

Magnetism and magnetocaloric effect study of $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$

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2015 Mater. Res. Express 2 046103

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Materials Research Express



PAPER

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9 December 2014REVISED
3 February 2015ACCEPTED FOR PUBLICATION
26 February 2015PUBLISHED
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Keywords: high pressure synthesis, magnetocaloric effect, ferromagnetic transition

Abstract

The $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$ single crystal was grown for the first time by a two-step method and its magnetism and magnetocaloric effect were investigated. This compound experiences a second-order paramagnetism-to-ferromagnetism transition in a wide temperature window between 200 and 150 K due to the presence of multiple ferromagnetic interactions. Since the spin entropy is gradually released above the ferromagnetic Curie temperature (~ 177 K), no sharp λ -type anomaly is observed in specific heat. On the basis of magnetization measurements, however, a considerable entropy change is found in this perovskite oxide. More interesting, this compound exhibits a broadening working temperature, and a significant refrigerant capacity (~ 355 J kg⁻¹ at 6 T) which is comparable with those found in some giant magnetocaloric alloys with first-order magnetic transitions. The present study therefore provides an example on how to enhance the refrigerant capacity by extending the working temperature of magnetocaloric material.

1. Introduction

Magnetic refrigeration is a promising technology with the potential to replace conventional gas compression refrigeration due to the advantages in energy efficiency, environment friendliness, and compact assembling etc [1–3]. Magnetocaloric effect (MCE) is the basis for magnetic refrigeration technology. The applying of an external magnetic field can decrease the spin entropy and therefore the heat will be delivered from a magnetic system to environment in an isothermal process. On the other hand, when the magnetic field is removed adiabatically, magnetic spins tend to randomize, giving rise to an increase in the magnetic entropy and a decrease in the lattice entropy and thus lowering the temperature of the system [4, 5]. The refrigerant capacity (RC) is an important quality factor for a refrigerant material, which determines the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. The RC is defined as $\text{RC} = -\int_{T_1}^{T_2} \Delta S_M dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of a temperature dependent entropy change (ΔS_M) peak. So it is desirable to combine a large ΔS_M with a wide working temperature for a promising MCE material in practical applications. At present, giant ΔS_M values have been found in several material systems such as $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ [6], Ni_2MnGa [7], and MnAs [8], etc. However, the giant entropy changes are often originated from a first-order magnetic transition associated with a structural phase transition. The narrow working temperature as well as the thermal and magnetic hysteresis severely limits the potential applications. Although much attention has been paid to search MCE materials with large ΔS_M , it is relatively little known on how to extend the working temperature to enhance the refrigerant capacity.

ABO_3 perovskite is a kind of very important functional materials. Since the crystal structures and the A-B ionic combinations are quite flexible, perovskite compounds show a wide variety of intriguing physical properties [9, 10]. For example, interesting magnetocaloric properties were found in Mn-based perovskites [11–13]. CaFeO_3 perovskite has attracted lots of interests due to the unique charge-disproportion transition of Fe^{4+} ions ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) as well as the peculiar spiral spin structure [14, 15]. When Co is used to partially substitute Fe, the magnetism of $\text{CaFe}_{1-x}\text{Co}_x\text{O}_3$ solid solution will change from antiferromagnetism with $x < 0.2$

to ferromagnetism with $x > 0.2$. Because the ferromagnetic (FM) ordering in this family is related to multiple double exchange interactions between Fe and Co ions as well as between Fe/Co ions and ligand holes [16–19], a broader FM transition temperature region is possible to occur in Co-doped CaFeO_3 magnets, which is favorable to enhance the RC by increasing the working temperature. In $\text{Ca/SrFe}_{1-x}\text{Co}_x\text{O}_3$ family, a single-crystal sample usually shows a larger saturated spin moment than the related polycrystalline sample [18, 19]. We therefore prepared $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$ (CFCO) single crystal for the first time and a considerable MCE was found in this perovskite compound.

2. Experimental details

Oxygen stoichiometric $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$ single crystal was grown by a two-step method [18, 19]. As the first step, oxygen-deficient polycrystalline sample $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_{2.5}$ with brownmillerite-type structure was prepared by a conventional solid-state reaction method [16], and then $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_{2.5}$ single crystal was grown by using a lamp-image-type floating-zone system with $\text{CaFeO}_{2.5}$ single crystal as a seed. Secondly, the obtained $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_{2.5}$ single crystal was treated in a cubic-anvil-type high pressure apparatus at 6.0 GPa and 1073 K for 30 min with the presence of KClO_4 oxidant. By combining these ambient and high pressure synthesis techniques, a CFCO single crystal with 3 mm in diameter and 4 mm in length was obtained. Thermogravimetric analysis confirmed the stoichiometry of oxygen content for the as-made single crystal.

