Journal of Magnetism and Magnetic Materials 324 (2012) 37–43

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Influence of Dy addition on the magnetocaloric effect of $La_{0.67}Ca_{0.33}Mn_{0.9}V_{0.1}O_3$ ceramics

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ARTICLE INFO

Article history:
Received 22 February 2011
Received in revised form
8 July 2011
Available online 26 July 2011

Keywords:
X-ray diffraction
Reitveld refinement
Magnetocaloric effect
Relative cooling power

ABSTRACT

The influence of partial substitution of La by Dy on the magnetocaloric response of $(La_{1-x}Dy_x)_{0.67}Ca_{0.33}Mn_{0.9}V_{0.1}O_3$, where $x=0.03$, 0.15 and 0.25 is studied. Rietveld refinement of X-ray diffraction pattern using GSAS method shows that the compounds adopt the orthorhombic structure with Pnma space group. The systematic change in lattice parameters and magnetic phase transition indicates the substitution effect of Dy. From the magnetization isotherms at different temperatures, magnetic entropy change close to their respective transition temperatures (T_C) has been evaluated. The maximum value of entropy change near T_C is found to be about 4.8 J/kg K at 187.5 K for $LCMVDy_{0.03}$, 2.45 J/kg K at 107.5 K for $LCMVDy_{0.15}$ and 2.15 J/kg K at 92.5 K for $LCMVDy_{0.25}$ at 4 T. Dy addition produces a reduction in T_C and in magnitude of the magnetic entropy change. Even though the entropy change decreases with increasing Dy substitution the refrigerant temperature range, ΔT, is found to be 10 K for $LCMVDy_{0.03}$, 31 K for $LCMVDy_{0.15}$ and 35 K for $LCMVDy_{0.25}$ compounds [90%] at 4 T. The field dependence of the magnetic entropy change is also analyzed showing the power law dependence, $\Delta S_M \propto H^n$ where $n=0.75(2)$ for $LCMVDy_{0.03}$, $n=0.80(4)$ for $LCMVDy_{0.15}$ and $n=0.92(8)$ for $LCMVDy_{0.25}$ compounds at their respective transition temperatures. The relative cooling power and its field dependance are also analyzed.

1. Introduction

Magnetocaloric effect (MCE) is becoming a field of increasing research interest. Perovskite manganites of the type $R_{1-x}A_xMnO_3$ (R: rare-earth ions such as La^{3+}, Pr^{3+} and Nd^{3+}, A: divalent alkaline-earth ion such as Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.) are well known for high magnetostriction, magnetocaloric effect (MCE) and magnetoresistance (MR) [1–6]. Basic mechanism of such phenomenon has been explained with double exchange (DE) theory. In these manganite systems, the hopping of e_g electrons between two partially filled d orbitals of neighboring Mn^{3+} and Mn^{4+} ions through the orbital overlap e_g–O_{2px}–e_g and strong Hunds coupling between the t_{2g} core spins and the mobile e_g electron spins cause the ferromagnetic (FM) interaction between Mn^{3+} and Mn^{4+} ions. However, recent studies reveal that additional factors such as lattice distortion, orbital ordering etc. are required to understand the whole picture of the manganite physics [7,8]. Substitution of divalent ions at A-site of $R_{1-x}A_xMnO_3$ converts some of the Mn^{3+} ions ($3d^4$, $t_{2g}^3e_g^1$) into Mn^{4+} ions ($3d^3$, $t_{2g}{}^3e_g^0$) resulting in fascinating physical phenomena such as paramagnetic (PM) insulator to FM conductor or various mixed magnetic phases viz. canted antiferromagnet (AFM)/spin glass (SG) coupled with charge/orbital ordered states in a particular doping range. A useful parameter, which decides the efficiency of a magnetocaloric material for magnetic refrigeration applications, is the relative cooling power (RCP) or the refrigerant capacity [9–12]. High RCP values depend on both the height and the width of the ΔS_M curve. Although compounds with second order transition (SOT) show smaller ΔS_M^{peak} than materials with first order transition (FOT), a compromise between an optimal RCP and the lack of hysteresis currently makes compounds with SOT better candidates for the development of magnetic cooling devices [13,14].

It has been recently shown that there exists a universal curve for the magnetic entropy change for SOT materials [15,16]. It can be constructed using a phenomenological procedure which does not require the knowledge of either the equation of state or the critical exponents of the material. Expressing the field dependence as $\Delta S_M \propto H^n$, this approach allows us to find a relationship between the exponent n and the critical exponents of the material and to propose a phenomenological universal curve for the field dependence of ΔS_M, which was successfully tested for different series of soft magnetic amorphous alloys and lanthanide based crystalline materials. Up to now very little attention has been paid to the field dependence of RCP [17].

