ZFC and FC magnetizations of $EuTi_{1-x}Co_xO_3$ ($x = 0.1$ (a), 0.075 (b), 0.05 (c), 0.025 (d), 0 (e)) under the magnetic field of 0.1 kOe.

In Fig. 3, the magnetization data of the magnetic field increases coincide with the decreases at 2 K, indicating no magnetic hysteresis; there is a beneficial effect on the magnetic entropy and cooling capacity of the material without magnetic hysteresis. The inset of Fig. 3 shows the magnetic moment calculated per Eu^{2+} atom in $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) compounds for 50 kOe at 2 K. With doping Co^{2+} ions, the magnetic moment decreases from 6.1μ_B ($x = 0$) to 5.5μ_B ($x = 0.025$) and from 6.0μ_B ($x = 0.05$) to 5.6μ_B ($x = 0.075$, 0.1). It is possible that some Eu^{2+} ions were converted to Eu^{3+} ions (without magnetic moments), leading to the decrease of total magnetic moments as the Co^{2+} ion content increases. On the other hand, the Eu^{2+} ions did not convert to Eu^{3+} ions, but produced the oxygen vacancies. However, Co^{2+} ions have a certain magnetic moment, the exchange may decrease the total magnetic moment which comes from Eu^{2+}4f spins and the Co^{2+}3d spins (further research is needed to confirm the exchange mechanism between Eu^{2+}4f spins and the Co^{2+}3d spins).

Figure 4 shows the isothermal magnetization curves from 2 K to 5 K with an increment of 1 K at 0–50 kOe applied magnetic field. In Fig. 4 ($x = 0$), the high temperature magnetization is greater than the value at low temperatures under low fields. On the contrary, the situation is the opposite in higher fields. It is consistent with the AFM ordering of the compound below T_N.[12] However, there are no intersections among the curves as shown in Fig. 4 ($x = 0.025$, 0.05, 0.075, 0.1), which can be seen in the FM magnetic ground state. The FM coupling gradually increases, and slightly dominates in the delicate balance between AFM and FM phases, when the Ti is substituted by Co. Figure 5 shows the Arrott curve (the curve of M^2 for H/M in the case of isothermal) of $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1). When the slope of the curve is negative, the magnetic transition is the first order, whereas it will be of second order based on the Banerjee criterion.[26] The $EuTiO_3$ is the first order with the negative slope of the Arrott plots below T_N. The results of $EuTi_{1-x}Co_xO_3$ ($x = 0.025$, 0.05, 0.075, 0.1) suggest that the phase transition is second order for the positive slope of the Arrott plot.

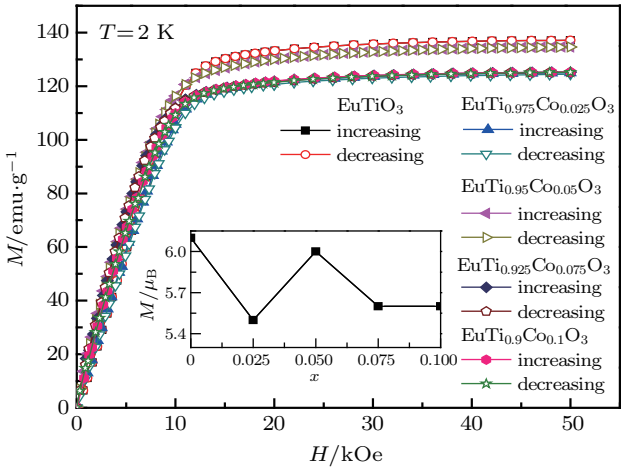


Fig. 3. (color online) The field dependences of magnetization data both increasing and decreasing field model at 2 K. Inset: the μ_B–x curve.

