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Review

Magnetocaloric properties in the Cr-doped $La_{0.7}Sr_{0.3}MnO_3$ manganites

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ABSTRACT

Single-phase polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ with nominal composition of $x = 0.00$, 0.20, 0.40 and 0.50 were prepared by a conventional solid-state reaction method in air. Investigations of magnetization were carried out in the temperature range 5–400 K and magnetic field range 0–8 T. It was found that the Curie temperature T_C decreases with increasing x and the maximum magnetic entropy change $(-\Delta S_M)$ for $x = 0.20$ is $\sim$1.203 and $\sim$2.653 J/kg K, respectively for 2 and 6 T magnetic field near the temperature of 280 K.

Contents

1. Introduction

Magnetic refrigeration has many advantages over gas refrigeration. It has been attracting attention for decades [1]. During the last years, we notice a renewed and increasing interest devoted to the study of magnetocaloric properties of materials. This is due to the possibility of technological application of magnetic materials, which present a magnetocaloric effect, to be the substitute of non-green chemicals such as chlorofluorocarbons and hydro-chlorofluorocarbons used for refrigeration at room temperature [2]. Even at lower temperatures, the magnetic refrigeration still has drawn attention, mainly to be applied to gas liquefaction as natural gas, hydrogen and helium. Therefore, it is important to characterize new promising magnetic materials for magnetic refrigeration in a large temperature span. The key in using magnetic refrigeration at room temperature is to seek the proper material whose Curie temperature should be near room temperature and which can produce a large entropy variation when it goes through a magnetization–demagnetization process. For a long time, the rare-earth elemental Gd was considered to be the only usable material that exhibits a large magnetocaloric effect near room temperature. Over the past few years much work on the ABO_3-type perovskite manganite has attracted considerable attention in scientific studies not only due to its magnetoresistance effect, but also due to its magnetocaloric effect [3–8].

Ceramic preparation route, such as the conventional solid-state reaction method, the sol–gel method and combustion thermal spray techniques were used to prepare rare-earth perovskite materials. The method of synthesis plays an important role on the quality and the magnetocaloric properties of materials [9,10].

In this work, we present our study of magnetic and magnetocaloric properties of perovskite $La_{0.7}Sr_{0.3}MnO_3$ with Mn partly substituted by Cr.

2. Experiment

$La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ ($x = 0.00$, 0.20, 0.40 and 0.50) polycrystalline compounds were prepared by a conventional solid-state reaction method in air. The starting reagents La_2O_3, $SrCO_3$, Cr_2O_3

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and MnO_2, were weighted in stoichiometric proportions. The mixed powders were first heated in air at 1173 K for 72 h to achieve decarbonation. After grinding, they were heated again at 1473 K for 24 h in air to ensure homogenization. Intermediate cooling and mechanical grinding steps were repeated in order to get an accurate homogenization and complete reaction. The powders were pressed into pellet forms under 4 tons/cm^2 and sintered at 1673 K for 2 days in air with several periods of grinding and repelleting. Finally, these pellets were quenched to room temperature. This step was carried out in order to conserve the structure at an annealed temperature. The magnetic properties were explored with a vibrating sample magnetometer, working at temperatures between 5 and 400 K and fields between 0 and 8 T.

3. Results and discussion

Structural characterizations have been reported elsewhere [11,12]: all samples are single-phased and can be indexed in a rhombohedral structure of $R\bar{3}c$ space group. The Cr doping does not change the rhombohedral structure of $La_{0.7}Sr_{0.3}MnO_3$ sample. Fig. 1 shows magnetization versus temperature measured in an applied field of 0.05 T using zero field cooling (ZFC) processes.

All samples show a single magnetic transition from ferromagnetic (FM) to paramagnetic (PM) behaviour as the temperature increases. It can be seen that the FM–PM transition occurs in a narrow temperature range, which means a good homogeneity of the samples.

The FM–PM transition temperature T_C is defined as a maximum in the absolute value of $(\mathrm{d}M/\mathrm{d}T)$. T_C is defined also as an inflection point of $M(T)$ curves. The data show that T_C shifts towards lower temperature with increase in the Cr content ($T_C = 369$ K for $x = 0.00$ and $T_C = 226$ K for $x = 0.50$). The values of magnetization decrease when the doping level of Cr increases. Ferromagnetism in undoped $La_{0.7}Sr_{0.3}MnO_3$ sample is linked to FM Mn^{3+}–O–Mn^{4+} double exchange interactions leading to a maximum magnetic transition temperature of 380 K [13] with the ratio $Mn^{4+}/(Mn^{4+}+Mn^{3+}) = 0.30$. Doping at the Mn site could be of interest in modifying the double exchange strength and hence influences the magnetic behaviour of a doping manganite. With Cr substitution Cr^{3+}–O–Mn^{3+} and Cr^{3+}–O–Cr^{3+} interactions appear; as Cr^{3+} and Mn^{4+} exhibit the same t_{2g} electronic configurations, Mn^{3+}–O–Cr^{3+} interaction is also FM whereas Mn^{4+}–O–Cr^{3+} and Cr^{3+}–O–Cr^{3+} interactions are antiferromagnetic (AFM) like Mn^{4+}–O–Mn^{4+} (two cations with empty e_g orbitals establish a weak AFM superexchange interaction) [14,15]. The magnetization decreases in Cr-doped compounds as x increases and is therefore in good agreement with the gradual development of Cr^{3+}–O–Cr^{3+} and Mn^{4+}–O–Cr^{3+} AFM interactions and the weakening of Mn^{3+}–O–Mn^{4+} and Mn^{3+}–O–Cr^{3+} FM interactions (as Mn^{3+} is progressively replaced by Cr^{3+}).

