Magnetocaloric Effect in La_{0.8}Sr_{0.2}MnO₃ Film

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(Received September 2, 2014; in final form February 28, 2015)

Thin epitaxial film of $La_{0.8}Sr_{0.2}MnO_3$ has been deposited on yz-cut LiNbO₃ by pulsed laser ablation. The film was characterized by X-ray diffraction and magnetic measurements as a single phase. The magnetic properties and the magnetocaloric effect have been measured as a function of magnetic field and temperature. A reasonably high magnetocaloric effect indicates that this film might provide an efficient material for micro magnetic refrigerators.

DOI: 10.12693/APhysPolA.128.56

PACS: 75.30.Sg, 75.47.Lx, 75.70.Ak

1. Introduction

Recently, there has been a growing interest in developing a new magnetic refrigeration technology based on magnetocaloric effect (MCE). It was established that a good magnetic refrigerant material requires large magnetic entropy change (ΔS_m) and large adiabatic temperature change (ΔT_{ad}) for a certain magnetic field change (ΔH) [1]. The large ("giant") magnetocaloric effect near the room temperature was discovered in several families of compounds [2]. Among them, especially interesting are manganites [3]. In contrast to other compounds with the giant magnetocaloric effect, most of the manganites are characterized by the second order paramagnetferromagnet phase transition. Therefore, no thermal hysteresis between cooling and warming cycles is observed for them during the phase transition. Recently, it has been shown [4, 5] that the magnetic entropy change in La-based manganites is very large, even larger than that is exhibited by gadolinium.

While the magnetocaloric effect is most frequently studied in bulk materials, there have been some efforts recently to explore the MCE in nanoscale materials. It is connected with developed recently concept of a solidstate micro magnetic refrigerator (SSMMR) which could be used to cool microdevices [6]. In this paper, the magnetocaloric effect was studied in the La_{0.8}Sr_{0.2}MnO₃ thin film deposited on the yz-cut LiNbO₃ single crystal substrate. The La_{0.8}Sr_{0.2}MnO₃ compound was chosen for his reasonably high magnetocaloric effect [7, 8] and for our previous experience in growing high quality La-based films [9].

2. Experimental results

Lanthanum manganite films were grown on the yz-cut optically polished piezodielectric LiNbO₃ substrate by pulsed laser-deposition technique with the use of $La_{0.8}Sr_{0.2}MnO_3$ stoichiometric ceramics as a target. For the laser ablation targets, the polycrystalline $La_{0.8}Sr_{0.2}MnO_3$ samples were prepared by the sol-gel combustion method. The obtained powder was then pressed into a pellet underwent to a series of annealing in order to increase its densification.

During the deposition, the substrate temperature was equal to 750 °C and the oxygen pressure was 300 mTorr. The deposited film, 150 nm thick, was cooled to room temperature at the same oxygen pressure. X-ray diffraction data show that the film is single phase, epitaxial and (2 1 1) oriented with the pseudocubic lattice parameter a = 0.3853 nm. Chemical composition of the film was checked by electron probe microanalysis. According to the chemical analysis data, the chemical composition of the film was differed from that of the ceramic target within 2%.

Magnetization measurements were carried out by a 7 T superconducting quantum interference device SQUID magnetometer (Quantum Design MPMS-XL).



Fig. 1. Temperature dependence of magnetization for the $La_{0.8}Sr_{0.2}MnO_3$ sample for zero field cooling (ZFC) and field cooling (FC) regimes. Inset: plot of dM/dT versus T.

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Figure 1 shows temperature dependence of magnetization for the La_{0.8}Sr_{0.2}MnO₃ sample measured at the magnetic field of 600 Oe. The divergence of the *FC* and *ZFC* magnetization seems to be due to a magnetic domain structure. From the temperature dependence of magnetization, the Curie temperature, $T_{\rm C}$, was determined by differentiation dM/dT (see inset in Fig. 1). It was found that the Curie temperature is equal to 239 K. This value is considerably lower than that for the bulk counterpart having $T_{\rm C} = 287$ K [8]. Moreover, in this manganite $T_{\rm C}$ for nanopowders is higher than that for bulk sample [7].



Fig. 2. Isofield magnetization curves versus temperature for the $La_{0.8}Sr_{0.2}MnO_3$ sample (the results of measurement are not corrected for substrate diamagnetism).

