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Effect of substitution of Fe for Mn on the structural, magnetic properties and magnetocaloric effect of LaNdSrCaMnO$_3$

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ABSTRACT

We have studied the structural, magnetic and magnetocaloric properties of La$_{0.6}$Nd$_{0.1}$Sr$_{0.15}$Ca$_{0.15}$Mn$_{1-x}$Fe$_x$O$_3$ (LNSCMFe$_x$) perovskite samples. The samples were synthesized using the solid-state reaction at high temperature and were analyzed by XRD data based on the Rietveld refinement technique. LNSCMFe$_x$ samples crystallized in orthorhombic symmetry with Pnma space group. Besides, the curves of magnetization reveals that all samples exhibit a magnetic transition from the paramagnetic to ferromagnetic phase at the Curie temperature T_C, which decreases from 327 K to 296 K with the increase of the Fe doping level from $x=0$ to $x=0.1$. The thermal evolution of magnetization in the ferromagnetic phase at low temperature varies as $T^{3/2}$ in accordance with Bloch's law. The magnitude of the isothermal magnetic entropy, ($-\Delta S_M^{max}$), at the FM Curie temperature increases from 3.79 J/kg K for $x=0$ composition to 5.8 J/kg K for $x=0.1$, under a magnetic field of 5 T. For an applied magnetic field of 5 T, the relative cooling power (RCP) values are found to vary between 173.66 and 231.76 J/kg. These results suggest that these materials could be used as an active magnetic refrigerant around room temperature.

1. Introduction

The perovskite-like rare-earth manganese Ln$_{1-x}$D$_x$MnO$_3$ (Ln: rare earth ions such as La^{3+}, Pr^{3+}and Nd^{3+}…, D: divalent alkaline-earth ions such as Ca^{2+}, Sr^{2+}, Ba^{2+}…) compounds have been an intensive topic in scientific studies and potential technological application because of their charge and orbital ordering, magnetic phase transition, colossal magnetoresistance (CMR) effect as well as magnetocaloric effect (MCE) [1–5]. The close relation between transport and magnetism in these materials has been explained bythe double exchange (DE) interaction [6], polaronic effects [7] and phase separation [8]. Such magnetic parameters are very sensitive to the substitution of Mn by other 3d elements because this substitution causes the change of ratio of amount Mn^{3+}/Mn^{4+} in these manganites. The presence of mixed valence states of Mn ions in the doped manganites gives rise to the competing double exchange (DE) and super-exchange (SE) interactions [9,10]. It modifies the Mn^{3+}–O^{2-}–Mn^{4+} network and in turn largely affects their magneto-transport properties as well as MCE [11–14].

La$_{0.7}$Sr$_{0.3}$MnO$_3$ is one of the extensively studied manganites which undergoes a paramagnetic-ferromagnetic transition around $T_C=375$ K and it shows a ($-\Delta S_M^{max}$) of 4.6 J.kg^{-1} K^{-1} under $\mu_0 H=5$ T around its T_C [15]. The T_C of this compound is well above room temperature. However, for domestic refrigeration purposes, the T_C is required to be near room temperature with considerable MCE. The ferromagnetic transition of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ can be brought down to room temperature either by a partial replacement of the bigger ionic size La^{3+} by a smaller size of Nd^{3+}or Pr^{3+}ion or by partial replacement of Mn ions by other transition metal ions such as Cr, Fe, Zn, Ti, etc. [16]. From this point of view, the main objective is to tune the T_C from 370 K to near room temperature. Hence, the present study deals with structural, magnetic and magnetocaloric properties of La$_{0.6}$Nd$_{0.1}$Sr$_{0.15}$Ca$_{0.15}$Mn$_{1-x}$Fe$_x$O$_3$($x=0$, 0.05 and 0.1) synthesized by the solid state method.

2. Experimental

The La$_{0.6}$Nd$_{0.1}$Sr$_{0.15}$Ca$_{0.15}$Mn$_{1-x}$Fe$_x$O$_3$ (LNSCMFe$_x$) polycrystalline samples were prepared by the conventional solid-state ceramic method. The powders in stoichiometric amounts of La$_2$O$_3$, Nd$_2$O$_3$, SrCO$_3$, CaCO$_3$, MnO$_2$ and Fe$_2$O$_3$ were well-mixed and calcined at 1173 K/24 h, 1273 K/24 h and 1473 K/24 h with intermediate grinding to ensure homogenization. The powder, thus obtained was ground, pelletized and sintered at 1673 K/24 h to get

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the phase pure material. The structure and phase purity were checked by powder X-ray diffraction (XRD) using CuKα radiation ($\lambda = 1.54053$ Å) at room temperature. The patterns were recorded in the $20^\circ \leq 2\theta \leq 90^\circ$ angular range with a step of 0.017° and a counting time of 18 s per step. According to our measurements, this system is able to detect up to a minimum of 3% of impurities. Structural analysis was carried out with the Rietveld structural refinement program using FULLPROOF software (Version 1.9c-May 2001-LLB-JRC) [17].

Magnetization measurements versus both temperature and magnetic field ($\mu_0 H$) curves were carried out using BS1 and BS2 magnetometer developed in Louis Neel Laboratory of Grenoble.

