

## Large Magnetic Entropy Change in $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ Perovskite

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In this paper, magnetic property and magnetocaloric effect (MCE) in perovskite manganites of the type  $\text{La}_{(0.75-x)}\text{Ce}_x\text{Ca}_{0.25}\text{MnO}_3$  ( $x = 0.0, 0.2, 0.3$  and  $0.5$ ) synthesized by using the standard solid state reaction method have been reported. From the magnetic measurements as a function of temperature and applied magnetic field, we have observed that the Curie temperature ( $T_C$ ) of the prepared samples strongly dependent on Ce content and was found to be 255, 213 and 150 K for  $x = 0.0, 0.2$  and  $0.3$ , respectively. A large magnetocaloric effect in vicinity of  $T_C$  has been observed with a maximum magnetic entropy change ( $|\Delta S_M|_{\text{max}}$ ) of 3.31 and 6.40 J/kgK at 1.5 and 4 T, respectively, for  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ . In addition, relative cooling power (RCP) of the sample under the magnetic field variation of 1.5 T reaches 59 J/kg. These results suggest that  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$  compound could be a suitable candidate as working substance in magnetic refrigeration at 213 K.

**Keywords :** manganites, magnetocaloric effect, entropy change, magnetization

### 1. Introduction

Recently, a series of doped lanthanum-manganese oxides have been the object of extensive research due to the exotic physics and possible potential spintronic applications [1-3]. More recently, an interesting property has been found in the ferromagnetic manganites near the Curie temperature, the magnetocaloric effect (MCE) [4, 5]. The origin of this effect is based on the adiabatic demagnetization: the application of a magnetic field in a ferromagnetic material induces a spin reorientation thus decreasing the spin entropy. This process is accompanied by a rise of the lattice entropy when the field is applied adiabatically. On the contrary, if we remove off the applied magnetic field, the spin system tends to randomize which increases the spin entropy, reduces the lattice one and consequently lowers the temperature of the system. The main requirements for a magnetic material to possess a large magnetic entropy change are the large spontaneous magnetization as well as the sharp drop in the magnetization associated with the ferromagnetic to paramagnetic transition at  $T_C$  [5, 6].

Many series of substituted perovskite were reported to display a large MCE comparable to that of pure Gd [7]. It has been revealed that the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  based manganite

materials doped with Sr, Pb, Dy, Gd etc. presents a large isothermal entropy change upon an application of a low and modest magnetic field around  $T_C$  [2, 4, 8, 9]. Moreover, the  $T_C$  and magnetization of perovskite manganites can be adjusted by Mn-site substitution [10, 11]. The MCE of the perovskite manganites family can be tuned from low temperature to near and above room temperature, which is beneficial for operating magnetic refrigeration in various temperature ranges.

In this work, we present the magnetic and magnetocaloric properties of  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$  compound. This compound belongs to the family of  $\text{La}_{(0.75-x)}\text{Ce}_x\text{Ca}_{0.25}\text{MnO}_3$  perovskite, for which we have shown that the magnetic phase transition is of the first order. It has high  $\Delta S_M \sim 3.31$  J/kgK at 1.5 T, which is beneficial for technological applications.

### 2. Experimental

Powder samples of  $\text{La}_{(0.75-x)}\text{Ce}_x\text{Ca}_{0.25}\text{MnO}_3$  (LCCMO) ( $x = 0.0, 0.2, 0.3, 0.5$ ) have been synthesized using the standard solid state reaction method at high temperature. Stoichiometric amounts of high-purity analytical grade (99.99%)  $\text{La}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{CeO}_2$ , and  $\text{Mn}_2\text{O}_3$  were mixed and ground in an agate mortar for about four hours. The mixed powders were first heated at 950 °C in air for 12 hours and then heated up to 1100 °C for 48 h. The obtained powders were then pressed into pellets (of about 1mm

