Large magnetic entropy change above 300 K in a La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ single crystal

Manh-Huong Phana,*, Hua-Xin Penga, Seong-Cho Yub, Nam Hwi Hurc

aDepartment of Aerospace Engineering, Bristol University, Queen's Building 2.29, University Walk, Bristol BS8 1TR, UK
bDepartment of Physics, Chungbuk National University, Cheongju 361-763, South Korea
cCenter for CMR Materials, Korea Research Institute of Standards and Science, Yusong, P.O. Box 102, Taejon 305-600, South Korea

Available online 14 December 2004

Abstract

A detailed study of the magneto-caloric effect in a single crystal of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ has been made. The magnetic entropy change ($\Delta S_M$) reaches a maximum value of $\sim 7.45$ J/kg K at $\sim 308$ K for a 50 kOe field change, which is ideal for room-temperature magnetic refrigeration applications. Due to the absence of grains in the manganite single crystal, the $\Delta S_M$ distribution of this sample is much more uniform than that of gadolinium and polycrystalline manganites, which is desirable for an Ericson-cycle magnetic refrigerator. The single crystal has the large magnetic entropy change induced by low magnetic field change, which is beneficial for the household application of active magnetic refrigerant (AMR) materials. These results indicate that the present single crystal is an excellent candidate as a working material for room-temperature AMR.

© 2004 Elsevier B.V. All rights reserved.

PACS: 75.30.Sg

Keywords: Entropy; Magnetocaloric effect; Magnetic refrigeration; Single crystal

1. Introduction

Magnetic refrigeration, which is based on the magneto-caloric effect (MCE), has attracted much attention from the aspects of fundamental and applied research. The MCE is an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material caused by an applied magnetic field. Generally, there are two key requirements for a magnetic material to possess a large MCE. One is a large enough spontaneous magnetization, belonging to a class of heavy rare-earth metals [1,2], and the other is a sharp drop in magnetization which is associated with the ferromagnetic-paramagnetic transition at the Curie temperature, as was found in perovskite manganites [3]. It has been shown that, due to their high magnetic moments, heavy-rare-earth elements and their compounds are the best candidate materials for finding a large MCE. For example, the highest MCE involving a second-order transition is found in gadolinium, which can be used to achieve cooling between 270 and 310 K [1]. Recently, Pecharsky and Gschneidner [2] have discovered an extraordinarily large MCE in Gd$_5$(Si$_2$Ge$_2$), which undergoes a simultaneous first-order structural and magnetic-phase transition that is believed to be responsive for the large MCE. This new compound exhibits the MCE about two times as large as that exhibited by gadolinium, the best known magnetic

*Corresponding author. Tel.: +44 0117 928 7697; fax: +44 0117 927 2771.
E-mail address: M.H.Phan@bristol.ac.uk (M.-H. Phan).

0304-8853/$-see front matter © 2004 Elsevier B.V. All rights reserved.
refrigerant material for near-room-temperature applications. However, further efforts to seek for new materials, especially materials without rare-earth elements [3–5], and exhibiting large MCE in response to low applied field, are of significant importance. In streamlining this interest, colossal magnetoresistance (CMR) in perovskite manganites has also generated growing interest in the science community, due to their excellent performance in magnetic and sensing sensor technology, especially for magnetic recording. Since the magnetic properties of perovskite manganites, Curie temperature and saturation magnetization, are strongly doping-dependent, these typical materials are believed to be good candidates for magnetic refrigeration at various temperatures. In a recently remarkable work [6], we have reported that such lanthanum manganite single crystals can meet the requirements for an active magnetic refrigeration (AMR) material that should have large magnetic entropy change induced by low magnetic field change and showing a uniform $\Delta S_M$ distribution—which is desirable for an Ericson-cycle magnetic refrigerator.

In this work, we present the results of a detailed study of MCE in a single crystal of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$, which is currently considered as an excellent candidate for room-temperature magnetic refrigeration applications.

2. Experimental

Single crystals of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ were prepared by the floating zone method using an infrared radiation convergence-type image furnace that consists of four mirrors and halogen lamps; details of the growth conditions can be found elsewhere [7]. The starting ceramic rods were obtained from the solid-state reaction of a stoichiometric mixture of La$_2$O$_3$, CaCO$_3$, SrCO$_3$ and MnCO$_3$. X-ray diffraction data and electron-probe microanalysis confirmed the quality of the crystal. The magnetic measurements were performed using a Quantum Design MPMS-5 SQUID magnetometer or a PPMS-7 magnetometer.

