Thermal hysteretic behaviour of La0.67Ca0.33MuO3

Neves Bez, Henrique; Nielsen, Kaspar Kirstein; Smith, Anders; Bahl, Christian

Published in:
Proceedings of the 6th IIF-IIR international Conference on Magnetic Refrigeration

Publication date:
2014

6th IIF-IIR International Conference on Magnetic Refrigeration
Victoria, BC, 7-10 September 2014

THERMAL HYSTERETIC BEHAVIOUR OF $La_{0.67}Ca_{0.33}MnO_3$

H. N. BEZ, K. K. NIELSEN, A. SMITH, C. R. H. BAHL
Department of Energy Conversion and Storage, Technical University of Denmark
Risø Campus, Roskilde, Denmark – hnbe@dtu.dk

ABSTRACT — $La_{0.67}Ca_{0.33}MnO_3$ has been reported for the past years as a possible material for magnetocaloric applications. In this circumstance, hysteresis is unappealing due to losses during the thermal cycles. It is usually related with first-order phase transitions and large magnetocaloric effect. In this context, we report thermal hysteresis of single phase $La_{0.67}Ca_{0.33}MnO_3$ characterized by heating and cooling procedures of heat capacity in zero field, magnetic susceptibility and magnetic entropy change.

1. INTRODUCTION

A broad range of materials display the magnetocaloric effect (MCE). An example is the La-manganites, in particular $La_{0.67}Ca_{0.33}MnO_3$. It has an O'-type orthorhombic structure, with a distortion on the MnO_6 octahedra due to the so-called Jahn-Teller effect [1]. Furthermore, it has been shown that different processing may lead to different properties [2].

Even though this ceramic has been researched throughout the past years and characterized by different methods, only a few scientific papers discuss whether the material presents a first or second-order phase transition (FOPT and SOPT, respectively). One of the characteristics of a FOPT, thermal hysteresis, has not been studied much in this material. Also, many papers about perovskites showing magnetocaloric temperature-dependent properties do not investigate whether the property behaves differently under heating and cooling procedures, respectively. Here we report on the hysteretic behaviour of $La_{0.67}Ca_{0.33}MnO_3$ produced by solid-state reaction.

2. METHODS

$La_{0.67}Ca_{0.33}MnO_3$ polycrystalline material was synthesized by solid-state reaction. La_2O_3, $CaCO_3$ and MnO_2 in the powder form were ground and mixed stoichiometrically by roll milling during 48 h with a rotation speed of 180 rpm. After that, the powder was calcinated at 1123 K for 24 h. Then the powder was isostatically pressed into pellets and sintered at 1403 K for 48 h. Both calcination and sintering were performed in air. Single phase material was identified by XRD measurement and Rietveld refinement. The heat capacity, c_p, was measured at a rate of 1K/min in a custom-built differential scanning calorimeter (DSC). Furthermore, vibrating sample magnetometry (VSM) was used to derive the magnetic entropy change, ΔS_m, from isothermal magnetization curves. All measurements were performed both while cooling and heating in order to investigate the thermal hysteresis of this perovskite.

3. RESULTS

From the Rietveld refinement the unit cell parameters, a, b and c were calculated to be 5.4828(2) Å, 7.7169(2) Å, 5.4641(2) Å, respectively, resulting in a unit cell of and 231.191(2) Å^3, which is in agreement with the literature [4]. Figures 1(a)-(c) show the characterizations performed in order to analyse the thermal hysteresis of $La_{0.67}Ca_{0.33}MnO_3$. Figure 1(a) shows the magnetic susceptibility calculated from magnetization under an external fixed magnetic applied field of 0.01 T. The Curie temperature, T_C, can be estimated as the temperature where the inverse magnetic susceptibility tends to zero [3] (in a very low applied field), when the linear fit of the inverse magnetic susceptibility for $T > T_C$ is used (dashed lines). For the paramagnetic (PM) state to ferromagnetic (FM) state transition T_C is 266.5 K and from FM to PM it is 267.3 K, thus there is an observed hysteretic temperature difference (ΔT_{hyst}) of 0.8 K. Figure 1(b) shows the heat capacity measurement of $La_{0.67}Ca_{0.33}MnO_3$. The measurement was performed in zero applied magnetic field, both during heating and cooling procedures. Here, one can observe that the ΔT_{hyst} is around 0.7 K in good agreement with the value determined from magnetic susceptibility technique (the inherent temperature lag from the device has been corrected for in the data). Moreover, the c_p measurements show maximum peak values of 820 J/kg·K. The c_p maximum value is also in agreement with the literature [5,6], where a measured value of around 800 J/kg·K is given.