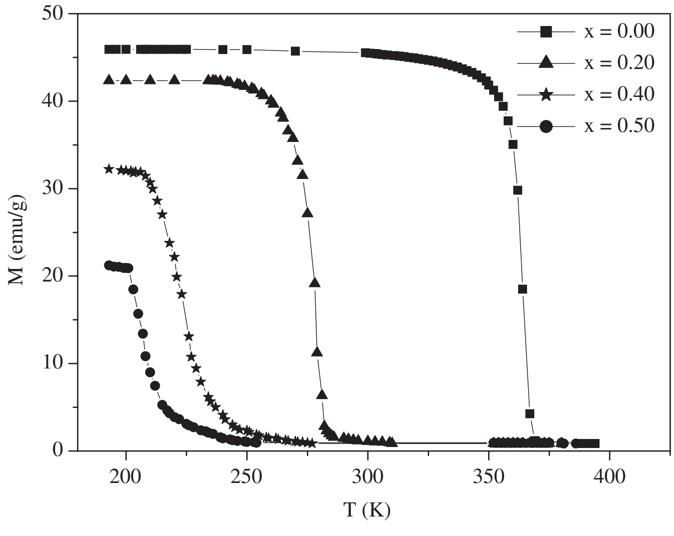

Fig. 1. Magnetization (M) versus temperature (T) curves measured in an applied magnetic field of 0.05 T. The measurements are carried out through ZFC processes.

Fig. 2 shows the evolution of magnetization versus the applied magnetic field obtained at different temperatures (isothermal magnetization), i.e. by measuring the magnetization under a variable field from 0 to 8 T for each temperature. Below T_C, $M(B = \mu_0 H)$ increases sharply with applied magnetic field for $B < 0.5$ T and then saturates above 1 T. The saturation magnetization shifts to higher values of magnetic field with decreasing temperature. This result confirms the FM behaviour of our samples at low temperatures. The evolution of magnetization obtained at different temperatures for the undoped $La_{0.7}Sr_{0.3}MnO_3$ sample and doped with Cr reveals a strong variation of magnetization around the Curie temperature. It indicates that there is a possible large magnetic entropy change associated with the FM–PM transition temperature, occurring at T_C.

In order to investigate this idea, we calculate the magnetic entropy change $(-\Delta S_M)$, which result from spin ordering (i.e., FM ordering). Hence, $(-\Delta S_M)$ can be measured through the adiabatic change of temperature by the application of a magnetic field.

According to a thermodynamic Maxwell's relationship: $(\partial S/\partial H)_T = (\partial M/\partial T)_H$, the magnetic entropy change ΔS_M produced by the variation of a magnetic field from 0 to H is given by [9,16,17]

$$\begin{aligned}\Delta S_M(T,H) &= S_M(T,H) - S_M(T,0)\\ &= \int_0^H \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \qquad (1)\end{aligned}$$

For magnetization measured at discrete field and temperature intervals, the magnetic entropy change defined in Eq. (1) can be approximated by [9,17]

$$\Delta S_M\left(\frac{T_1+T_2}{2}\right) = \left(\frac{1}{T_2-T_1}\right)\left[\int_0^H M(T_2,H)\mu_0 \mathrm{d}H - \int_0^H M(T_1,H)\mu_0 \mathrm{d}H\right] \qquad (2)$$

If one measures the magnetization as a function of field at various temperatures, then the magnetic entropy change is proportional to the area enclosed between any two isothermal magnetization curves divided by the temperature difference between the isotherms. Based on the experimental data, the integral in Eq. (2) can be calculated numerically.

In Fig. 3, we plot the magnetic entropy data $(-\Delta S_M)$ as a function of temperature for $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ sample with $x = 0.00$, 0.20, 0.40 and 0.50. The peak of magnetic entropy changes in the vicinity of the Curie temperature T_C, where the variation of magnetization with temperature is fastest. In addition, we note that the present density of the experimental points location of the $(-\Delta S_M)$ maximum is practically independent of the applied magnetic field strength.

The magnitude of this maximum rises approximately proportional to the magnetic field and reaches maximal values of $(-\Delta S_M^{max})$. For the undoped sample $La_{0.7}Sr_{0.3}MnO_3$, the maximum entropy change $(-\Delta S_M^{max})$ around 365 K are ~1.27 and ~2.782 J/kg K, respectively, for 2 and 6 T magnetic fields. The maximum entropy change $(-\Delta S_M^{max})$ of $La_{0.7}Sr_{0.3}Mn_{0.8}Cr_{0.2}O_3$ around 280 K are ~1.203 and ~2.653 J/kg K, respectively, for 2 and 6 T magnetic fields. For the sample with $x = 0.40$ the maximum entropy change are ~0.473 and ~1.178 J/kg K,