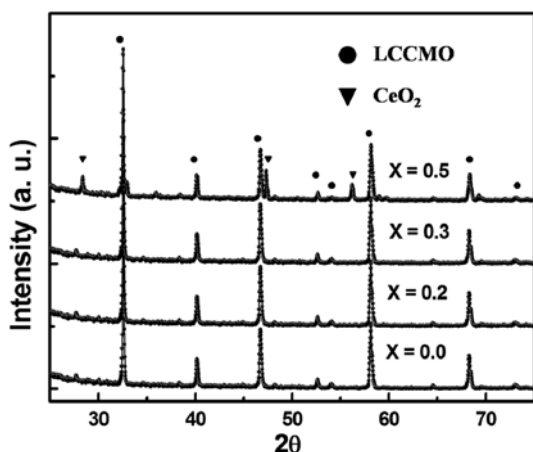
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thickness) and sintered at 1300 °C in air for 48 h with intermediate grinding and repelling. Finally, these pellets were cooled to room temperature at a cooling rate of 1 °C/min. in air in order to get single phase. The structure and phase purity of the samples were checked at room temperature by means of X-ray diffraction (XRD) using Phillips X'pert (MPD 3040) X-ray diffractometer with  $\text{Cu K}\alpha$  radiations ( $\lambda = 1.5406 \text{ \AA}$ ) operated at voltage of 40 kV and current of 30 mA. The morphology of grain boundaries and surfaces were investigated by scanning electron microscope (SEM-JSM5610). The magnetic measurements in the temperature range 100–350 K with a frequency of 40 Hz were performed on a quantum design vibrating sample magnetometer PPMS-6000 VSM.

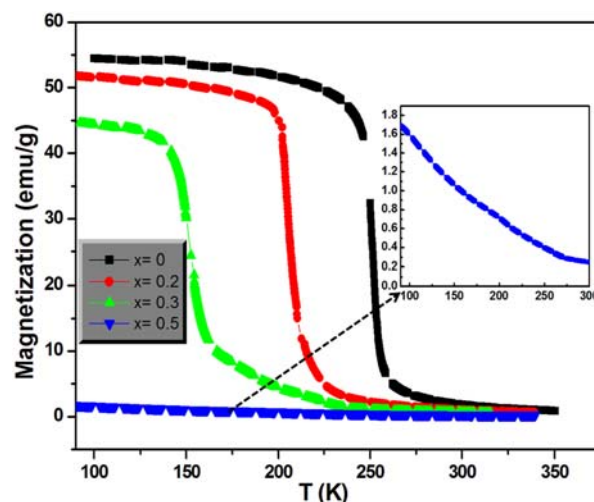
### 3. Results and Discussion

The results of the X-ray diffraction studies (Fig. 1) at room temperature of LCCMO ( $0 \leq x \leq 0.3$ ) compounds indicate that all the samples were found to be single phase and have the same perovskite structure. As the cerium content increases to  $x = 0.5$ , impurity phase ( $\text{CeO}_2$ ) appears in XRD patterns. It has been found that the samples (with  $x = 0.0, 0.2$  and  $0.3$ ) have orthorhombic structure with  $\text{Pnma}$  (PDF NO. 89-8080) space group. The inset of Fig. 4 shows the SEM micrograph of  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ , it also revealed that the sample is homogeneous with micron grain size.

The temperature dependence of magnetization for the LCCMO samples is measured at the constant field of 0.5 T as shown in Fig. 2. The Curie temperature ( $T_C$ ), defined by the maximum in the “absolute value” of  $dM/dT$ , has been determined from the magnetization versus temperature (M-T) curve and found to be 255, 213 and 150 K for  $x = 0.0, 0.2$  and  $0.3$ , respectively. This means  $T_C$



**Fig. 1.** Room-temperature XRD patterns of  $\text{La}_{(0.75-x)}\text{Ce}_x\text{Ca}_{0.25}\text{MnO}_3$  with  $X = 0.0, 0.2, 0.3$  and  $0.5$ .



**Fig. 2.** (Color online) Temperature dependence of magnetization measured at  $H = 0.5 \text{ T}$ .

decreases with increasing Ce content. Since change in  $T_C$  of perovskite manganese oxides with an  $\text{ABO}_3$ -type structure is governed by two factors. One is the A-site average ionic radius  $\langle r_A \rangle$ , and another is the charge carrier density [8, 12]. Since the ionic radii of lanthanum and cerium,  $r_{\text{La}^{3+}} = 1.216 \text{ \AA}$  and  $r_{\text{Ce}^{3+}} = 1.196 \text{ \AA}$  [13], are very close, the substitution of  $\text{La}^{3+}$  by 20% of  $\text{Ce}^{3+}$  does not affect the structure. This fact strengthens the supposition that cerium is trivalent. Thus, the substitution of  $\text{La}^{3+}$  by  $\text{Ce}^{3+}$  would not change the charge carrier density. Hence the decrease in  $T_C$  with increasing Ce content for samples can only be attributed to the change in A-site ionic radius  $\langle r_A \rangle$ . As Ce content increases, the average A-site ionic radius  $\langle r_A \rangle$  decreases, leading to a change in Mn–O bond length and Mn–O–Mn bond angle. This causes weakening an exchange effect. Consequently, the Curie temperature decreases. The phenomenon has also been revealed in the  $\text{LaCaMnO}_3$ -based manganite materials doped with R (R = Nd, Gd, and Tb) [8, 14]. In order to get a deeper insight of the type of magnetic transition, we carried out magnetization measurements versus applied magnetic field (M-H) up to 4 T at several temperatures near  $T_C$  (Fig. 3). The magnetization below  $T_C$  sharply increases up to 0.5 T and then saturates. We derive the Arrott plots ( $H/M$  vs.  $M^2$ ) from M-H measurements and the results plotted are shown in Fig. 4. It shows the first order magnetic phase transition (ferromagnetic to paramagnetic) behavior because of negative slope in the high-field regions [15].

