The Magnetic Entropy Change on La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ Compound

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The magnetocaloric effect and magnetization behavior have been analyzed in the double-perovskite La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ compound with the sintering temperature at 1273 K. Samples were fabricated by the conventional solid-state reaction method. X-ray diffraction measurement revealed that all the samples had a single phase in orthorhombic. Detailed investigations of the magnetic entropy behavior of the samples were discussed with the variation of $T_C$. The magnetic entropy changes, $\Delta S_M$ of approximately 0.36-1.14 J/kg K were obtained in the temperature range of 145-350 K for the La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ compound. The enhancement of the magnetic entropy change is believed to be due to changes in the microstructure, which changes the magnetic part of the entropy of a solid around the magnetic ordering temperature.

Keywords: magnetic entropy change, perovskite materials, magnetization behavior

1. Introduction

The magnetic caloric effect (MCE) is intrinsic to magnetic solids and is induced via the coupling of the magnetic sub-lattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change in the magnetic field. It can be measured and calculated as the adiabatic temperature change $\Delta T_{ad}(T, \Delta H)$ or as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$ [1]. Traditionally, diluted paramagnetic slats and rare earth intermetallic compounds that display significant MCE have been considered as attractive materials for cryogenic applications [2, 3]. Especially, double perovskite La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ demonstrates room temperature magnetoresistance and a ferrimagnetic phase transition with a Curie temperature of 145-350 K [4-7]. Therefore, it would be very interesting to study the magnetocaloric effect for this kind of material because of the Curie temperature being near room temperature. We have already published reports on the magnetocaloric effect of the Ba$_{1.8}$La$_{0.2}$FeMoO$_3$ compound [8]. The magnetic entropy change can be tuned by a suitable sintering process. In this work, the magnetocaloric effect of the La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ compound was investigated. Materials with proper Curie temperature and large spontaneous magnetization have many peculiar properties that are attractive for applications as magnetic refrigerants [9-11].

2. Experiments

Polycrystalline La$_{0.7}$Ba$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07$) samples were prepared by a standard solid-state reaction in a stream of 5% H$_2$/Ar gas at a sintering temperature of 1273 K for 12 hrs. After sintering a stoichiometric mixture of high purity Fe$_2$O$_3$ (99.99%), FeO (99.99%), BaO (99.99%) and MnO$_2$ (99.999%) powders were fired in an Al$_2$O$_3$ crucible at 1573 K in an electric furnace. X-ray diffraction patterns were taken with a Phillips diffractometer using Cu K$\alpha$ radiation. The temperature dependence of the magnetization was measured with a commercial vibrating sample magnetometer (VSM) at various temperatures from 80 K to 500 K in fields up to 10 kOe.

3. Results and Discussion

On the basis of the thermodynamic theory, the magnetic entropy change caused by the variation of the external magnetic field from 0 to $H_{\text{max}}$ is given by

$$\Delta S_M = \int_0^{H_{\text{max}}} \left(\frac{\partial S}{\partial H}\right) dH$$

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From the Maxwell’s thermodynamic relationship:

\[
\left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H
\]

Eq. (1) can be rewritten as follows:

\[
\Delta S_M = \int_{H_0}^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H dH
\]  

(3)

Numerical evaluation of the magnetic entropy change was carried out from formula (3) using isothermal magnetization measurements. In spite of magnetization measurements at small discrete field and temperature intervals, \(\Delta S_M\) can be computed approximately from Eq. (3) by:

\[
\frac{\partial}{\partial H} \left( \frac{\partial M}{\partial T} \right)_H = \frac{\partial}{\partial T} \left( \frac{\partial M}{\partial H} \right)_T = \frac{\partial^2 M}{\partial T \partial H}
\]
\[ \Delta S_M = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \]  

(4)

Thus, the magnetic entropy changes associated with applied field variations can be calculated from Eq. (4).

Figure 1 presents the X-ray diffraction patterns for the La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) compound sintered at 1273 K. It revealed that all La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) samples had a single phase with an orthorhombic structure, and there are no additional diffraction peaks related to the initial powders.

Figure 2 shows the temperature dependence of magnetization for the La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) compound measured at 100 Oe from 80 K to 500 K. The magnetic transition temperature, \(T_c\), is defined as the minimum temperature of the \(dM/dT\) vs. \(T\) curve [12]. The sharp decrease in magnetization implies the occurrence of magnetic ordering [13]. As shown in Fig. 3, the Curie temperature decreased from 346 to 132 K with increasing Fe concentration.

The top panel of Figs. 4-6 demonstrates the isothermal magnetization curves in the vicinity of Curie temperature for the La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) (\(x = 0.02, 0.04, 0.05\)) compound sintering at 1273 K. To determine the type of the phase transition for the La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) compound, the measured data for the M-H isotherms were transferred into H/M versus \(M^2\) plots and displayed in the bottom panel of Figs. 4-6. According to the Banerjee criterion, the negative slope in H/M versus \(M^2\) plots means that the ferromagnetic to paramagnetic phase transition is first order [14]. As shown in Fig. 4, the negative slopes in the lower \(M^2\) region, implies that this sample belongs to the materials displaying a first-order transition. Figure 7 presents the temperature dependence of the magnetic entropy change for the La\(_{0.7}\)Ba\(_{0.3}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) compound with an external field of 10 kOe. The magnetic entropy change, a
function of temperature and magnetic field, produced by the variation of the magnetic field from 0 to $H_{\text{max}}$ is calculated by Eq. (4). As can be seen in Fig. 7, with a magnetic field varying from 0 to 10 kOe, $\Delta S_M$ is approximately 0.36-1.14 J/kg K. Our results show that the maximum value of $\Delta S_M$ obtained at the $x = 0.02$ compound. Especially, the magnetocaloric effect takes place around room temperature about 300 K. The interesting features of this compound make it a working material in room temperature magnetic refrigeration due to the proper substitution of Fe. This, most likely, opens promising applications in magnetic cooling systems.

4. Conclusion

The magneto-caloric effect and magnetization behavior have been analyzed in the double-perovskite $\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compound with a sintering temperature of 1273 K. X-ray diffraction measurements revealed that all the samples had a single phase in orthorhombic. The magnetic entropy changes, $\Delta S_M$ of about 0.36-1.25 J/kg K were obtained in the temperature range of 145-350 K. The maximum values of $\Delta S_M$ obtained at the $x = 0.02$ compound with Curie temperature of 297 K. Compared with Gd and other candidate materials, these oxide materials are much easier to fabricate and possess higher chemical stability, which is beneficial for many application fields.

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References