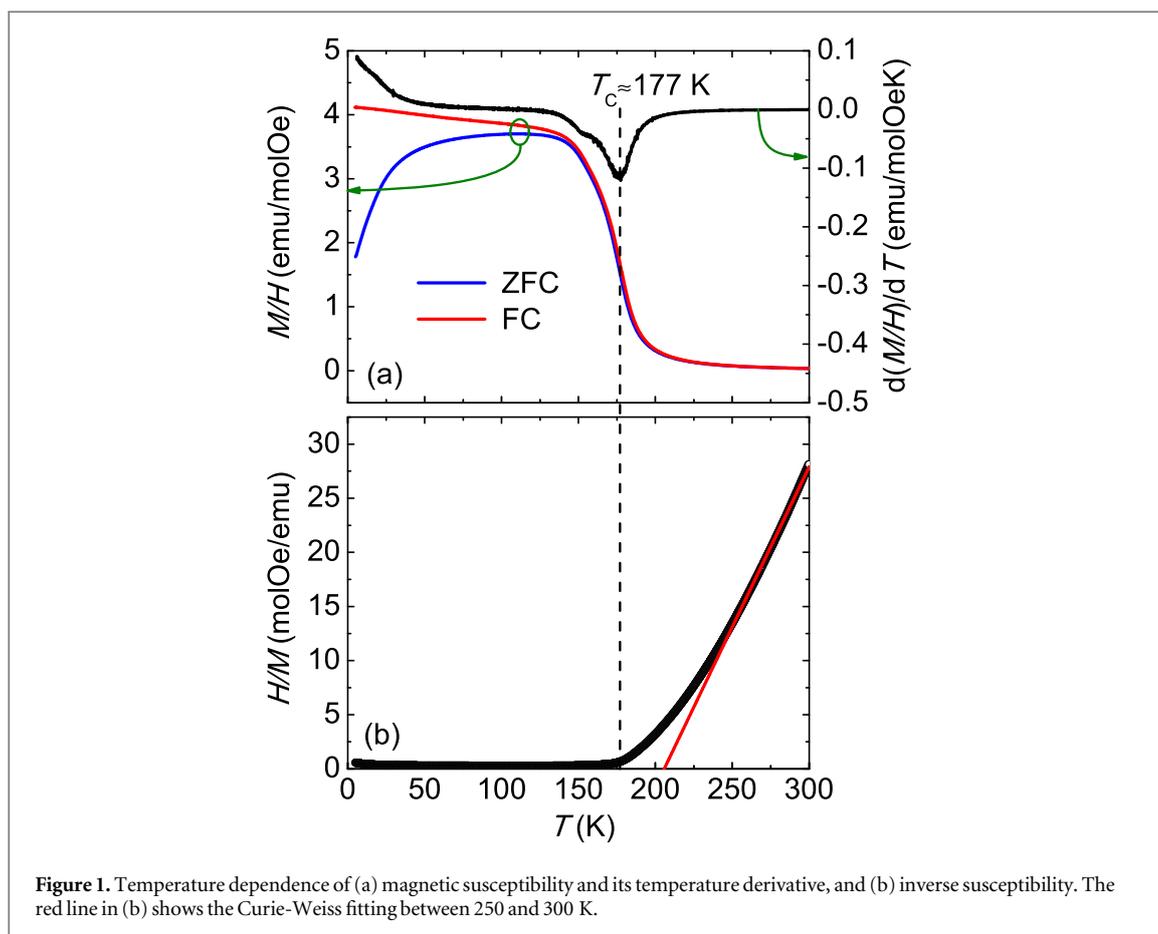
The phase purity was checked by powder x-ray diffraction using a Rigaku diffractometer with $\text{Cu-K}\alpha$ radiation (40 kV, 300 mA). The quality of single crystal was identified by Laue diffraction. The magnetic susceptibility and magnetization (M) were measured using a Quantum Design vibrating sample magnetometer. The resistivity and heat capacity (C_p) data were collected with a Quantum Design physical property measurement system.