The magnetic entropy, which is associated with the MCE, can be calculated from the isothermal magnetization curves (Fig. 3) under the influence of a magnetic field. According to the classical thermodynamical theory,

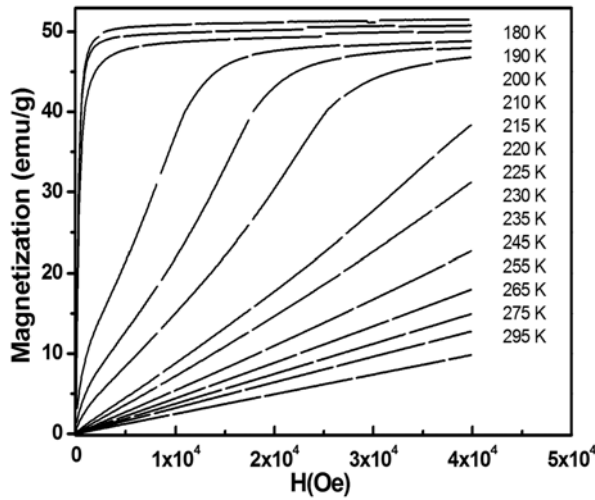


Fig. 3. Isothermal magnetization curves (M-H) measured at different temperatures around  $T_C$  for the  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ .

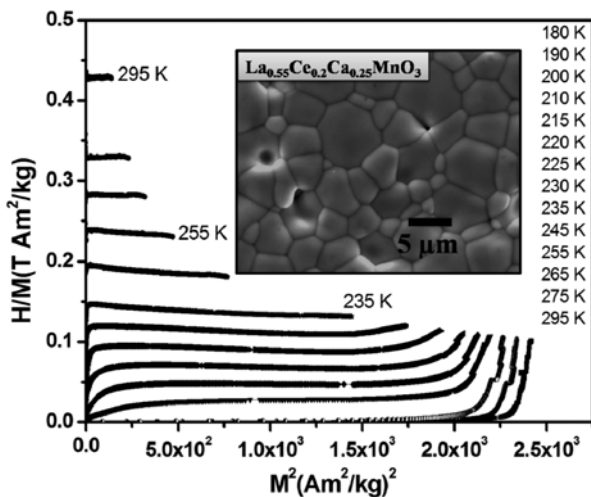


Fig. 4.  $H/M$  versus  $M^2$  isotherms for  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ . Inset shows the morphology of the sample.

the magnetic entropy change  $\Delta S_M$  produced by the variation of a magnetic field from 0 to  $H_{\max}$  is given by [7]

$$\Delta S_M(T, H) = \int_0^{H_{\max}} \left( \frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

To evaluate the magnetic entropy change ( $\Delta S_M$ ), numerical approximation of the integral in Eq. (1) is required. The usual method is to use isothermal magnetization measurement at small discrete field intervals and then  $\Delta S_M$  can be approximated from Eq. (1) by

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \quad (2)$$

Where,  $M_i$  and  $M_{i+1}$  are the experimental values of the

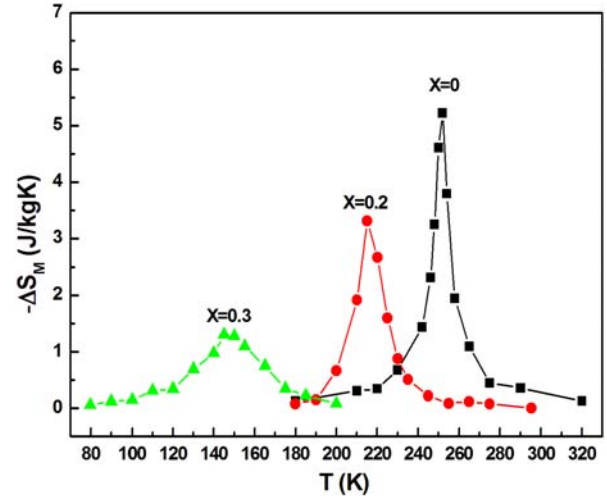


Fig. 5. (Color online) Magnetic entropy change, for a magnetic field change of 1.5 T, obtained for the  $\text{La}_{(0.75-x)}\text{Ce}_x\text{Ca}_{0.25}\text{MnO}_3$  ( $x=0.0, 0.2, 0.3$ ) compounds.

