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Effect of sintering temperature on structure, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ manganite

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Abstract: The effect of sintering temperature on the structure, magnetic transition and magnetic entropy of $La_{0.6}Ca_{0.4}MnO_3$ manganite was studied. It was observed that this compound belongs to the orthorhombic structure with the *Pnma* space group without any impurity phase. The effect of sintering temperature on the Curie temperature (T_C) was studied. The small increment in T_C is found with increasing the sintering temperature. The magnetocaloric study exposes a quite large change of the magnetic entropy, which varies with sintering temperature. For an applied magnetic field of 3 T and sintering temperature of 1300 °C, the relative cooling power (RCP) is 89 J/kg. As a result, the studied compound can be considered as potential material for magnetic refrigeration near and below room temperature.

Key words: manganite; magnetocaloric effect; sintering temperature; colossal magnetoresistance

1 Introduction

Magnetic refrigeration has been paid much attention in recent years due to its high energy efficiency and being environment friendly, in contrast to the traditional gas-compression refrigeration technology [1,2]. More recently, an interesting property has been found in the manganites near the Curie temperature, the magnetocaloric effect (MCE) for refrigeration [3]. The phenomenon was firstly observed by WARBURG [4] in 1881. In ferromagnetic manganites, the magnetic spins align with an applied magnetic field, reducing the magnetic entropy of that spin system. If this process is performed adiabatically, this reduction in the spin entropy is accompanied by an increase in the lattice entropy. And then the temperature of the material rises. In contrast, when the field is removed, the spins tend to randomize, increasing the magnetic entropy and lowering the lattice entropy and the temperature. The possible use of the MCE at near room temperature requires the exploration of new kind of magnetic materials [5]. Most important requirements for magnetic refrigeration are large magnetic entropy change, magnetic phase transition, and Curie temperature near room temperature. The giant MCE in the pseudo-binary alloy $Gd_5(Si{-}Ge)_4$ in the range of 50 to 280 K [6,7] and at about 300 K has been measured in $MnFeP(O_{0.45}As_{0.55})$ [8]. Gd based materials are considered for a large magnetocaloric effect near its Curie temperature (293 K) [9,10]. Although they are good candidates for magnetic refrigeration, they are limited either by the dangerous pnictides used in their fabrication or by expensiveness. In recent years, various types of ferromagnetic manganese oxides have attracted attention as alternative candidates to replace Gd for this purpose [11,12].

In this work, the experiment was carried out on the bulk polycrystalline samples of $La_{0.6}Ca_{0.4}MnO_3$ manganite. the effects of sintering temperature on structure, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ manganite were investigated. The MCE properties of the samples were analyzed by computing the magnetic entropy change using magnetization data.

2 Experimental

Polycrystalline sample of nominal composition $La_{0.6}Ca_{0.4}MnO_3$ was fabricated by using standard

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solid-state reaction procedure under ambient condition. Stoichiometric amounts of high-purity analytical grade (99.99%) La_2O_3, CaO and Mn_2O_3 powders were mixed by ball-mill process for 24 h in ethanol medium. The mixed powder was first calcined at 950 °C in air for 10 h and then heated up to 1050 °C for 10 h. After grinding, mixed powder was pressed into pellets and sintered at 1000 °C for 20 h and cooled down to room temperature. This sintering process was repeated at 1100, 1200, 1300 °C for 20 h. The structure and phase purity of the sample were checked at room temperature by means of X-ray diffraction (XRD) using Phillips X'pert (MPD 3040) X-ray diffractometer with Cu K_α radiations (λ=0.15406 nm) operated at voltage of 40 kV and current of 30 mA. The morphologies of grain boundaries and surfaces were investigated by scanning electron microscope (SEM-JSM5610). The magnetic measurements in the temperature range of 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 (Fig. 1) of $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at various temperatures indicate that all the samples have single phase without a detectable secondary phase. The absence of any kind of impurity phase suggests the complete reaction among the reactants during the sintering process. As the sintering temperature increases, the increase in the crystallinity is found, as shown in the XRD patterns.