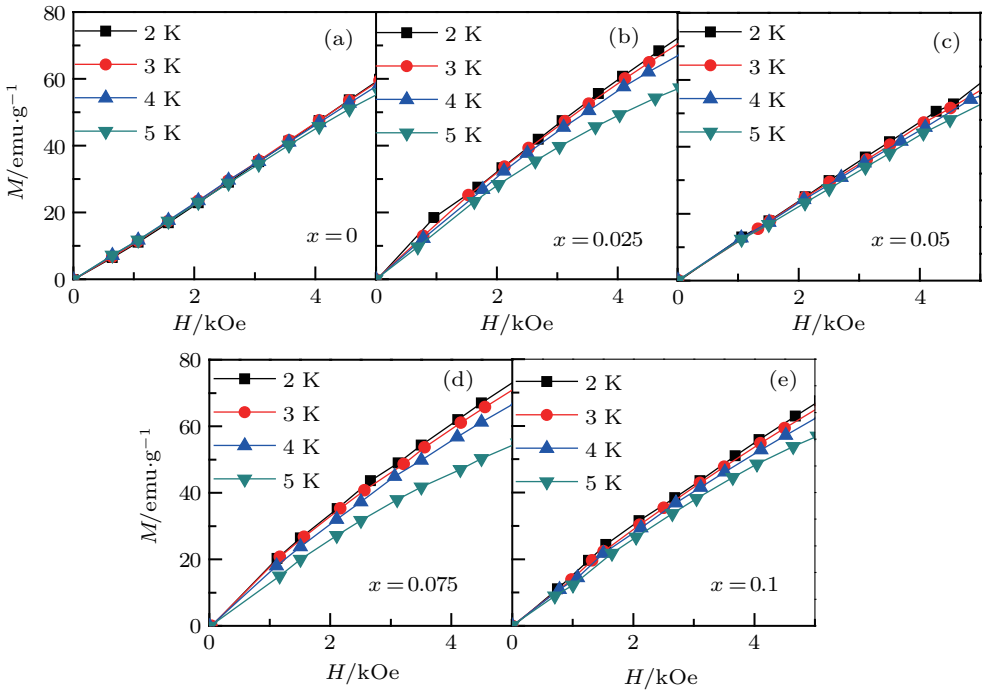


Fig. 4. (color online) Magnetization isotherms of $EuTi_{1-x}Co_xO_3$ compounds collected at 2, 3, 4 and 5 K under low fields ($x = 0$ (a); $x = 0.025$ (b); $x = 0.05$ (c); $x = 0.075$ (d); x =0.1(e)).

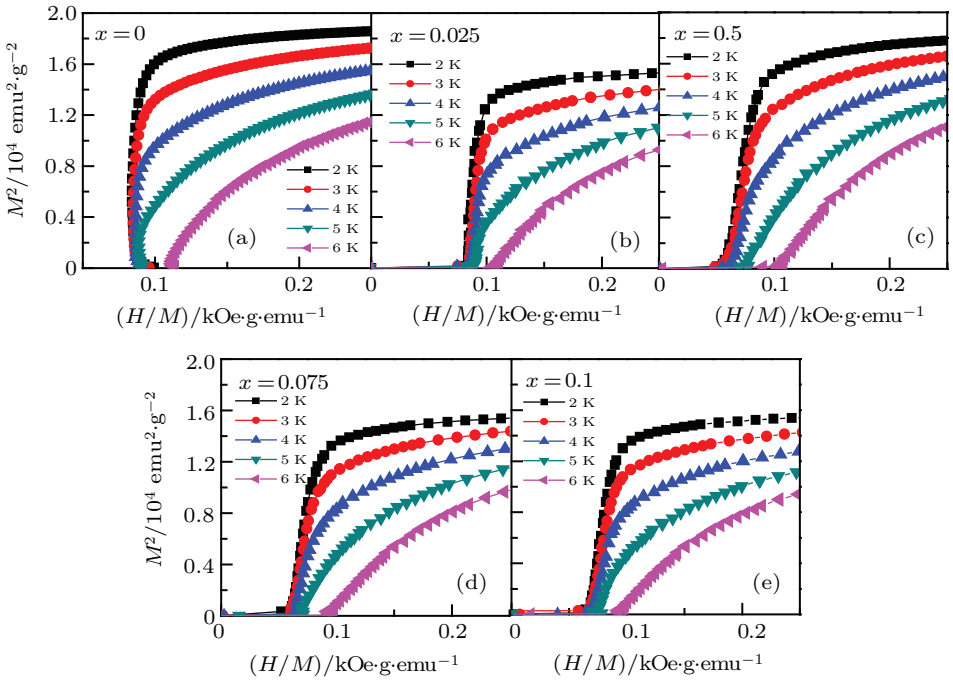


Fig. 5. (color online) The Arrott plot of the $EuTi_{1-x}Co_xO_3$ compounds at 2, 3, 4, 5, and 6 K under low fields ($x = 0$ (a); $x = 0.025$ (b); $x = 0.05$ (c); $x = 0.075$ (d); x =0.1(e)).