3. Results and discussion

Fig. 1 shows temperature dependences of the magnetization of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ measured in the fields of 100 Oe and 5 kOe (the inset of Fig. 1). The Curie temperature ($T_C$), defined by the maximum in the “absolute value” of $dM/dT$, has been determined from the $M$–$T$ curve and found to be $\approx 307$ and $\approx 308$ K at $H = 100$ Oe and 5 kOe, respectively. It is noted that, at $H = 5$ kOe, the shape of the $M$–$T$ curve remains almost unchanged, while the $T_C$ is shifted to a higher temperature ($\approx 308$ K). Therefore, the material in the present study could be expected to show large MCE near its Curie temperature [6].

It can be seen clearly from Fig. 2 that there is a drastic change of the magnetization around $T_C$, indicating a large magnetic entropy change. This coincides with the rapid reduction of magnetization at $T_C$ (Fig. 1). Another feature to be noted is that a large proportion of changes of the magnetization occurs in a relatively low-field range (<20 kOe), which is beneficial for the household application of MCE materials.
In order to evaluate the MCE of the present material, we calculated changes of the magnetic entropy ($\Delta S_M$) caused by the application of external magnetic fields from the isothermal curves of magnetization versus the applied field by using the following expression [3]:

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i,$$

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

In Fig. 3, the magnetic entropy change is plotted against temperature for the sample at $\Delta H = 10, 30$ and $50$ kOe. Upon $50$ kOe applied field, the highest value of $\sim 7.45$ J/kg K for the sample is found at a temperature of $\sim 308$ K. It is found that the MCE value of the present single crystal is comparable with that of gadolinium [1] and is clearly larger than that found in several other manganese oxides [8–10]. It is worth noting that, due to the absence of grains in the present manganite single crystal, the $\Delta S_M(T)$ distribution of this sample is much more uniform than that of gadolinium and polycrystalline manganites. This is desirable for an Ericson-cycle magnetic refrigerator. Furthermore, the large magnetic entropy changes in the present sample are observed to occur at temperatures above $300$ K. This allows water to be used as a heat transfer fluid in the room-temperature magnetic refrigeration regime [11]. In addition, compared with gadolinium and its compounds, perovskite-like structured materials are easier to fabricate and possess a higher chemical stability as well as a higher resistivity. The high resistivity is beneficial to lowering the eddy current heating. All these characteristics make the present manganite a competitive material for room-temperature magnetic refrigeration applications.

In general, the large magnetic entropy change in perovskite manganites results mainly from the considerable variation of magnetization near $T_C$. In addition, the spin–lattice coupling in the magnetic ordering process also plays an important role [3,6,9]. Due to strong coupling between spin and lattice, significant lattice change accompanying magnetic transition in perovskite manganites has been observed [3]. The lattice structural change in the $\langle$Mn–O$\rangle$ bond distance as well as the $\langle$Mn–O–Mn$\rangle$ bond angle would, in turn, favor the spin ordering. Thereby, a more abrupt reduction of magnetization near $T_C$ occurs and results in a significant magnetic-entropy change. In this way, a conclusion might be drawn that a strong spin–lattice coupling in the magnetic transition process would lead to additional magnetic entropy change near $T_C$, and consequently enhances the MCE.

Hence, the large magnetic entropy changes in the present manganite must have originated from the abrupt reduction of magnetization which is associated with a ferromagnetic-to-paramagnetic phase transition near the Curie temperature [3,9]. The additional entropy change can probably be attributed to the fact that the magnetic transition greatly enhances the effect of the applied magnetic field. This is also the reason why a sharp magnetic phase transition remains almost unchanged even under high fields. Another remarkable feature is that the present sample exhibited a relatively small magnetic hysteresis with a coercivity of $\sim 30$ Oe near its $T_C$, which is beneficial to the magnetic cooling efficiency.

![Fig. 3. The magnetic entropy change as a function of temperature in various fields for La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$.](image-url)

**4. Conclusion**

The large magnetic entropy changes in the La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ single crystal are found to occur at temperatures above $300$ K, allowing water to be used as a heat transfer fluid in the room-temperature magnetic refrigeration regime. This is ideal for room-temperature magnetic refrigeration applications. Due to the absence of grains in the single crystal, the $\Delta S_M$ distribution of this sample is much more uniform than that of gadolinium and polycrystalline manganites, which is desirable for an Ericson-cycle magnetic refrigerator. The single crystal has the large magnetic entropy change induced by low magnetic field change, which is beneficial for the household application of active magnetic refrigerant materials. All these make the present single crystal a promising candidate possible to be used as an active magnetic refrigerant in magnetic refrigerators.
Acknowledgements

This work was supported by the Korean Science and Engineering Foundation through the Research Center for Advance Magnetic Materials at Chungnam National University.

References