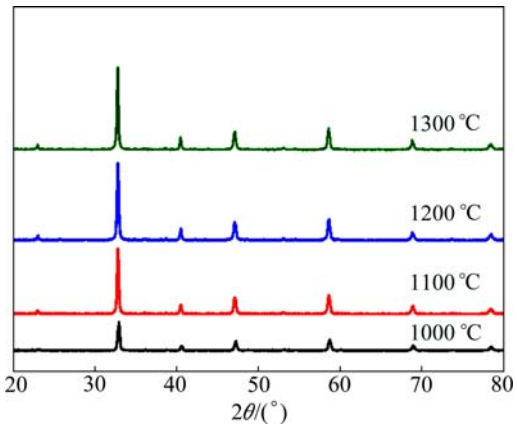

Fig. 1 XRD patterns of $La_{0.6}Ca_{0.4}MnO_3$ samples sintered at various temperatures

All the observed XRD peaks were indexed to the orthorhombic structure with *Pnma* space group using powder-X software, which matches very well with the PDF card No. 89-8080. The SEM image (Fig. 2) reflects a smooth polycrystalline structure with inhomogeneous grain size distribution. By increasing the sintering temperature, the average grain size increases.

The temperature dependence of magnetization for the samples was measured at the constant field of 0.5 T, as shown in Fig. 3. The Curie temperature (T_C), defined by the maximum in the "absolute value" of dM/dT, has been determined from the magnetization versus

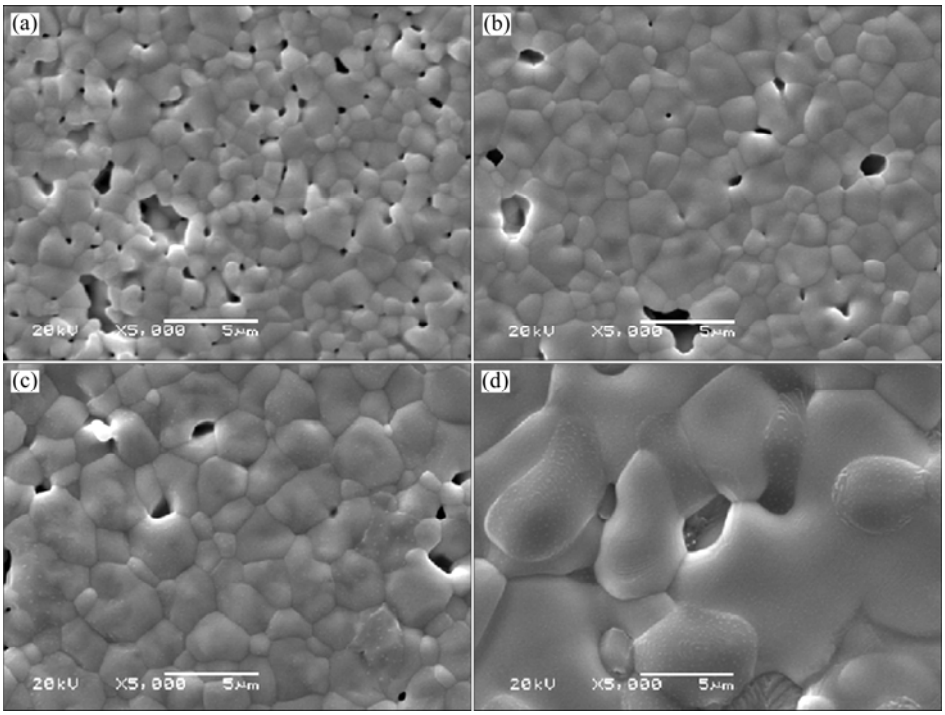

Fig. 2 SEM images of $La_{0.6}Ca_{0.4}MnO_3$ samples sintered at various temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C

temperature (M−T) curve and found to be 270, 271, 272 and 272 K for samples sintered at 1000, 1100, 1200, 1300 °C, respectively. There is no significant change at T_C with changing the sintering temperature. In order to investigate the behaviour of magnetization as a function of magnetic field, the evolution of magnetization versus the applied magnetic field obtained at different temperatures for the samples sintered at 1000 and 1300 °C are shown in Fig. 4. The M−H curves reveal a strong variation of magnetization around the Curie temperature.

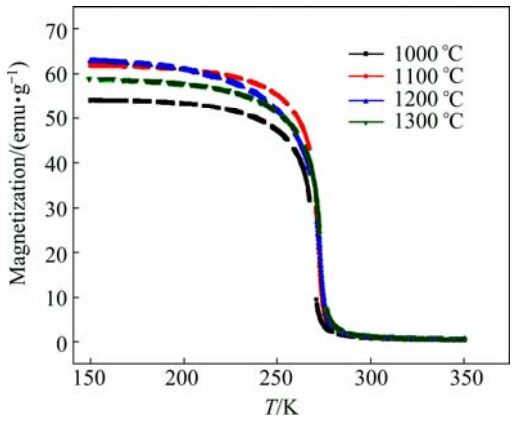

Fig. 3 Temperature dependence of magnetization for $La_{0.6}Ca_{0.4}MnO_3$ samples sintered at various temperatures