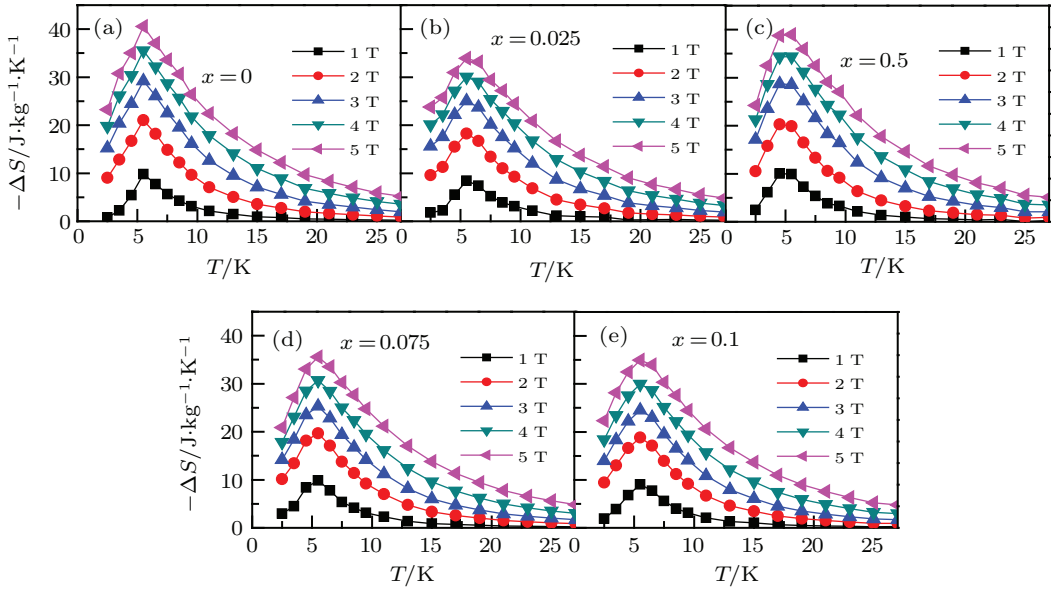


Fig. 6. (color online) Temperature dependences of magnetic entropy change for $EuTi_{1-x}Co_xO_3$ under different magnetic fields ($x =$ 0 (a); $x = 0.025$ (b); $x = 0.05$ (c); $x = 0.075$ (d); $x = 0.1$ (e)).

The values of ΔS_M can be calculated by the magnetization isotherms using the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$.[27] Figure 6 shows the values of $-\Delta S_M$ in the samples of $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) under different magnetic fields and different temperatures. The $-\Delta S_M^{\max}$ for $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) reach 40.5 J·kg^{-1}·K^{-1}, 33.9 J·kg^{-1}·K^{-1}, 38.9 J·kg^{-1}·K^{-1}, 35.6 J·kg^{-1}·K^{-1}, and 34.9 J·kg^{-1}·K^{-1}, respectively. The values of $-\Delta S_M$ monotonically increase as the applied magnetic field increases and the maximum values of $-\Delta S_M(-\Delta S_{\mathrm{M}}^{\max})$ are obtained near the magnetic transition temperature. Figure 7 shows the values of $-\Delta S_M$ of $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) as a function of the temperature with the magnetic field changed from 10 kOe, 20 kOe to 50 kOe. Since the value of $-\Delta S_M$ below the transition temperature is increased with the increase of the doping Co ion content, it can be obviously observed that the value of $-\Delta S_M$ below the transition temperature is significantly increased, under a mag-

netic field change 0–10 kOe, the value of $-\Delta S_M^{\max}$ reaches 10 J·kg^{-1}·K^{-1} for $EuTi_{0.95}Co_{0.05}O_3$. Meanwhile, the values of $-\Delta S_M$ are almost the same under a magnetic field change 0–20 kOe and 0–50 kOe. Therefore, the decrease of magentic moment caused by Co and Eu interactions in the large magnetic field is disadvantageous. It is larger and more comparable than those of most potential magnetic refrigerant materials in a similar magnetic transition temperature under the same field change (20 kOe), such as TmCuAl (17.2 J·kg^{-1}·K^{-1}),[28] $ErMn_2Si_2$ (20 J·kg^{-1}·K^{-1}),[29] $ErRu_2Si_2$ (11 J·kg^{-1}·K^{-1}).[30]

RC is a measure of how much heat can be transferred between the cold and the hot sinks in an ideal refrigeration cycle, which is another important parameter. The RC, defined as a cooling capacity of RC $= \int_{T_1}^{T_2} |\Delta S_M| \mathrm{d}T$, where T_1 and T_2 are the temperatures at half maximum of the peak taken as the integration limits.[31] The RC values of $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) were calculated under 10 kOe, 20 kOe, and 50 kOe of the magnetic field, as shown in Table 1. The maximum values of RC reach 38.5 J·kg^{-1} and 296.1 J·kg^{-1} for $EuTi_{0.95}Co_{0.05}O_3$ under the magnetic field changes of 10 kOe and 50 kOe, respectively. Therefore, $Eu_{1-x}Co_xTiO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) compounds appear to be promising materials for low temperature refrigeration.

