RAPID COMMUNICATION

Magnetocaloric effect study of $SrFe_{0.8}Co_{0.2}O_3$ single crystal prepared under high pressure*

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A high-quality $SrFe_{0.8}Co_{0.2}O_3$ single crystal is prepared by combining floating-zone and high-pressure treatment methods. Its Magnetocaloric effect is investigated by magnetic measurements. A paramagnetism-to-ferromagnetism transition is found at about 270 K and this transition is a second-order one in nature as confirmed by Arrott plots. The saturated moment obtained at 2 K and 7 T is 3.63 μ_B/f.u. The maximal value of magnetic entropy change measured at 5 T is about 4.0 $J\cdot kg^{-1}\cdot K^{-1}$. The full wide at half maximum for a magnetic entropy change peak observed in $SrFe_{0.8}Co_{0.2}O_3$ is considerably large. As a consequence, the relative cooling power value of $SrFe_{0.8}Co_{0.2}O_3$ obtained at 5 T is 331 J/kg, which is greatly higher than those observed in other perovskite oxides. The present work therefore provides a promising candidate for magnetic refrigeration near room temperature.

Keywords: high pressure synthesis, magnetocaloric effect, ferromagnetic phase transition

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1. Introduction

The magneto-thermodynamic phenomenon known as the magnetocaloric effect (MCE) was first discovered by Warburg in 1881.[1] Its application in magnetic refrigeration provides a unique way to realize refrigeration from ultralow to room temperature (RT).[2–4] The MCE refers to the temperature change in response to the variation in the external magnetic field. For a paramagnetic solid near absolute zero or a ferromagnetic material near its Curie temperature (T_C), when the applied magnetic field increases in an adiabatic way, the magnetic part of the total entropy is released to the lattice, resulting in temperature rising in the material. In the reverse demagnetizing process, the zero field magnetic entropy of the material or refrigerant is restored from the lattice part, leading to the falling of the refrigerant temperature.[5,6]

Compared with conventional gas compression refrigeration, the ozone depletion substance and compressor are not needed in the magnetic refrigeration. Moreover, the efficiency of magnetic refrigeration can be as high as 30–60% of Carnot cycle, which is much higher than that of the gas compression refrigeration (5–10%).[7] Therefore, magnetic refrigeration is very environmentally friendly and energy saving as well as noiseless and stable as compared with gas compression refrigeration.[4,8–10] At present, much attention has been paid to searching for room-temperature MCE materials such as Gd,[11] MnAs,[12] $Gd_5Si_2Ge_2$,[13] $MnFeP_{0.45}As_{0.55}$,[14] etc, owing to the potential environmental and economic benefits.[15,16] However, these materials usually are expensive, poisonous and have hystereses in magnetic and thermal cycles arising from the fist-order ferromagnetic transition. Hysteresis can depress the efficiency of magnetic refrigeration. By comparison, the second-order MCE materials have no magnetic and thermal hysteresis and usually have comparable or even larger refrigerant capacity (RC), although they sometimes exhibit relatively low values of magnetic entropy change (ΔS_M). It is therefore very desirable to search for MEC materials with second-order ferromagnetic transition and considerable RC near RT.[6]

ABO_3-type perovskite is a kind of very important functional materials due to its versatile crystal structures and physical properties.[16,17] The MCE was studied in a few of perovskite compounds such as $BaFeO_3$,[19] $La_{1-x}Ca_xMnO_3$,[20,21] $Ba_2Fe_{1+x}Mo_{1-x}O_6$,[22] etc. As for the solid solution of $SrFe_{1-x}Co_xO_3$ perovskite, with increasing Co content (x), the ground state magnetism changes from antiferromagnetism ($x \leq 0.05$) through cluster glass to ferromagnetism ($x > 0.15$) with high ferromagnetic Curie temperatures between 245 and 337 K.[23] The tunable curie temperature near RT makes this solid solution an interesting candidate for MCE study. Actually, the MCE of $SrFe_{0.5}Co_{0.5}O_3$ polycrystalline sample was investigated by Yin *et al.*, which exhibits a second-order magnetic transition around 330 K.[24] The ΔS_M

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is an important parameter to qualify MCE for a refrigerant material. A large saturated moment is favorable to enhancing the value of ΔS_M. In the $SrFe_{1-x}Co_xO_3$ solid solution, the largest saturated moment emerges near $x = 0.2$.[23] Moreover, the value of saturated moment in this family is related to sample quality. For example, in $SrCoO_3$ polycrystalline samples, the saturated moments obtained in experiments are between 1.0 and 1.8μ_B/f.u.,[25,26] which is much less than that observed in the single-crystal sample (2.5μ_B/f.u.).[23,27] We thus prepare high-quality $SrFe_{0.8}Co_{0.2}O_3$ single crystal and study the magnetocaloric effect in this paper.