3. Results and discussion

The x-ray powder diffraction shows that CFCO single crystal crystallizes to an orthorhombic GdFeO_3 -type perovskite structure with lattice parameters $a = 5.323 \text{ \AA}$, $b = 5.312 \text{ \AA}$, and $c = 7.516 \text{ \AA}$. The cell volume is a little smaller than that of the parent compound CaFeO_3 due to partial substitution of Fe^{4+} by Co^{4+} ions with a smaller ionic radius [14, 20]. Unfortunately, however, for this orthorhombic compound with $a \approx b$, the obtained single crystal is highly twinned as found in CaFeO_3 single crystal [21]. Therefore, a moderate crystal with a random plane was used for the present MCE study.

Figure 1(a) shows the temperature dependence of magnetic susceptibility measured at magnetic field $H = 0.1 \text{ T}$ in zero-field-cooled (ZFC) and field-cooled (FC) modes. Both ZFC and FC curves show a paramagnetic (PM) to FM transition in a wider temperature region between 200 and 150 K. Based on the temperature derivative of the ZFC magnetic susceptibility (figure 1(a)), the FM Curie temperature (T_C) was assigned to be about 177 K. As shown in figure 1(b), the inverse susceptibility above 250 K can be well fitted by the Curie–Weiss law, producing the Curie constant $C = 3.38 \text{ emuK molOe}^{-1}$ and the Weiss constant $\theta = 206 \text{ K}$. The positive Weiss constant is in agreement with the FM interactions. According to the Curie constant, the fitted effective moment is $\mu_{\text{eff}} = 5.20 \mu_B \text{ f.u.}^{-1}$. In CaFeO_3 and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ solid solution, high-spin and intermediate-spin configurations were assigned to Fe^{4+} and Co^{4+} ions, respectively [14, 18, 19]. If identical spin configurations are considered in the present CFCO, the spin-only effective moment in theory should be $4.62 \mu_B \text{ f.u.}^{-1}$. This value is a little smaller than the fitted one probably due to the presence of some orbital moment of Co^{4+} ions as found in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ by magnetic circular x-ray dichroism measurements [22].

