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Observation of giant magnetocaloric effect in $EuTiO_3$

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ABSTRACT

A giant reversible MCE and large RC in $EuTiO_3$ compound were observed. Under the magnetic field changes of 5 T, the maximum value of $-\Delta S_M$ is evaluated to be 40.4 J/kg K, and the value of RC is 328 J/kg in $EuTiO_3$ compound. Especially, for the magnetic field changes of 1 and 2 T, the large values of $-\Delta S_M$ are 11 and 22.3 J/Kg K without magnetic and thermal hysteresis are also obtained, respectively. The giant MCE is attributed to field-induced AFM-FM transition and FM-PM transition. Therefore, the giant reversible MCE and large RC make the $EuTiO_3$ compounds could be considered as a good candidate material for low-temperature and low-field magnetic refrigerant.

1. Introduction

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) has attracted much attention due to its high energy-efficiency, compactness and environmental benignness compared to the conventional gas refrigeration [1–3]. Researchers have paid much attention to this field and explored a range of potential magnetic materials with large magnetocaloric effect (MCE). The search of magnetic refrigerants in industrial applications near room temperature has been paid much attention. Numerous ferromagnetic materials exhibiting giant $-\Delta S_M$ around their transition temperatures have been found, such as $LaFe_{13-x}Si_x$[3,4], $MnAs_{1-x}Sb_x$[5], $MnFeP_{0.45}As_{0.55}$[6] and $Gd_5Si_2Ge_2$[7] et al. On the other hand, the magnetic refrigeration also have drawn attention at low temperature, mainly to be applied to gas liquefaction as helium, hydrogen and natural gas and potential applications in space science [8]. Many studies reported the low field giant MCEs and large RC together with small or zero hysteresis loss materials, such as, TmGa [9], TmCuAl [10], $ErMn_2Si_2$[11], HoCoAl [12], $ErCr_2Si_2$[13] and $ErRu_2Si_2$[14] et al.

$EuTiO_3$ is one of the $ATiO_3$ perovskite members which presents quantum paraelectricity and G-type antiferromagnetic (AFM) order of the Eu sublattice. It as a potential multiferroic material has received considerable interests due to its rich physical properties [15–20]. To our knowledge, the magnetocaloric properties of $EuTiO_3$ are not to particularity investigate yet since rare earth can always contribute large magnetic moment. In the present paper, we report on the magnetic properties and giant reversible ΔS_M and large refrigerant capacity (RC) under a low field with negligible thermal and field hysteresis loss in $EuTiO_3$ compound.

2. Experiment

Europia (Eu_2O_3), and tetra-butyl titanate ($Ti(OC_4H_9)_4$) in stoichiometric proportions were dissolved in nitric acid (HNO_3) respectively. Then, these two solutions were mixed and stirred for about an hour. Glycol ($C_2H_6O_2$) in 1:1 M ratio with respect to the metal nitrates was added and stirred for half an hour to the solution as a dispersant. The solution was kept at 90 °C for 6 h to form the dried gel. Then, the obtained gel was heated in a furnace at 400 °C in air for about 4 h and annealed at 800 °C in air for an hour to remove carbon. The final powder was annealed at 900 °C in 5% H_2 and 95% Ar atmosphere for 2 h to obtain $EuTiO_3$ materials.

The structure of the $EuTiO_3$ was investigated by X-ray diffraction (XRD) with Cu Kα radiation at room temperature. It indicates a cubic crystal structure described by the prototype perovskite Pm3m space group and the lattice parameters were determined to be $a=b=c=3.905$ Å as shown in Fig. 1. Magnetizations were

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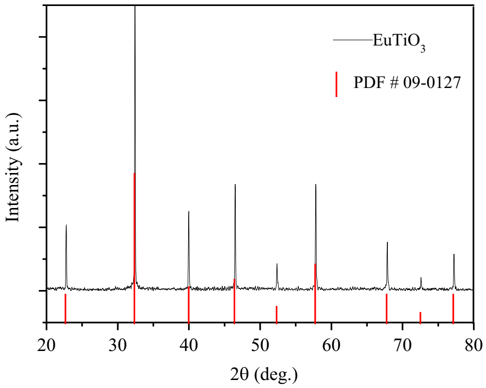

Fig. 1. : XRD patterns of the EuTiO$_3$.