2. Experiments and characterizations

Oxygen stoichiometric $SrFe_{0.8}Co_{0.2}O_3$ single crystal was grown by a two-step method.[23,27] Firstly, oxygen-deficient polycrystalline sample $SrFe_{0.8}Co_{0.2}O_{2.5}$ with brownmillerite-type structure was prepared by a standard solid-state reaction method by using high-purity $SrCO_3$, Fe_2O_3, and Co_3O_4 as starting materials. These reactants were thoroughly mixed and then sintered at 1373 K for 24 h in air. The product was ground again and pressed into a rod with 5 mm in diameter and 10 cm in length. This rod was treated at 1373 K for 12 h in Ar atmosphere. Single crystal of $SrFe_{0.8}Co_{0.2}O_{2.5}$ was grown by a floating-zone method with using the prepared rod. Finally, the obtained $SrFe_{0.8}Co_{0.2}O_{2.5}$ single crystal was treated in a cubic-anvil-type high pressure apparatus at 6.0 GPa and 1023 K for 30 min in the presence of $KClO_4$ oxidant. Thermogravimetric analysis confirmed that the final product treated by high oxygen pressure is $SrFe_{0.8}Co_{0.2}O_3$ with stoichiometric oxygen content. The crystal structure of $SrFe_{0.8}Co_{0.2}O_3$ was checked by a Rigaku diffractometer with Cu-Kα radiation (40 kV, 300 mA).The quality of single crystal was identified by Laue diffraction. The magnetic data were measured by using a quantum design vibrating sample magnetometer. The temperature dependence of magnetic susceptibility was acquired at applied magnetic field $H = 0.1$ T in zero-field-cooled (ZFC) and field-cooled (FC) modes.

3. Results and discussion

The as-prepared sample after high-oxygen-pressure treatment is proved to be a high-quality single crystal by Laue diffraction measurements. Figure 1 shows the x-ray powder diffraction pattern measured at room temperature. All the diffraction peaks can be well indexed in terms of a simple cubic perovskite structure with space group *Pm*-3*m*. The obtained lattice constant is $a = 3.8480(1)$ Å, which is in agreement with previously reported result.[23] The temperature dependences of magnetic susceptibility measured at magnetic field $H = 0.1$ T in ZFC and FC modes are shown in Fig. 2. A ferromagnetic transition is observed at $T_C \approx 270$ K in the present $SrFe_{0.8}Co_{0.2}O_3$ single crystal. No substantial hysteresis is found in the transition temperature region, implying that the magnetic transition is second-order in nature.

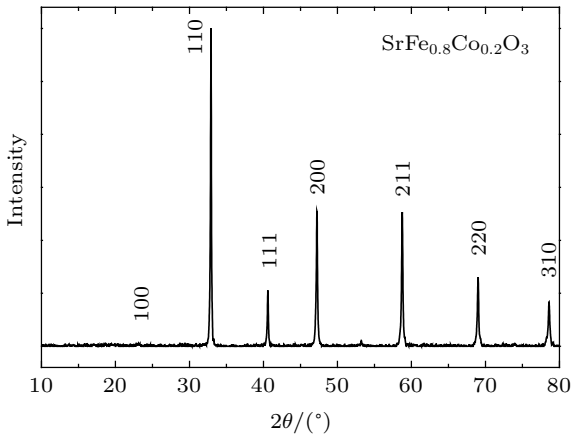


Fig. 1. Powder x-ray diffraction pattern and corresponding Miller indices of $SrFe_{0.8}Co_{0.2}O_3$ single crystal.