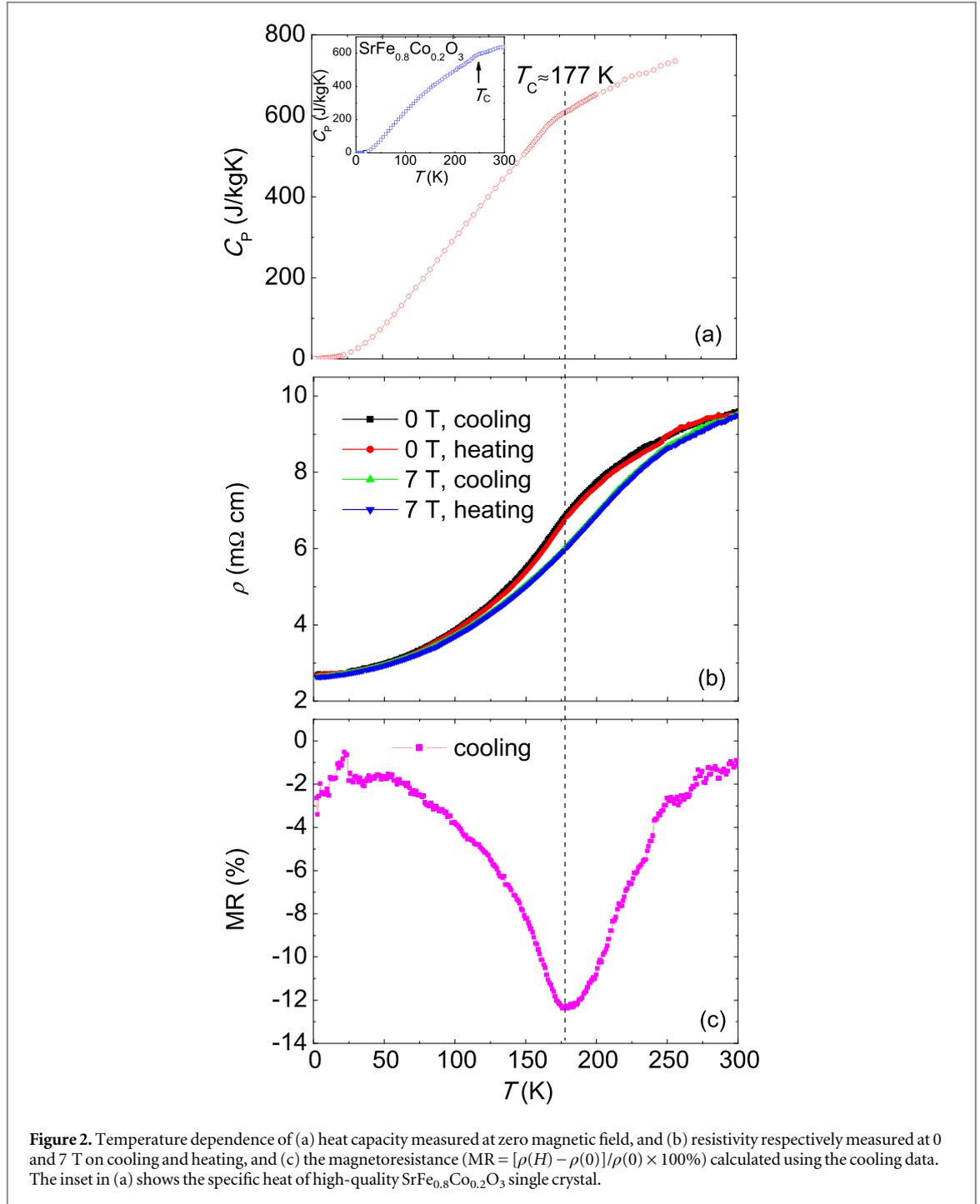
The broader PM-FM transition is further confirmed by specific heat and electric transport measurements. As shown in figure 2(a), near T_C , a broadening C_p hump instead of a sharp λ -type anomaly, which is usually presented for a long-range second-order magnetic phase transition, is observed in the temperature dependence of specific heat in CFCO. This observation can be attributed to that the spin entropy is partially released well above T_C due to the presence of some short-range FM interactions probably occurred between Fe and Co ions and/or between Fe/Co ions and oxygen holes on account of the negative p - d charge transfer energy discovered in the perovskite oxides with unusually high Fe^{4+} and Co^{4+} ions [23, 24]. Correspondingly, one cannot find coherent anomaly in electric transport at T_C . As shown in figure 2(b), the resistivity experiences a smooth change with temperature across T_C . This behavior is different from that of SrCoO_3 , where a resistivity anomaly is found near the FM Curie temperature [18]. When magnetic field is used, however, the resistivity of CFCO is considerably decreased in a wider temperature region centered at T_C (figures 2(b) and (c)). As a result, a negative magnetoresistance effect ($\text{MR} = [\rho(H) - \rho(0)]/\rho(0) \times 100\%$) is obtained thanks to the reduction of spin fluctuation and spin scattering under field, as reported in many other ferromagnetic metals [25, 26]. As shown in figure 2(c), the maximum MR value ($\sim -13\%$) is clearly observed around T_C .



Note that in addition to the presence of multiple magnetic interactions, other effects such as imperfect and inhomogeneous crystal may also lead to broad transitions in magnetism, electricity and specific heat etc. In order to figure out this question, we prepared a high-quality $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ single crystal with a simple cubic perovskite structure [19]. Our measurement results show that $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ exhibits very similar phase transitions in magnetism and transport properties with those of CFCO. As an example, the specific heat of $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ single crystal was shown in the inset of figure 2(a), and a broad hump was also observed near the Curie temperature (~ 250 K). We therefore conclude that the cooperated effects of multiple FM interactions instead of sample quality should be responsible for the broad FM transition in the present CFCO.

Figure 3 shows the field dependent isothermal magnetization curves measured at several representative temperatures. Above T_C , the observed linear magnetization behavior is consistent with the PM feature. Below T_C , the magnetization increases sharply with field and tends to saturate with field up to about 2 T. The saturated moment obtained at 7 T and 5 K is $3.1 \mu_B \text{ f.u.}^{-1}$, which is slightly smaller than the completely local spin moment ($3.7 \mu_B \text{ f.u.}^{-1}$) for the high-spin Fe^{4+} and intermediate-spin Co^{4+} ions in CFCO due to the metallic conductivity as presented in figure 2(b). The observed coercive field is about 0.1 T at 5 K. With increasing temperature to 120 K, the coercive field considerably decreases to < 0.01 T (inset of figure 3). It is therefore expected that the magnetic hysteresis should be negligible around T_C .