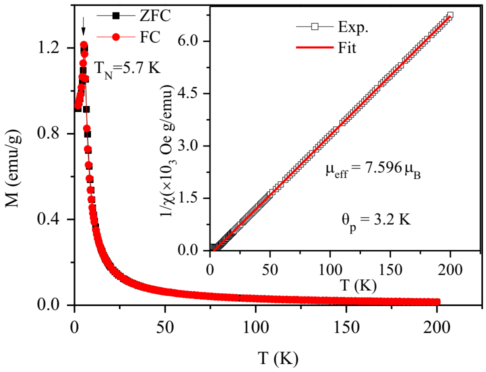

Fig. 2. : Temperature dependences of ZFC and FC magnetizations of EuTiO$_3$ under the magnetic field of 0.01 T. Inset: the temperature variation of the ZFC inverse susceptibility fitted to the Curie-Weiss law.

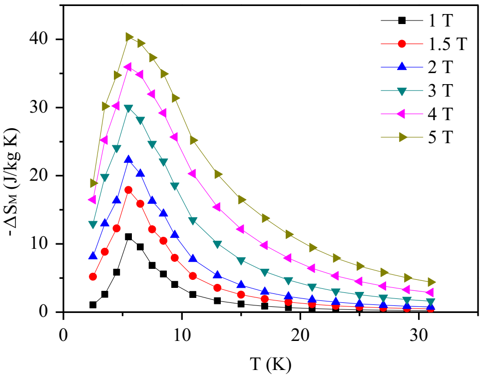

Fig. 4. : Temperature dependences of magnetic entropy change for EuTiO$_3$.

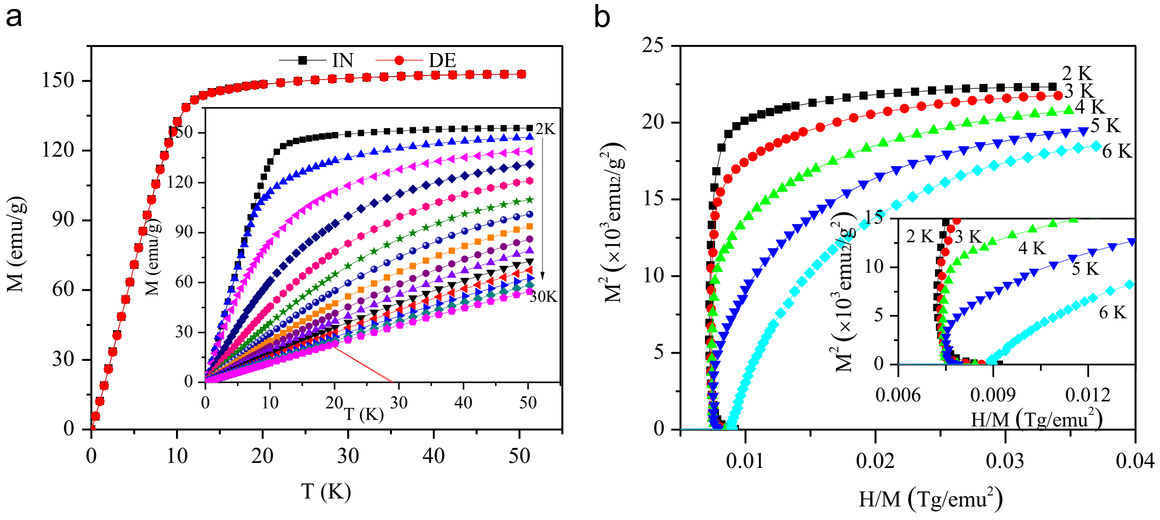

Fig. 3. : (a) Magnetization isotherms of EuTiO$_3$ measured in the temperature range of 2-30 K and the mold increasing and decreasing field at 2 K and (b) the Arrott plot of the EuTiO$_3$.

measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

3. Result and discussion

Fig. 2 shows the zero-field-cooling (ZFC) and field-cooling (FC) temperature dependence of magnetization for EuTiO$_3$ compound under an applied magnetic field of 0.01 T. It exhibits an antiferromagnetic (AFM) to paramagnetic (PM) magnetic transition at T_N=5.7 K, which agrees with previous reported [15–17]. The ZFC and FC curves are well overlapped, which indicates that there is no thermal hysteresis. On the other hand, we also notice that the reciprocal magnetic susceptibility ($\chi_m{}^{-1}$) of the EuTiO$_3$ compound follows 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 moment μ_{eff}=7.596 μ_B is obtained based on the value of C$_m$. The localized 4f moments on the Eu^{2+} (S=7/2, L= 0) sites order [21], and the Eu^{2+} 4f^7 band is a reason for narrowing of the optical band gap in the title compounds [22].The value of the Eu^{2+} magnetic moment (μ=7 ± 1 μ_B) was found to be consistent to the free ion as previously reported [21]. The value of θ_p is positive and equals to 3.2 K, which implies that the EuTiO$_3$ compound is a weak intiferromagnetic.

Fig. 3(a) shows the isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T during both increasing (black line) and decreasing (red line) fields at 2 K. No magnetic hysteresis can be observed, implying that EuTiO$_3$ compound is a soft ferromagnet. The *M* (*H*) data show a linearly increase at considerably low fields and in strong magnetic fields the magnetization isotherm tends to saturate, which exhibit typical AFM nature. The Eu magnetic moments ordering along the *a*,*b*-plane diagonal are consistent with an AFM G-type pattern [23]. The magnetic moment calculated at 5 T is about

6.58 μ_B. This value is smaller than the expected value for Eu^{2+} ion, which connects with the AFM state and crystal field. The negative slope of the Arrott plots below T_N, which is shown in Fig. 2(b) and the inset, further confirms the occurrence of the first order AFM-to-FM metamagnetic transition [24].

As is well known, the ΔS_M value can be calculated either from the magnetization isotherms by using the Maxwell relation$\Delta S(T, H) = \int_0^H (\partial M/\partial T)_H dH$[25]. Fig. 4 shows the values of $-\Delta S_M$ for different magnetic field changes as a function of temperature in $EuTiO_3$. The value of $-\Delta S_M{}^{max}$ is found to increase monotonically with the increase of applied magnetic field. The $-\Delta S_M{}^{max}$ reaches a value of 44.4 J /kg K at 5.5 K for a magnetic field change 0–5 T. Particularly, under the magnetic field changes of 1 and 2 T, which can be realized by permanent magnet and advantageous to applications, the maximum values of $-\Delta S_M$ are evaluated to be 11 and 22.3 J/kg K at 5.5 K, 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 [10], $ErMn_2Si_2$ (20 J/kg K) [11] and $ErRu_2Si_2$ (11 J/kg K) [14] et al. The RC, defined as a cooling capacity of$RC = \int_{T_1}^{T_2} \Delta S_M dT$, is calculated by numerically integrating the area under the $-\Delta S_M$-T curve, where $T_1$and T_2 are the temperatures at half maximum of the peak taken as the integration limits [25]. By using this method, the RC values of the $EuTiO_3$ are evaluated to be 106 and 328 J/kg for the magnetic field changes of 2 and 5 T, respectively. It can be seen that the MCE of $EuTiO_3$, especially under the low magnetic field change, is comparable with or even larger than those of other magnetocaloric materials around the liquid hydrogen temperature. Therefore, $EuTiO_3$ compound appears to be a very attractive candidate material for use in a magnetic refrigerator working in low temperature.

4. Conclusion

In summary, a giant reversible MCE and large RC in $EuTiO_3$ compound were observed. It exhibits an AFM to PM magnetic transition at T_N=5.7 K, the Eu magnetic moments order are consistent with an AFM G-type motif, with the moments lying within the *a*,*b*-plane along the plane diagonal. The effective magnetic moment μ_{eff} is7.596 μ_B, which indicates the localized 4f moments on the Eu^{2+} (S=7/2, L= 0) sites. Under the magnetic field changes of 5 T, the maximum value of $-\Delta S_M$ is evaluated to be 40.4 J/kg K in $EuTiO_3$ compound. Especially, for the low magnetic field changes of 1 and 2 T, which can be realized by permanent magnet, the maximum values of $-\Delta S_M$ are 11 and 22.3 J/Kg K, respectively. Therefore, the giant reversible MCE make the $EuTiO_3$ a promising candidate for magnetic refrigeration.