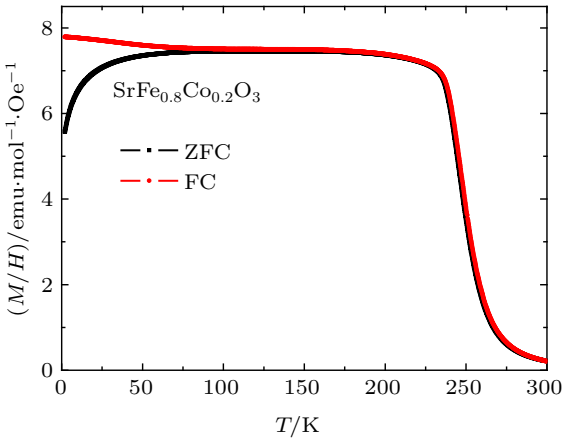


Fig. 2. (color online) Temperature dependence of magnetic susceptibility of $SrFe_{0.8}Co_{0.2}O_3$.

Figure 3 shows isothermal magnetization curves measured at several representative temperatures. At 300 K the magnetization does not show a linear dependence on magnetic field, suggesting the presence of some short-range ferromagnetic interactions above the Curie temperature. Actually, in the present $SrFe_{0.8}Co_{0.2}O_3$ system, multiple ferromagnetic double-exchange interactions are possible to occur between Fe^{4+} and Co^{4+} ions as well as between Fe^{4+}/Co^{4+} ions and oxygen holes due to the strong p–d hybridizations.[26,28] The saturated moment obtained at 2 K and 7 T is 3.63μ_B/f.u., which is slightly smaller than the completely local spin moment (3.8μ_B/f.u.) for the high-spin Fe^{4+} and intermediate-spin Co^{4+} ions in the metallic $SrFe_{0.8}Co_{0.2}O_3$ as proposed before.[23] Note that the saturated moment of $SrFe_{0.8}Co_{0.2}O_3$is largest in the ferromagnetic region in $SrFe_{1-x}Co_xO_3$ family. For example, the saturated moment observed in our sample is considerably larger than that of $SrFe_{0.5}Co_{0.5}O_3$ ($\sim 3.02\mu_B$/f.u.), suggesting a greater MCE for the present $SrFe_{0.8}Co_{0.2}O_3$.[24] Moreover, the coercive field at 2 K is only 200 Oe as shown in the inset of Fig. 3. With increasing temperature, the coercive field is reduced sharply. As an instance, almost no magnetic hysteresis is shown up above 200 K. This is favorable for the potential application for an MCE material.

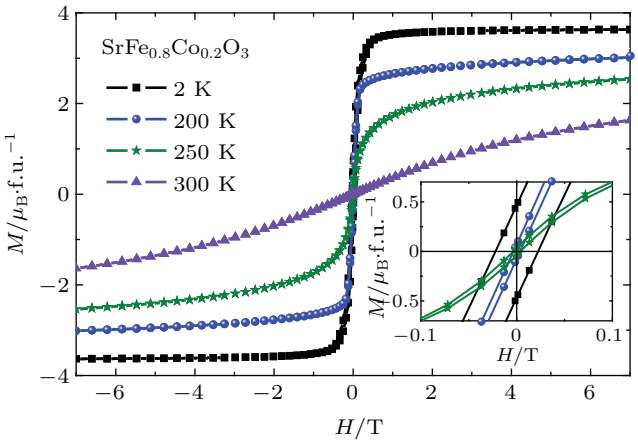


Fig. 3. (color online) Isothermal magnetization curves of $SrFe_{0.8}Co_{0.2}O_3$ measured at several representative temperatures. Inset shows the low-field magnetization curves to clarify the small coercive fields.

To study the MCE of $SrFe_{0.8}Co_{0.2}O_3$ single crystal, a series of isothermal magnetization curves is measured from 200 K to 300 K in steps of 2 K as shown in Fig. 4(a). On the basis of these measurements, the Arrott plots (H/M versus M^2) are obtained to identify the nature of the ferromagnetic phase transition. According to Banerjee's criterion,[29] if all the Arrott plots have positive slopes, the magnetic transition should be second-order. On the other hand, if a negative slope emerges, then the magnetic order is first-order. As presented in Fig. 4(b), all the Arrott plots show positive features, revealing that the ferromagnetic phase transition occurring in $SrFe_{0.8}Co_{0.2}O_3$ is second-order in nature, which is in agreement with magnetic susceptibility measurements mentioned above. The magnetic Curie temperature determined from the Arrott plots is about 274 K.