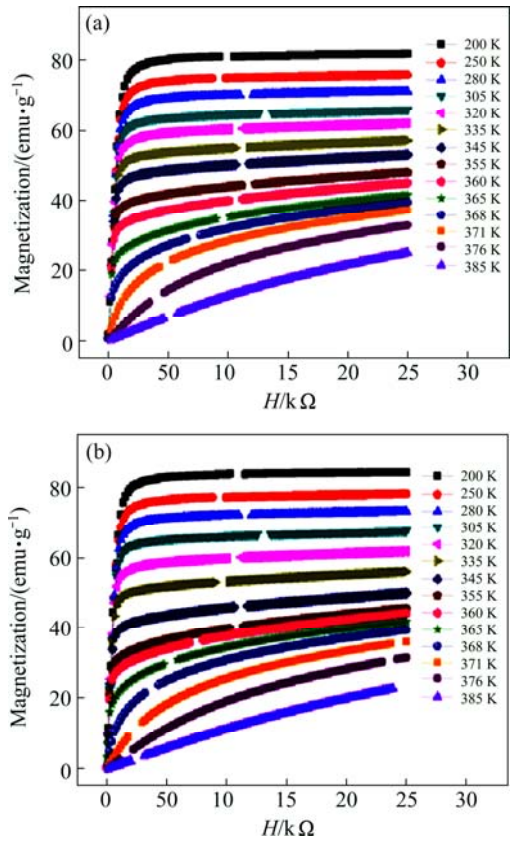

Fig. 4 Isothermal magnetization curves (M−H) measured at different temperatures around T_C for $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at 1000 °C (a) and 1300 °C (b)

It is indicated that there is a large magnetic entropy change associated with the ferromagnetic−paramagnetic transition near T_C. The magnetization measurements versus applied magnetic field (M−H) up to 3 T at several temperatures near T_C show that, below T_C magnetization increases sharply up to 0.5 T and then saturates. The magnetocaloric effect in terms of isothermal magnetic entropy change can be calculated either by using the adiabatic change of temperature under the application of a magnetic field or through the measurement of initial isothermal magnetization versus magnetic field at various temperatures. In the present case, the second method is to avoid the difficulties of adiabatic measurements. On the basis of the thermodynamical theory, magnetic entropy change, ΔS_M, associated with a magnetic field (H) variation is given by

$$\Delta S_M(T,H) = S(T,H) - S(T,O) = \int_0^H (\frac{\partial M}{\partial T})_H \, dH \quad (1)$$

For magnetization measured at discrete applied magnetic field, this equation can be approximated as [13]

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

where M_i and M_{i+1} are the magnetization values obtained at temperatures T_i and T_{i+1} in a field H_i, respectively.

Figure 5 shows the magnetic entropy change as a function of temperature for $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at various temperatures.

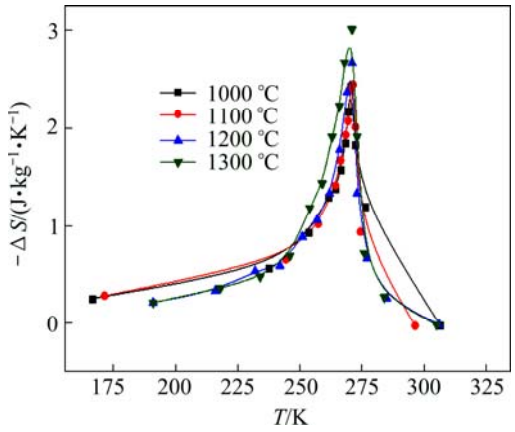

Fig. 5 Temperature dependence of magnetic entropy change (H=1 T) of $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at various temperatures

As seen from Fig. 5, the maximum in the magnetic entropy change, ΔS_M^{max}, is obtained near T_C with the applied magnetic field of 1 T. A clear plot of magnetic entropy change as a function of sintering temperature is shown in Fig. 6. It is clearly seen that, by increasing the sintering temperature, ΔS_M^{max} increases. The highest vaule 2.99 J/(kg·K) of ΔS_M^{max} is obtained for the sample

sintered at 1300 °C.