Figure 4(a) shows a series of isothermal magnetization curves between 150 and 210 K (applied field 0–6T) spanning the ferromagnetic transition region to study the MCE of CFCO. The area between two isotherms changes slightly, indicating a gradual variation in the magnitude of entropy change. As is well known, the Arrott plot (H/M versus M^2) provides evidence to identify the nature of magnetic phase transition [27]. In general, a negative slope of this plot indicates the occurrence of a first-order magnetic transition such as a magnetostrictive transition as observed in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ [28]. In contrast, a positive slope corresponds to a second-order magnetic transition [29, 30]. From the viewpoint of practical application of MCE, the material with a second-order magnetic transition is advantaged over that with a first-order one because of the low hysteresis in both thermal and magnetic cycles [5, 31]. As presented in figure 4(b), all the Arrott curves at the vicinity of T_C in CFCO show positive slopes, suggesting that the PM to FM transition in this compound is second-ordered. This is also in accordance with the temperature dependences of magnetic susceptibility and resistivity, where no thermal hysteresis behavior is found around T_C (figures 1(a) and 2(b)).

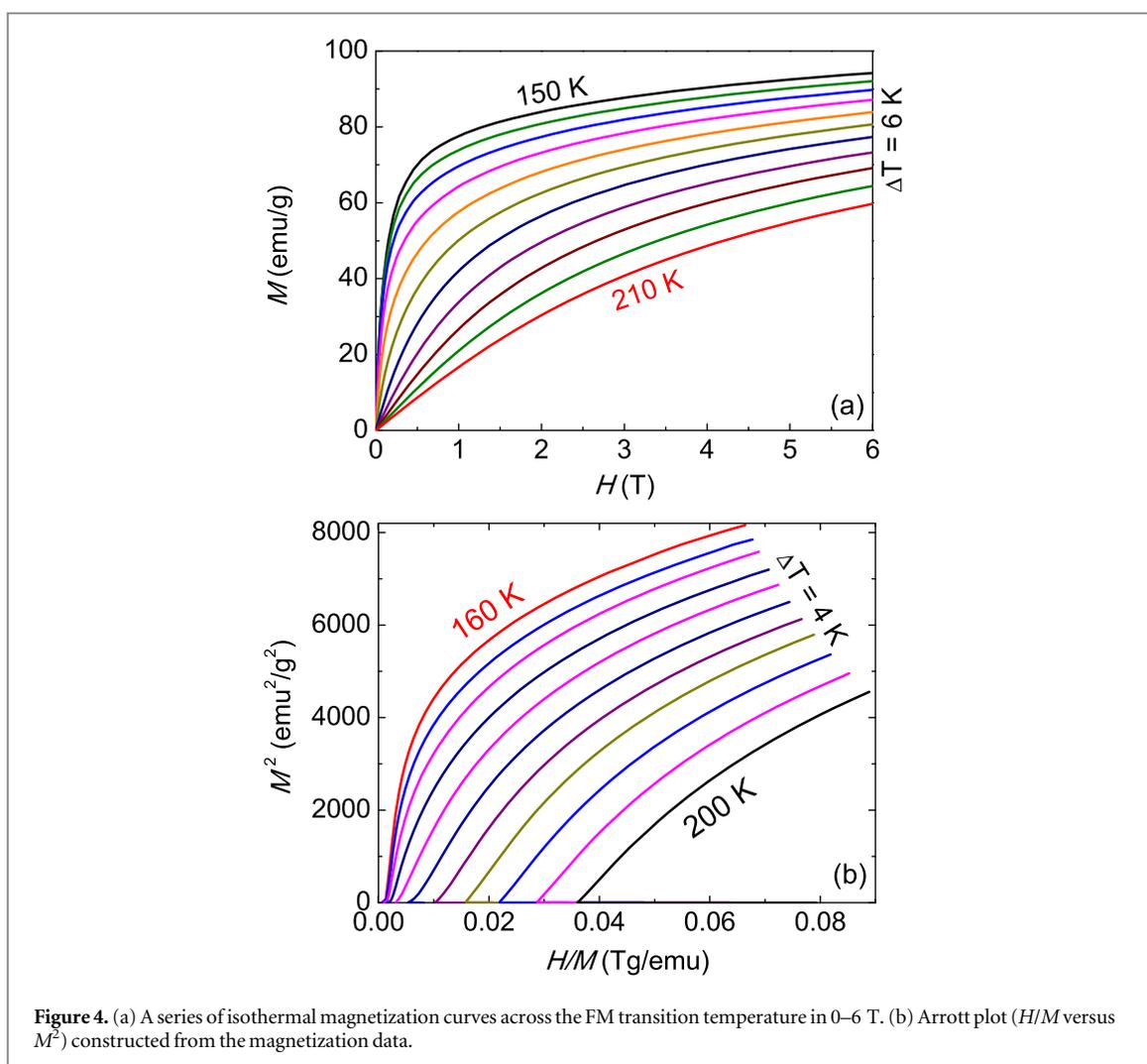
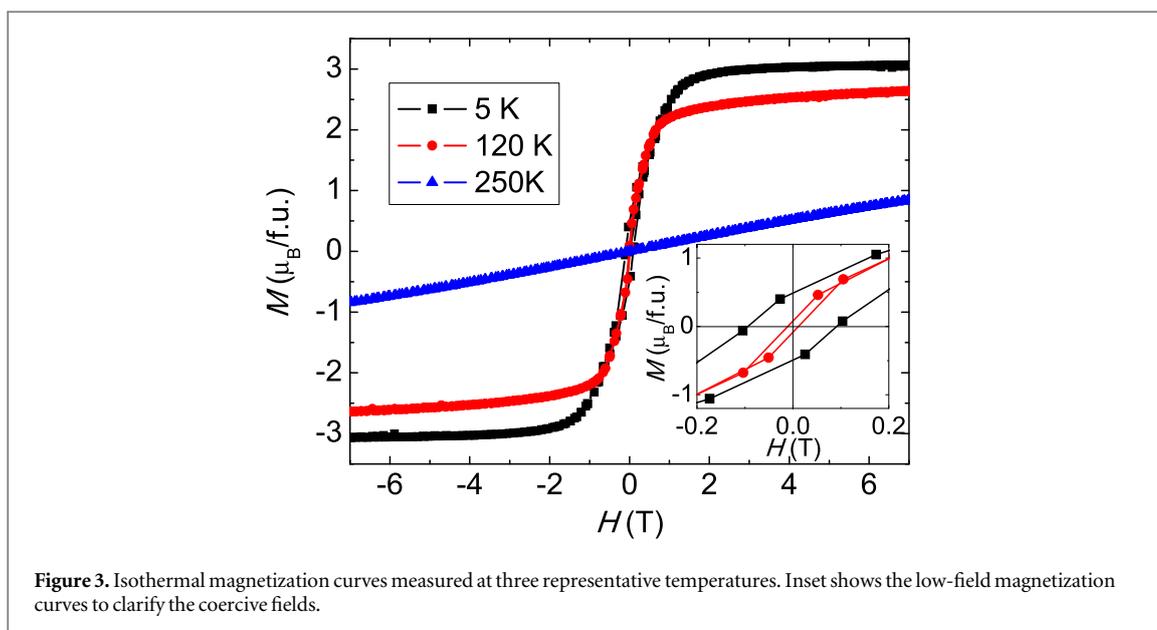