According to the thermodynamics theory, the ΔS_M can be calculated by using the following function:

$$\Delta S_M\left(\frac{T_2-T_1}{2}\right)=\frac{\Sigma}{T_2-T_1}.$$

Here, Σ is the area between two MH curves measured at temperatures T_1 and T_2, respectively. The calculated $-\Delta S_M(T)$ from the MH curves is shown in Fig. 5. The maximal value of $-\Delta S_M(T)$ measured at 5 T in $SrFe_{0.8}Co_{0.2}O_3$ is about 4.0 $J\cdot kg^{-1}\cdot K^{-1}$, which is comparable to that of $SrFe_{0.5}Co_{0.5}O_3$. However, the full width at half maximum (T_{FWHM}) for a $-\Delta S_M(T)$ peak observed in the former is clearly larger than that in the latter, indicating an enhanced refrigerant capacity in the present $SrFe_{0.8}Co_{0.2}O_3$ single crystal.

The refrigerant capacity and relative cooling power (RCP) are important parameters to evaluate magnetic cooling efficiency for a magnetocaloric material.[30–35] They can respectively be defined by the formulas

$$\mathrm{RC}=-\int_{T_1'}^{T_2'}\Delta S_M(T)\,\mathrm{d}T,\quad \mathrm{RCP}=-\Delta S_{\max}(T_2'-T_1').$$

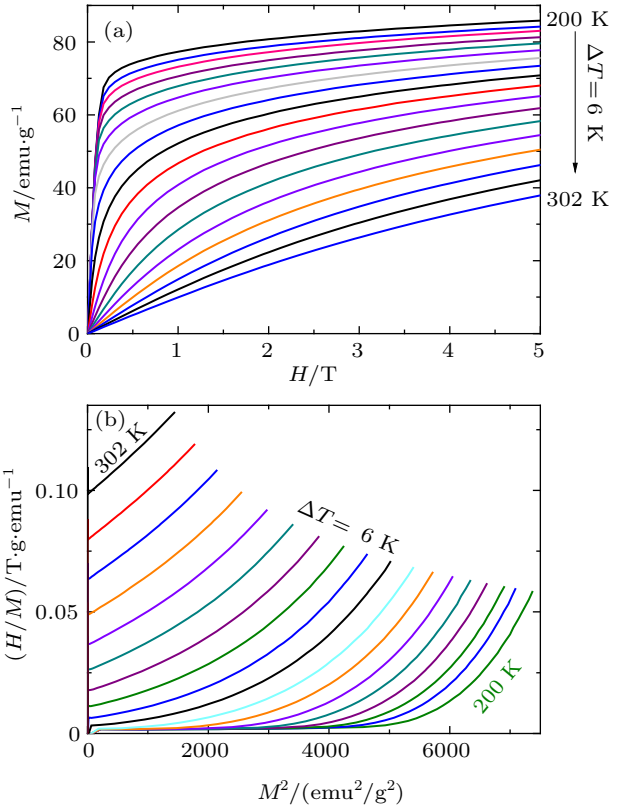


Fig. 4. (color online) (a) A series of isothermal magnetization curves of $SrFe_{0.8}Co_{0.2}O_3$ measured between 200 and 300 K, (b) Arrott plot (H/M versus M^2) constructed from the magnetization data.

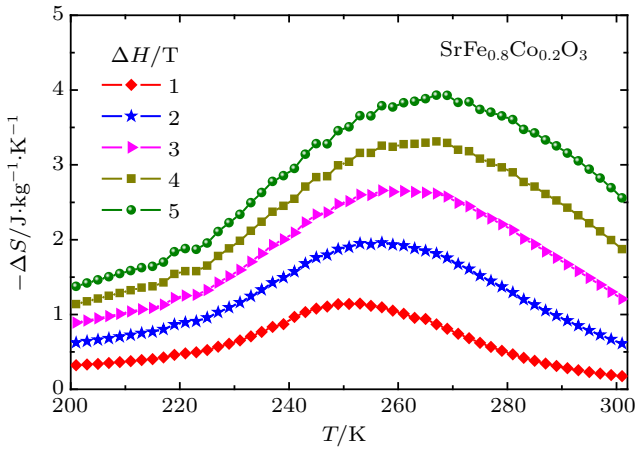


Fig. 5. (color online) Temperature dependences of entropy change $-\Delta S_M$ at different magnetic fields.