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References

[1] K.A. Gschneidner Jr, V.K. Pecharsky, A.O. Tsoko, Rep. Prog. Phys. 68 (2005) 1479.

[2] S.M. Benford, G.V. Brown, J. Appl. Phys. 52 (1981) 2110.

[3] B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, Z.H. Chen, Adv. Mater. 21 (2009) 4545.

[4] F.X. Hu, B.G. Shen, R. Sun, Z.H. Cheng, G.H. Rao, X.X. Zhang, Appl. Phys. Lett. 78 (2001) 3675.

[5] F. Wang, Y.F. Chen, G.J. Wang, B.G.J. Shen, D. Phys, Appl. Phys. 36 (2003) 1.

[6] H. Wada, Y. Tanabe, Appl. Phys. Lett. 79 (2001) 3302.

[7] O. Tegus, E. Bruck, K.H.J. Buschow, F.R. Boer de, Nature 415 (2002) 150.

[8] A.M. Gomes, M.S. Reis, A.P. Guimaraes, P.B. Tavares, J.P. Araujo, V.S. Amaral, J. Magn. Magn. Mater. 272–276 (2004) 2385–2386.

[9] Z.J. Mo, J. Shen, L.Q. Yan, C.C. Tang, J. Lin, J.F. Wu, et al., Appl. Phys. Lett. 103 (2013) 052409.

[10] Z.J. Mo, J. Shen, L.Q. Yan, J.F. Wu, L.W. Wang, C.C. Tang, et al., Appl. Phys. Lett. 102 (2013) 192407.

[11] L. Li, K. Nishimura, W.D. Hutchison, Z. Qian, D. Huo, T. Namiki, Appl. Phys. Lett. 100 (2012) 152403.

[12] X.X. Zhang, F.W. Wang, G.H. Wen, J. Phys.: Condens. Matter 13 (2001) L747.

[13] L. Li, W.D. Hutchison, D.X. Huo, T. Namiki, Z.H. Qian, K. Nishimura, Scr Mater 67 (2012) 237.

[14] Das I. Tapas Samanta, S. Banerjee, Appl. Phys. Lett. 91 (2007) 152506.

[15] K.S. Takahashi, M. Onoda, M. Kawasaki, N. Nagaosa, Y. Tokura, Phys. Rev. Lett. 103 (2009) 057204.

[16] V.V. Shvartsman, P. Borisov, W. Kleemann, S. Kamba, T. Katsufuji, Phys. Rev. B 81 (2010) 064426.

[17] T. Katsufuji, H. Takagi, Phys. Rev. B 64 (2001) 054415.

[18] S. Kamba, D. Nuzhnyy, P. Vanêk, M. Savinov, K. Knížek, Z. Shen, et al., J. Petzelt. Europhys. Lett. 80 (2007) 27002.

[19] V. Goian, S. Kamba, J. Hlinka, P. Vaněk, A.A. Belik, T. Kolodiazhnyi, et al., Eur. Phys. J. B 71 (2009) 429.

[20] C.J. Fennie, K.M. Rabe, Phys. Rev. Lett. 97 (2006) 267602.

[21] T.R. McGuire, M.W. Shafer, R.J. Joenk, H.A. Alperin, S.J.J. Pickart, Appl. Phys. 37 (1966) 981.

[22] T. Kolodiazhnyi, M. Valant, J.R. Williams, M. Bugnet, G.A. Botton, N. Ohashi, et al., J. Appl. Phys. 112 (2012) 083719.

[23] V. Scagnoli, M. Allieta, H. Walker, M. Scavini, T. Katsufuji, L. Sagarna, et al., Phys. Rev. B 86 (2012) 094432.

[24] S.K. Banerjee, Phys. Lett. 12 (1964) 16.

[25] K.A. Gschneidner Jr., V.K. Pecharsky, C.B. Zimm, Mater. Sci. Forum 315 (1999) 69.