The negative values of the entropy change $-\Delta S_M(T)$ can be calculated by the following formula [32]:

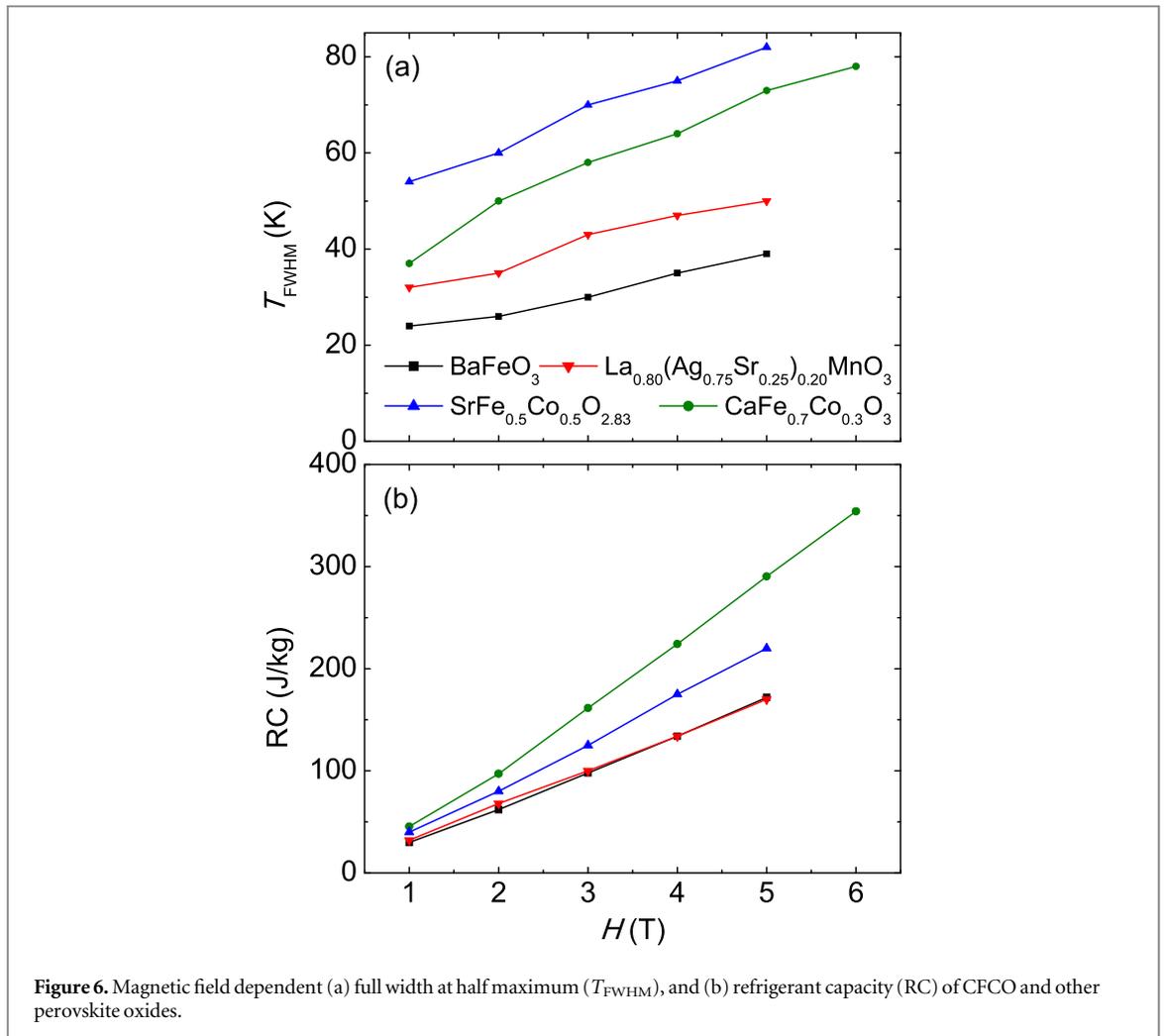
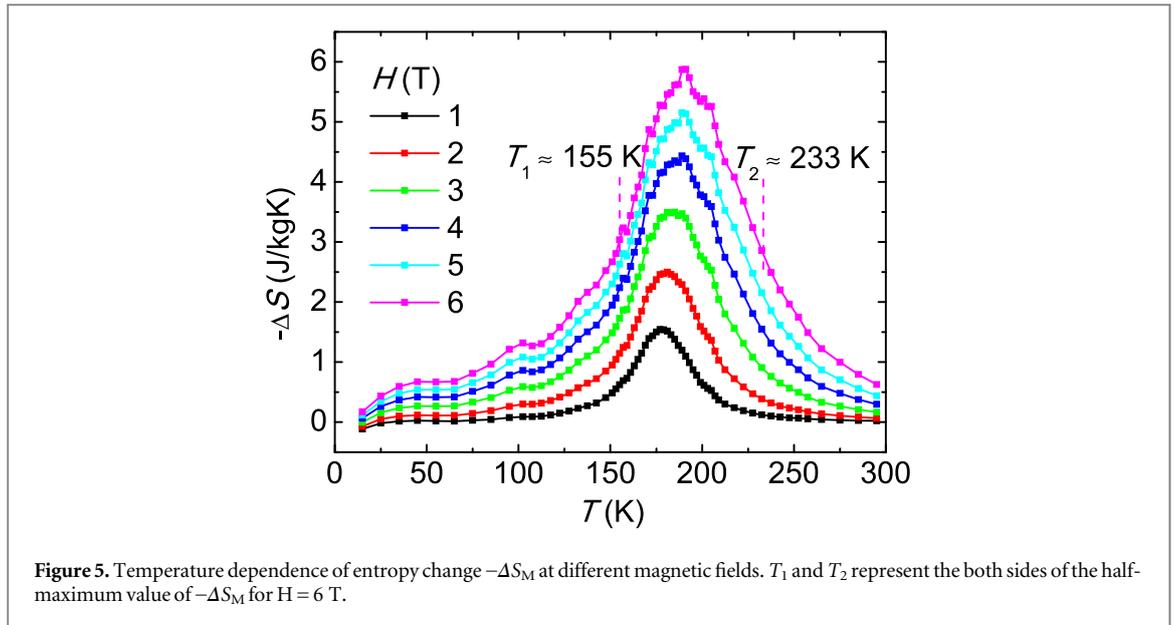
$$-\Delta S \left(\frac{T_1' + T_2'}{2} \right) = \frac{\Sigma}{T_2' + T_1'}$$