Here, T_1' and T_2' are the temperatures corresponding to both sides of the half-maximum value of a temperature dependent entropy change peaks, and ΔS_{max} is the maximum of a magnetic entropy change peak. We calculate the RC and RCP values of $SrFe_{0.8}Co_{0.2}O_3$ as shown in Fig. 6, where the relevant values of other perovskite oxides are also given for comparison. Apparently, both the RC and RCP increase with increasing magnetic field. The RC and RCP values of $SrFe_{0.8}Co_{0.2}O_3$ obtained at 5 T are respectively 277 J/kg and 331 J/kg, which are greatly higher than those observed in other perovskite oxides such as $SrFe_{0.5}Co_{0.5}O_3$ and $BaFeO_3$. By comparison, the RC of $SrFe_{0.8}Co_{0.2}O_3$ at 5 T is even

close to that of the well-studied giant magnetocaloric material $Gd_5Si_2Ge_2$ (RC = 305 J/kg) with a first-order ferromagnetic transition.[13]

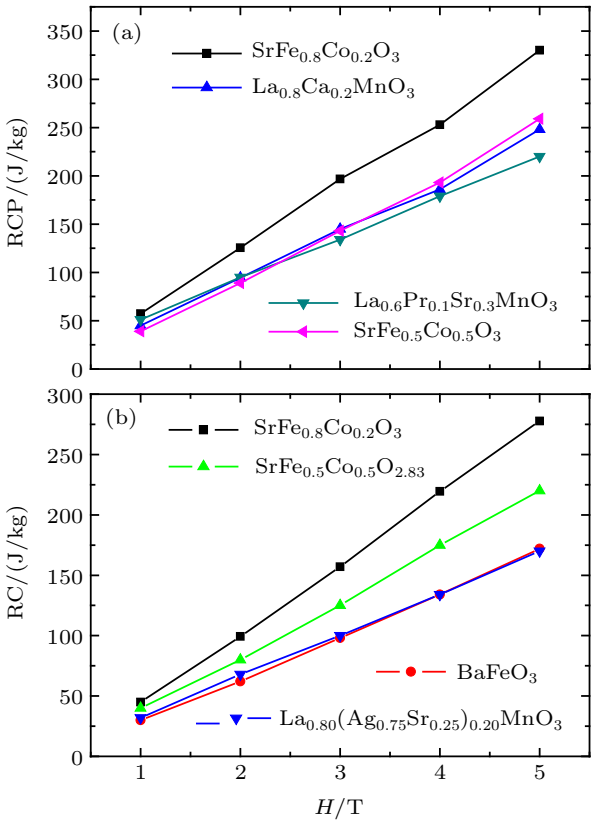


Fig. 6. (color online) (a) Relative cooling power (RCP), and (b) refrigerant capacity (RC) of $SrFe_{0.8}Co_{0.2}O_3$ and other perovskite oxides obtained at different magnetic fields.

4. Summary

Oxygen stoichiometric $SrFe_{0.8}Co_{0.2}O_3$ single crystal is grown by a two-step high-pressure single crystal growth method. Its magnetocaloric effect is investigated in detail by magnetic measurements. A paramagnetism-to-ferromagnetism transition is observed at about 270 K on the basis of the temperature dependence of magnetic susceptibility. No substantial thermal hysteresis is found in the transition temperature region. Isothermal magnetization curves each show a large saturated moment at 2 K and 7 T ($3.63\mu_B$/f.u.), and almost no magnetic hysteresis is found around the Curie temperature. All the Arrott plots show positive features, revealing that the ferromagnetic phase transition is second-order in nature. The maximal value of $-\Delta S_M(T)$ measured at 5 T in $SrFe_{0.8}Co_{0.2}O_3$ is about 4.0 J·kg^{-1}·K^{-1}, which is comparable to that of $SrFe_{0.5}Co_{0.5}O_3$. However, the T_{FWHM} for a $-\Delta S_M(T)$ peak observed in the former is clearly larger than in the later. As a consequence, enhanced RC and RCP values are obtained in $SrFe_{0.8}Co_{0.2}O_3$. These values (RC = 277 J/kg and RCP = 331 J/kg at 5 T) are considerably higher than those observed in most of other perovskite oxides, and even close to those of the well-studied giant magnetocaloric materials such as $Gd_5Si_2Ge_2$ with a first-order ferromagnetic transition. On account of the wide working temperature, large $-\Delta S_M$ and RC, as well as excluding rare elements, the present $SrFe_{0.8}Co_{0.2}O_3$ provides a potential candidate for magnetic refrigeration near room temperature.

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