In the literature just a few references have cited hysteresis in this compound [1,5,6]. Lin et al. [5] measured the thermal hysteresis by DSC heat flux measurements with heating and cooling rate of 10 K/min, observing a ΔT_{hyst} of 5 K. However, one must consider here that the heating and cooling rates are of great importance for thermal hysteresis measurements, as the closer to equilibrium the smaller the ΔT_{hyst} due to extrinsic factors. Morrison et al. [6] have studied whether this manganite presents magnetic hysteresis using different methods. However, they have shown that apparent magnetic hysteresis can be observed due to extrinsic factors, e.g. magnetic field sweep rate, but when the sweep rate tends to zero no magnetic hysteresis is expected. Coey et al. [1] have shown that small magnetic hysteresis is expected as observed, however the sweep rate of the measurements were not cited. Figure 1(c) shows the ΔS_m calculated by isothermal magnetization measurements during cooling and heating, with $\mu_0 \Delta H$ = 0.5, 1.0 and 1.5 T (starting

from 0.01 T in each case). One may see that the maximum value is in agreement with the literature [1,5], and the transition temperature is around the ones shown in Fig. 1 (a) and (b). Furthermore, the ΔT_{hyst} was measured in the full width half maximum (FWHM). The values of ΔT_{hyst} in the FWHM were between 0.6 and 0.8 K, therefore in agreement with the previous measurements. Moreover, by applying the Bean-Rodbell model [7] we can fit the data and reproduce the size of the hysteresis (i.e. approximately 0.7 K) with a value of the Bean-Rodbell parameter, η, of 1.15. A value of $\eta > 1.0$ corresponds to a FOPT.

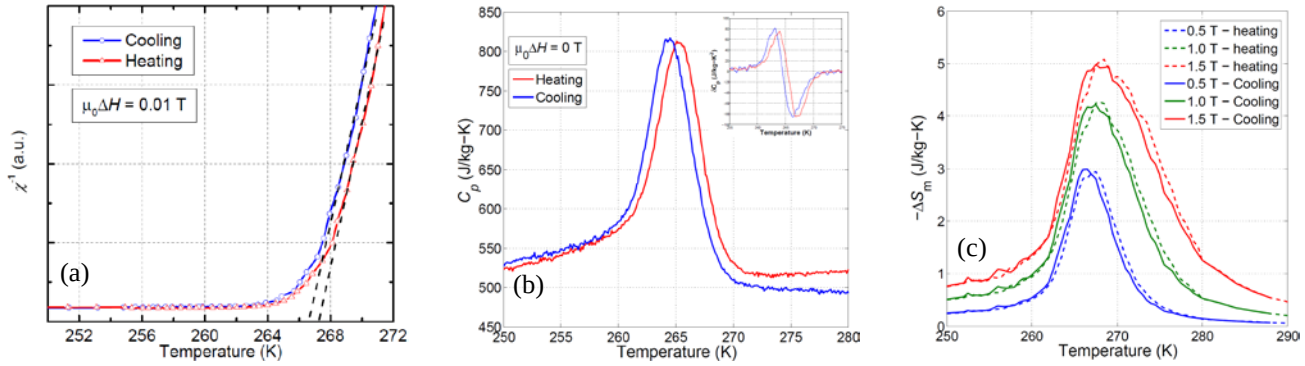

Fig. 1. $La_{0.67}Ca_{0.33}MnO_3$ characterizations: (a) The inverse susceptibility calculated by measurements of magnetization under a fixed applied field of 0.01 T in different temperatures; (b) Heat capacity measurement under no applied field. The inset shows the first derivative with respect to temperature; (c) Magnetic entropy change derived from magnetization curves in different temperatures.