magnetization at  $T_i$  and  $T_{i+1}$ , respectively. Using Eq. (2) and experimental M-H curves at various temperatures, the magnetic entropy change with the magnetic field variation can be calculated.

The magnetic entropy changes, determined numerically using Eq. (2) and the M-H curves, are shown in Fig. 5. It can be seen that all samples present large magnetic entropy change and that  $\Delta S_{M \max}$  decreases when increasing Ce concentration. From Eq. (1), it is obvious to find that the magnetic entropy changes depend on the value of  $(\partial M / \partial T)_H$ . Therefore, the large magnetic entropy change usually occurs near the  $T_C$  where the magnetization changes

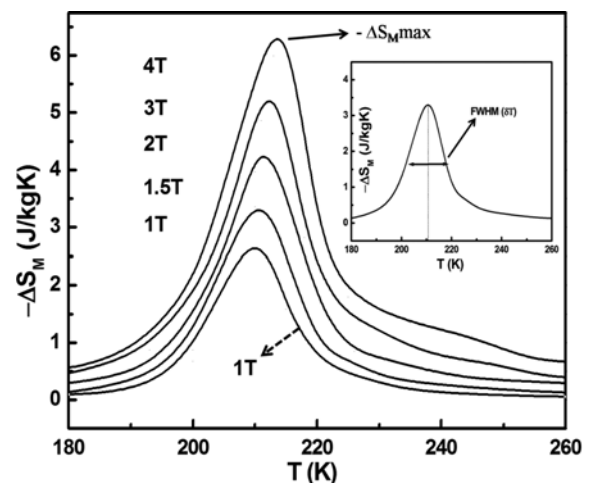


Fig. 6. Magnetic entropy change ( $-\Delta S_M$ ) plotted as a function of temperature at different applied fields; inset shows the  $-\Delta S_M$ -T curve at  $H = 1.5$  T, the line double arrows represents the full width at half maximum of the magnetic entropy change.

swiftly with the variation of temperature. Furthermore, the effect may be further maximized as the variation in magnetization with respect to temperature appears in a narrow temperature interval [16]. Similar to the above analysis, Fig. 6 shows that the maximum of magnetic entropy changes under the different applied magnetic fields, always concentrate on the  $T_C$  region. With the increase of magnetic field, the peak of magnetic entropy changes lightly moves to a higher temperature due to the shift of effective  $T_C$  by the applied magnetic field. Here, the maximum magnetic entropy change  $\Delta S_M$  is about 3.31 J/kgK with the magnetic field variation of  $\Delta H = 1.5$  T, large enough to be used in magnetic refrigeration.

Usually the most important factor for selecting magnetic refrigerants is based on the cooling power per unit volume, namely, the relative cooling power (RCP) [7]. The RCP has been defined as

$$RCP(S) = -\Delta S_M^{\max} \times \partial T_{FWHM} \quad (3)$$

Where,  $\Delta S_M$  is the maximum magnetic entropy change and  $\partial T_{FWHM}$  is the full width at half maximum of the magnetic entropy change curve. The material with a larger RCP value usually represents a better magnetocaloric substance due to its high cooling efficiency. Here, as shown in the inset of Fig. 6, the RCP of  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$  sample under the magnetic field variation of 0 to 1.5 T reaches 59 J/kg by using Eq. (3), further indicating that it can be used in magnetic refrigeration.

#### 4. Conclusions

We have investigated the structural, magnetic and magnetocaloric properties of  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$ . It has been observed that the magnetic phase transition from ferromagnetic to paramagnetic is of first order. A large magnetic entropy change of 3.31 J/kgK at field variation of  $\Delta H = 1.5$  T near the  $T_C$  has been observed. Additionally, a large relative cooling power of 59 J/kg has been

determined, which makes  $\text{La}_{0.55}\text{Ce}_{0.2}\text{Ca}_{0.25}\text{MnO}_3$  to an attractive candidate for magnetic refrigeration in the vicinity of the temperature 213 K.

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