Here Σ is the area between two MH curves measured at temperatures T_1' and T_2' , respectively. Figure 5 shows the temperature dependence of entropy change in a wide temperature region (15–295 K) measured under different magnetic fields. The peaks of these curves shift from T_C to ~ 190 K with increasing field applied from 0 to 6 T. When the applied field is 2 T, which is available for permanent magnet in industry, the maximum of $-\Delta S_M$ is 2.5 J kgK^{-1} . This is a large magnitude for perovskite MCE materials. Furthermore, when the applied field increases to 6 T, the maximal value of $-\Delta S_M$ increases to 5.9 J kgK^{-1} , which is similar with those of the well-studied Mn-based perovskite MCE materials such as $\text{La}_{0.87}\text{Sr}_{0.13}\text{MnO}_3$ (5.8 J kgK^{-1}) [2, 33].

Since the FM phase transition temperature window is rather wide in the present CFCO, a large working temperature is expected to occur. We therefore calculated the full width at half maximum (T_{FWHM}) for the



temperature dependent $-\Delta S_M$ peak by a Lorentz fitting. Figure 6(a) shows the magnetic field dependent T_{FWHM} of CFCO. For comparison, some reported T_{FWHM} values on other perovskite oxides are also plotted in this figure [28, 34, 35]. Apparently, the T_{FWHM} values of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.83}$ and CFCO are significantly larger than those of BaFeO_3 and the A-site doped LaMnO_3 , because several cooperated FM interactions coexist in the former two



compounds. It indicates that the performance of MCE can be enhanced by introducing multiple FM interactions to increase the working temperature. According to the obtained $-\Delta S_M$, we calculated the refrigerant capacity by the formula $RC = -\int_{T_1}^{T_2} \Delta S_M dT$ as mentioned before. The calculated RC values at different fields are shown in figure 6(b). Since the present CFCO possesses a wider working temperature (as characterized by the large

T_{FWHM}) and a considerable entropy change, it exhibits a promising refrigerant capacity. For example, the RC value of CFO obtained at 5 T (6 T) is 290 J kg^{-1} (355 J kg^{-1}), which is almost the largest one observed in perovskite oxides to the best of our knowledge and even is comparable with those exhibited by typical giant MCE alloys such as $\text{Gd}_5\text{Ge}_2\text{Si}_2$ (305 J kg^{-1}) with a first-order magnetic transition [2, 6, 32, 36].

4. Conclusions

The oxygen-full $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$ single crystal was obtained for the first time by integrating floating zone method and high-pressure treatment technique. Magnetization, specific heat, electric transport and magnetocaloric effect were studied in detail. A sluggish paramagnetic to ferromagnetic transition was observed in a broader temperature region between 200 and 150 K. All the Arrott curves at the vicinity of T_C showed positive slopes, suggesting that the magnetic transition was second-ordered in nature. Accompanying with the FM transition, no sharp anomaly was found in specific heat and resistivity at zero magnetic field. However, at high magnetic field, the resistivity decreased considerably near the FM transition temperature, and a maximum MR value was observed at T_C . On the basis of detailed isothermal magnetization measurements, the entropy change was obtained to be $-\Delta S_M(T) \approx 5.9 \text{ J kgK}^{-1}$ at 6 T, which was considerably large for perovskite MCE materials. Because of the broadening PM-FM transition in the present CFO single crystal, a wider working temperature region which was characterized by the value of T_{FWHM} of a $\Delta S_M(T)$ peak was found. As a result, a significant refrigerant capacity (355 J kg^{-1} at 6 T) was obtained. This value is almost the largest one in perovskite oxides and even comparable to conventional giant MEC alloys like $\text{Gd}_5\text{Ge}_2\text{Si}_2$ with a first-order magnetic transition. In consideration of the wide working temperature, large $-\Delta S_M(T)$ and RC, as well as excluding rare elements, the present $\text{CaFe}_{0.7}\text{Co}_{0.3}\text{O}_3$ provides a promising candidate for magnetic refrigeration.

Acknowledgments

The authors thank W He and Y J Ke for their useful discussion. This work was partly supported by 973 Project of the Ministry of Science and Technology of China (Grant No. 2014CB921500), and by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB07030300).

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