The most important factor, which provides the cooling efficiency of materials for magnetic refrigeration is based on the cooling power per unit volume, namely, the relative cooling power (RCP, P) [14−18]. It is evaluated by considering the magnitude of the magnetic entropy change, ΔS_M^{max}, and its full-width at half-maximum of the magnetic entropy change versus temperature curve and given as

$$P = -\Delta S_M^{max} \times \delta_{FWHM} \quad (3)$$

ΔS_M^{max} is found higher in the case of sample sintered at 1300 °C. However, RCP is lower as compared to the sample sintered at 1000 °C. This can be attributed to the broadening of the phase transition in the case of sample sintered at 1000 °C. On the other hand, RCP values for both samples exhibit a linear dependence on the applied magnetic field. As seen from Fig. 7, RCP increases with increasing applied magnetic field (Table1), which is indicative of a much larger entropy change being expected at higher magnetic fields. The material with a larger RCP value usually represents a better magnetocaloric efficiency.

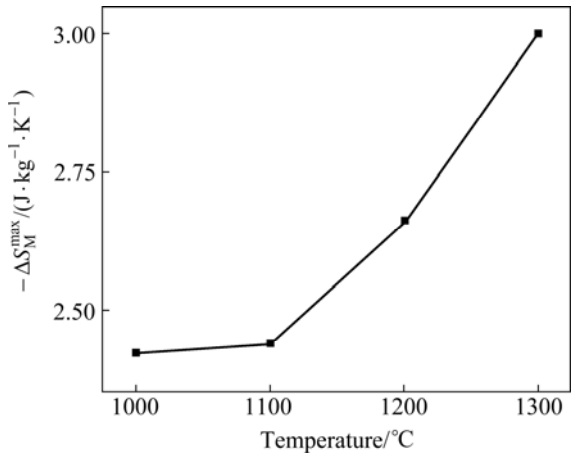

Fig. 6 Maximum in magnetic entropy change, ΔS_M^{max}, as a function of sintering temperature for $La_{0.6}Ca_{0.4}MnO_3$ sample

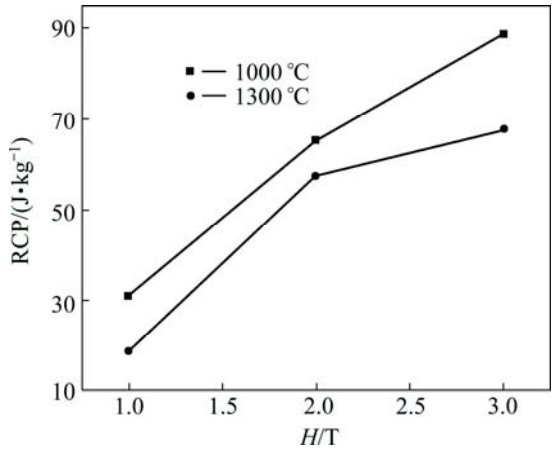

Fig. 7 RCP as a function of magnetic field for $La_{0.6}Ca_{0.4}MnO_3$ same sintered at 1000 and 1300 °C

Table 1 RCP values of $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at two different temperatures

Magnetic field/T	Temperature/°C	RCP/(J·kg^{-1})
1	1000	31.0
	1300	18.7
2	1000	65.4
	1300	57.5
3	1000	89.0
	1300	67.8

4 Conclusions

The structure, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at various temperatures were systematically investigated. All samples crystallize in orthorhombic structure with *Pnma* space group. The magnetic field versus temperature curves show that the transition from ferromagnetic to paramagnetic phase is near room temperature. The *M*−*H* curves reveal a strong variation of magnetization around the Curie temperature. A large magnetic entropy change of 2.99 J/(kg·K) at applied magnetic field of 1 T occurs for the sample sintered at 1300 °C. But the highest value of 89 J/kg of relative cooling power (RCP) with the applied magnetic field of 3 T is obtained for the sample sintered at 1300 °C, which makes $La_{0.6}Ca_{0.4}MnO_3$ a suitable candidate for magnetic refrigeration depending on its sintering temperature.

Acknowledgements

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烧结温度对 $La_{0.6}Ca_{0.4}MnO_3$ 结构、磁性和磁致热效应的影响

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摘　要：研究了烧结温度对 $La_{0.6}Ca_{0.4}MnO_3$ 的结构、磁转变和磁熵的影响。观察表明，该化合物属于具有 *Pnma* 空间群的斜方晶系结构，不含任何杂质。研究烧结温度对居里温度(T_C)的影响，发现提高烧结温度，T_C 稍有增大。磁致热效应研究显示，随着烧结温度的变化，磁熵会发生显著的变化。在外加磁场为 3 T、烧结温度为 1300 °C 时，相对冷却能(RCP)为 89 J/kg。因此，该化合物可以考虑作为在室温附近或低于室温的潜在磁制冷材料。

关键词：亚锰酸盐；磁热效应；烧结温度；巨磁阻

(Edited by Ai-hua CHEN)