Recently Xu et al. studied effect of Dy doping on magnetotransport properties in $La_{0.67}Sr_{0.33}MnO_3$ [18]. They observed an emergence of antiferromagnetic state at temperatures lower than

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doi:10.1016/j.jmmm.2011.07.032

transition temperature (T_C) for the studied compounds. Mitra et al. have reported the change of transport and magnetic properties with dysprosium doping in $(La_{(1-x)}Dy_x)_{0.7}Sr_{0.3}MnO_3 (x=0–0.4)$ [19]. Recently Terai et al. have investigated the electronic and magnetic states of $(La_{1-x}Dy_x)_{0.7}Ca_{0.3}MnO_3$ $(0<x<0.50)$ by measuring the electrical resistivity, magnetic susceptibility, magnetization and magnetoresistance [20]. They found that all the compounds except $x=0.5$ show a FM metal–PM insulator transition at T_C. In an earlier investigation by Nisha et al. the magnetocaloric properties of $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ synthesized by conventional solid state

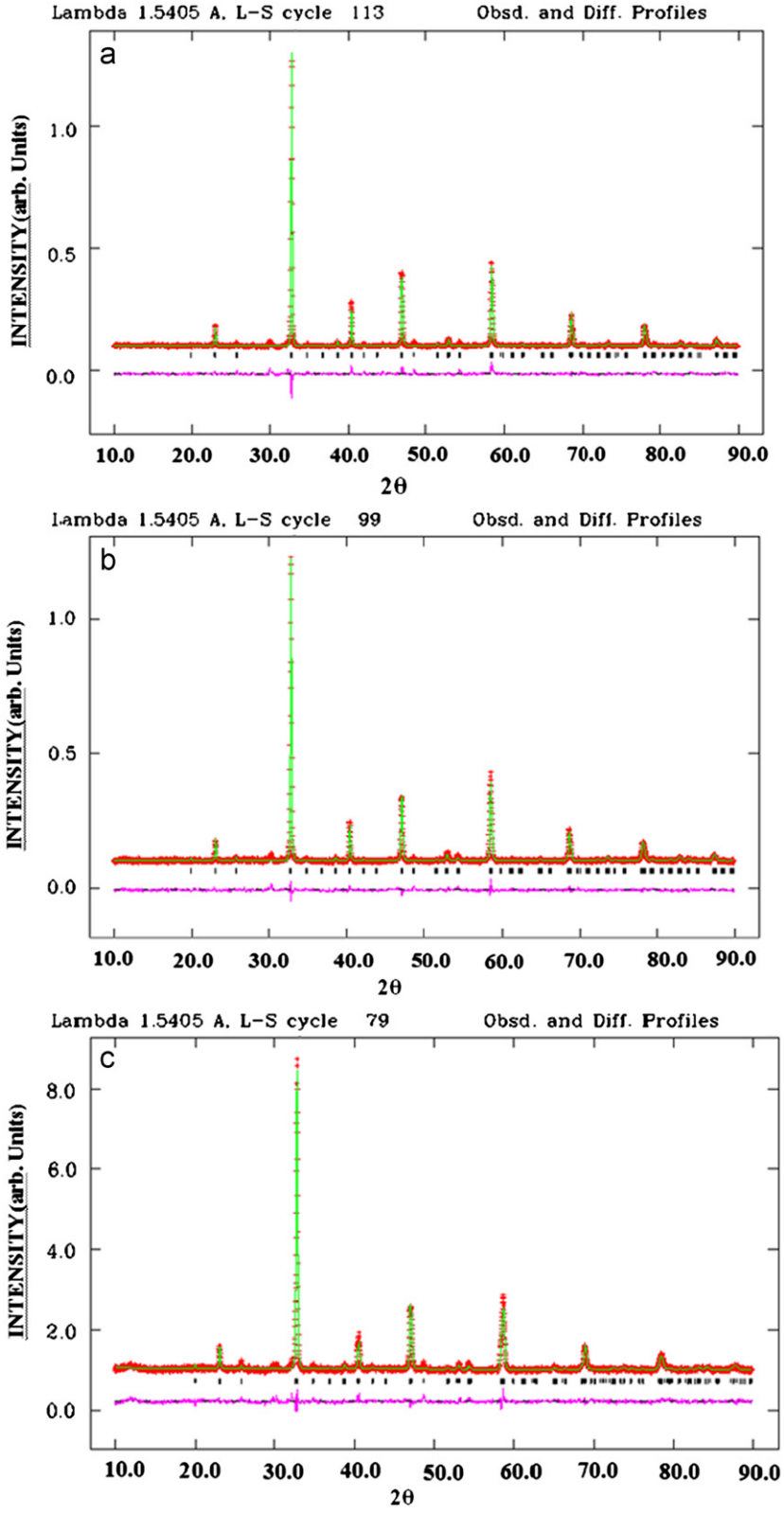

Fig. 1. Refined XRD pattern for (a) $LCMVDy_{0.03}$, (b) $LCMVDy_{0.15}$ and (c) $LCMVDy_{0.25}$. The plot at the bottom is the difference between the calculated and observed intensities.