From these measurements one can observe two facts: i) the material presents thermal hysteresis and ii) it presents a larger magnetic entropy change than Gd (at their respective transition temperatures). FOPT materials, as mentioned before, are expected to have thermal hysteresis. Usually thermal hysteresis is associated to crystalline structure (or volume) change. In the case of $La_{0.67}Ca_{0.33}MnO_3$, the ferromagnetism is related to the Mn^{+3}/Mn^{+4} coupling intermediate with a O^{2-}. Both Mn^{3+} and Mn^{4+} occupy interstitial octahedron sites, which are geometrically distorted by the so-called Jahn-Teller effect [1]. A possibility for the volumetric structural change is that the crystalline distortion is lost as the coupling becomes weaker around T_C, nevertheless in order to prove a hypothesis, a deeper understanding of the crystalline behaviour is needed, by means of synchrotron diffraction for example. Figure 2 shows c_p measurements of $La_{0.67}Ca_{0.33}MnO_3$ during the cooling procedures under 0,001 T, 0.5 T, 1.0 T and 1.5 T. One may observe as the field increases the c_p maximum values decreases, which is a typical behavior of SOPT. However, as the field increases the peak position also shifts to higher temperatures, which is a typical behavior of FOPT [8]. This 'mixed' behavior is consistent with a weakly FOPT (as previous work has shown by electron holography analyses [9]), and as the Bean-Rodbell analysis also suggests.

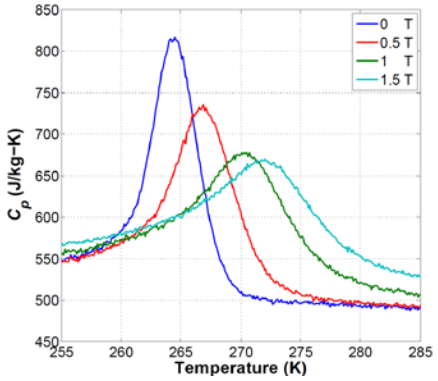

Fig. 2: c_p measurements during cooling procedures under different applied fields.

4. Acknowledgments

This work was financed by the ENOVHEAT project which is funded by the Danish Council for Strategic Research (contract no 12-132673) within the Programme Commission on Sustainable Energy and Environment.

References

[1] J. M. D. Coey, M. Viret, S. von Molnár, "Mixed-valence manganites", Advances in Physics, vol. 48 (2), 1999, pp. 167-293.

[2] M. Phan, S. Yu, "Review of the magnetocaloric effect in manganite materials", J. Magn. Mag. Mat., vol. 308 (2), 2007, pp. 325-340.

[3] B. C. Cullity, C. Grahan, "Introduction to Magnetic Materials", Sec. Ed., John Wiley & Sons Inc., 2009.

[4] J. Biasco, J. Garcia, J. M. de Teresa, M. R. Ibarra, P. A. Algarabel, C. Marquina, "A systematic study of structural, magnetic and electrical properties of $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$ perovskites", J. Phys. Cond. Mat. 8, 1996, pp. 7427-7442.

[5] G. C. Lin, Q. Wei, J. X. Zhang, "Direct measurements of the magnetocaloric effect in $La_{0.67}Ca_{0.33}MnO_3$", J. Magn. Mag. Mat., vol. 300, 2006, pp. 392-396.

[6] K. Morrison, A. Berenov, L. F. Cohen, "Origin of Hysteresis in $La_{0.67}Ca_{0.33}MnO_3$", Mater. Res. Soc. Symp. Proc., Vol. 1310, 2011.

[7] C.P. Bean and D.S. Rodbell, "Magnetic disorder as a first-order phase transformation", Phys. Rev. 126 (1), 104-115, 1962.

[8] A. Smith , C. R.H. Bahl , R. Bjørk , K. Engelbrecht, K. K. Nielsen, N. Pryds, "Materials Challenges for High Performance Magnetocaloric Refrigeration Devices", Adv. Energy Mater., vol. 2, 2012, pp. 1288-1318.

[9] J. C. Loudon and P. A. Midgley, “Micromagnetic imaging to determine the nature of the ferromagnetic phase transformation in $La_{0.7}Ca_{0.3}MnO_3$”, Phys. Lett. Rev. 96, 2006, 027214.