For the isothermal processes, the total magnetic entropy change of the magnetic system, $\Delta S_{\rm M}$, due to the application of a magnetic field, H, is [1]:

$$\Delta S_{\rm M}(T,H) = S_{\rm M}(T,H) - S_{\rm M}(T,0) = \int_{0}^{H_{\rm max}} \left(\frac{\partial M}{\partial T}\right)_{H} \mathrm{d}H, \qquad (1)$$

where T, H_{max} , and M are the temperature, maximum applied field and magnetization, respectively. Figure 2 presents results of magnetization M(T, H) measurements used for the calculation magnetic entropy changes at different magnetic fields for the La_{0.8}Sr_{0.2}MnO₃ film (Fig. 3). The obtained results indicate that the magnetocaloric effect found in the thin films at 20 kOe is equal to be about 50% of ΔS_{M} determined for their bulk counterparts. But it is interesting to notice that ΔS_{M} for the thin films is almost twice larger than that determined for nanopowders [7].

Quite different situation is in the case of Gd films [10]. Magnetocaloric properties of Gd films were found to be well comparable with one determined for Gd sheet. But these films were relatively thick (20–150 μ m).

The field dependence of the magnetic entropy change can be expressed as $\Delta S \sim H^n$. It is well established [11]



Fig. 3. Magnetic entropy change as a function of temperature.



Fig. 4. Temperature dependence of the exponent characterizing the field dependence of ΔS for La_{0.8}Sr_{0.2}MnO₃film.

that in the vicinity of second order magnetic phase transitions one should expect n = 1 well below the Curie temperature, n = 2 in the paramagnetic range, and n = 2/3for $T = T_{\rm C}$ in mean field approach. The deviations from this theoretical prediction seen in Fig. 4 seems to result from sample inhomogeneities. A very broad phase transition confirms this conclusion.

3. Discussion and conclusion

The paramagnetic to ferromagnetic transition was found to broaden and shift to lower temperatures in the thin-film sample. The broadening of this transition is responsible for reduction of the magnitude of the magnetocaloric effect in the $La_{0.8}Sr_{0.2}MnO_3$ film. The properties of thin film as compared to its bulk and nano counterparts suggest that the reduced dimensionality in the system is not responsible for the observed effects. It seems that it is rather extrinsic effect which can be attributed to the special environments of the surface and the interface atoms and also as a result of the strain which is induced by the substrate. This conclusion promises possibility to enhance the magnetocaloric effect in the $La_{0.8}Sr_{0.2}MnO_3$ films after careful technological treatment. This indicates that this film might provide an efficient material for micro magnetic refrigerators.

Acknowledgments

This study was financed by the National Centre for Research and Development, Research Project no. PBS2/A5/36/2013.

References

- A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect and Its Applications*, IOP Publishing Ltd, Bristol 2003.
- [2] B.F. Yu, Q. Gao, B. Zhang, X.Z. Meng, Z. Chen, Int. J. Refriger. 26, 622 (2003).
- [3] V. Markovich, A. Wisniewski, H. Szymczak, *Handbook of Magnetic Materials*, Vol. 22, Amsterdam 2014, Ch. 1.

- [4] R. Szymczak, M. Czepelak, R. Kolano, A. Kolano-Burian, B. Krzymanska, H. Szymczak, J. Mater. Sci. 43, 1734 (2008).
- [5] A. Kolano-Burian, R. Szymczak, R. Kolano, H. Szymczak, A. Burian, Ł. Hawełek, P. Zackiewicz, M. Czepelak, J. Phys. Conf. Series 303, 012070 (2011).
- [6] T. Tsukamoto, M. Esashi, Sh. Tanaka, J. Micromech. Microeng. 22, 094008 (2012).
- [7] M. Pekala, V. Drozd, J. Non-Cryst. Solids 354, 5308 (2008).
- [8] M. Pekala, V. Drozd, J. Alloys Comp. 456, 30 (2008).
- [9] Y. Ilisavskii, A. Goltsev, K. Dyakonov, V. Popov, E. Yakhkind, V.P. Dyakonov, P. Gierłowski, A. Klimov, S.J. Lewandowski, H. Szymczak, *Phys. Rev. Lett.* 87, 146602 (2001).
- [10] K.P. Shinde, B.B. Sinha, S.S. Oh, H.S. Kim, H.S. Ha, S.K. Baik, K.C. Chung, D.S. Kim, S. Jeong, *J. Magn. Magn. Mater.* **374**, 144 (2015).
- [11] V. Franco, J.S. Blázquez, A. Conde, Appl. Phys. Lett. 89, 222512 (2006).