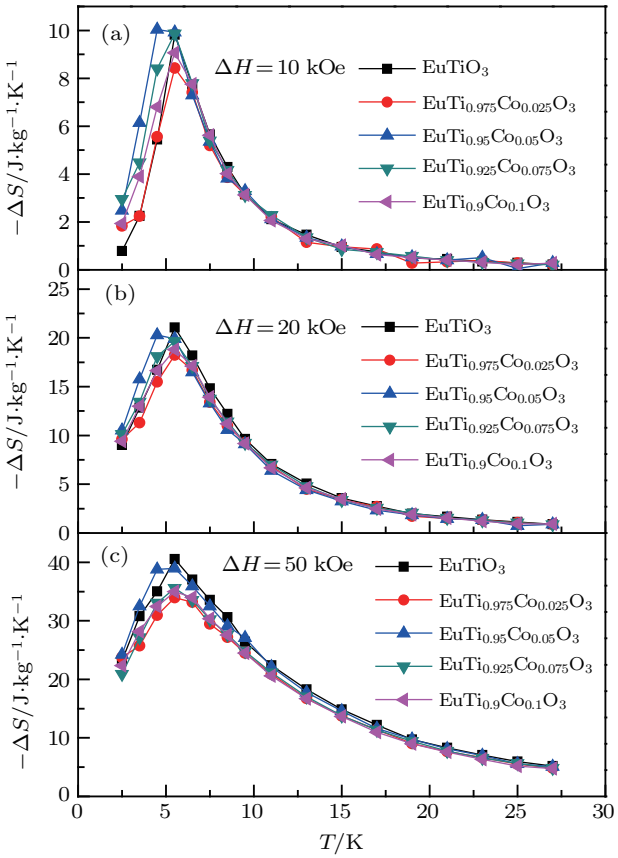


Fig. 7. (color online) Temperature dependences of magnetic entropy change for $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) under magnetic field 10 kOe (a), 20 kOe (b), and 50 kOe (c).

Table 1. The content of Co^{3+} dependences of RC for $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) under magnetic fields of 10 kOe, 20 kOe, and 50 kOe.

Samples	$\Delta H = 1$ T		$\Delta H = 2$ T		$\Delta H = 5$ T	
	$-\Delta S_M^{\max}$/ J·kg^{-1}·K^{-1}	RC/ J·kg^{-1}	$-\Delta S_M^{\max}$/ J·kg^{-1}·K^{-1}	RC/ J·kg^{-1}	$-\Delta S_M^{\max}$/ J·kg^{-1}·K^{-1}	RC/ J·kg^{-1}
$EuTiO_3$	9.8	27	21.1	98	40.5	291.5
$EuTi_{0.975}Co_{0.025}O_3$	8.4	30.6	18.2	96.0	33.9	274.7
$EuTi_{0.95}Co_{0.05}O_3$	10.0	38.5	20.3	99.2	38.9	296.1
$EuTi_{0.925}Co_{0.075}O_3$	9.8	36.7	19.7	100.1	35.6	278.5
$EuTi_{0.9}Co_{0.1}O_3$	9.1	34.8	18.8	98.7	34.9	275.2

4. Conclusion

A giant reversible MCE in $EuTi_{1-x}Co_xO_3$ ($x = 0$, 0.025, 0.05, 0.075, 0.1) compounds was observed under low fields. Due to the larger size of Co^{2+} ion (~ 0.745 Å) than that of Ti^{4+} ion (~ 0.605 Å), the diffraction peaks showed a left shift after Co^{2+} ion doping. The $EuTiO_3$ exhibited the G-type AFM, while the delicate balance between AFM and FM phases in the $EuTiO_3$ compound was changed, when the Ti^{4+} ions were substituted by Co^{2+} ions in the compound. Under a low magnetic field change (0–10) kOe, the values of $-\Delta S_M^{\max}$ achieved 10 J·kg^{-1}·K^{-1} and the RC reached 38.5 J·kg^{-1} for $EuTi_{0.95}Co_{0.05}O_3$. In conclusion, the experimental results show that $EuTi_{1-x}Co_xO_3$ compounds can be considered as promising materials for low-temperature and low-field magnetic refrigerant.

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