3. Results and discussion

3.1. Structural properties

In order to make sure that the samples LNSCMFe$_x$ were single phase without any other detectable secondary phases, X-ray diffraction (XRD)data was analyzed. Fig. 1 shows the observed and calculated peak profile and bragg position of a typical X-ray diffraction patterns for the example LNSCMFe$_x$ ($x = 0.1$) at room temperature. The XRD patterns indicate the formation of monophase perovskite oxides having an orthorhombic structure with space group Pnma. The structure refinement was performed in the orthorhombic setting of Pnma space group ($Z = 4$), with (La/Nd/Sr/Ca) at 4c(x, 0.25, z) position, (Mn/Fe) at 4b(0, 0, 0.5), O_1 at 4c(x, 0.25, z) and O_2 at 8d(x, y, z).The structural parameters are refined by the standard Rietveld technique and the fitting between the experimental spectra and the calculated values is relatively good, based on the consideration the low χ^2 values. Structural refinements of the XRD data, namely the cell parameters and fitting results are presented in Table 1 for all samples. We can see that the lattice parameters and the unit cell volume increase with increasing iron content in the samples. This increase is due to the fact that the ionic radius of iron (Fe^{3+}) is larger than the manganese one ($r_{Fe3+} = 0.785$ Å and $r_{Mn3+} = 0.72$ Å) [18].

We can calculate the average grain size (D) from the XRD peaks using the Scherrer formula:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \tag{1}$$

where λ is the X-ray wave length employed, $\beta$is the full width at half maxima of the most intense peak and θ is the diffraction angle. The as obtained (D) are estimated to be mostly of 76.65 nm, 78.16 nm and 97.76 nm for the $x = 0$, 0.05 and 0.1 samples, respectively. By another way, from the XRD peaks (for example that shown in Fig. 1**)**, we have estimated the crystallite size D of LNSCMFe$_x$ by analyzing the broadening of X-ray diffraction peaks, using the Williamson–Hall approach, can be written as [19]:

$$\beta \cos \theta = (k\lambda / D) + 2(\Delta\xi / \xi) \sin \theta \tag{2}$$

where $\Delta\xi/\xi$ is the lattice strain in the system. After plotting β cos (θ) vs sin(θ), lattice strain was calculated from the slope of the line and the particle size D was calculated from the intersection ($K\lambda/D$=intersection) with the vertical axis, the average crystal size has been calculated and it is found to be in the range of 68.21–86.77 nm. The particle size, calculated in the present system using Williamson–Hall technique, is lower as compared to the particle size obtained from Debye–Scherer method because the broadening effect due to strain is completely excluded in Debye–Scherer technique [20].

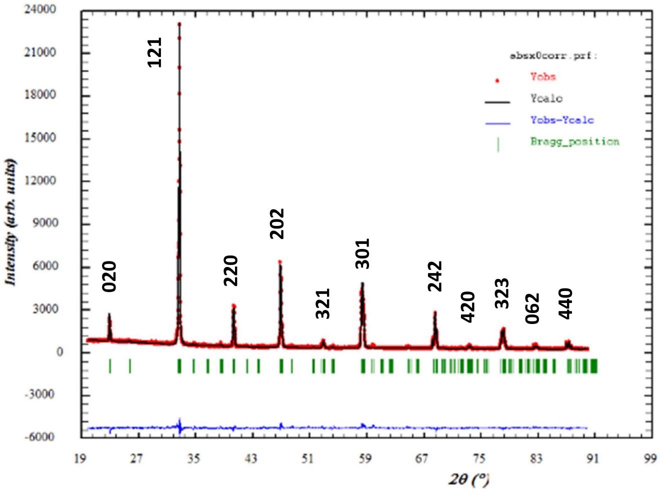

Fig. 1. X-ray diffraction pattern and the corresponding Rietveld refinement of LNSCMFe$_x$ ($x = 0.1$).

Table 1
Refined structure parameters for $La_{0.6}Nd_{0.1}Sr_{0.15}Ca_{0.15}Mn_{1-x}Fe_xO_3$ after the Rietveld refinements of X-ray diffraction data at room temperature.

Compounds	LNSCM	LNCSMFe$_{0.05}$	LNCSMFe$_{0.1}$
a (Å)	5.483 (1)	5.491 (1)	5.492 (1)
b (Å)	7.702 (2)	7.715 (2)	7.723 (2)
c (Å)	5.452 (1)	5.461 (1)	5.464 (1)
Cell volume (Å^3)	230.32 (1)	231.40 (1)	231.83 (1)
Bond lengths and bond angles			
Mn–O$_1$ (Å)	1.965 (5)	1.957 (3)	1.957 (4)
Mn–O$_1$–Mn (°)	157.11 (19)	160.40 (12)	161.34 (18)
Mn–O$_2$ (Å)	1.74 (2) 2.13 (2)	1.840 (14) 2.05 (1)	1.89 (2) 2.01 (2)
Mn–O$_2$–Mn (°)	173.5(9)	167.6(5)	166.0(9)
R_{exp} (%)	3.88	4.27	4.15
R_p (%)	4.45	4.54	4.60
R_{wp} (%)	5.73	6.29	6.33
χ^2 (%)	2.19	2.18	2.33

3.2. Magnetization investigation

Fig. 2 shows the temperature dependence of magnetization in field-cooled mode$\left(\mu_0 H = 0.05\ T\right)$. $M(T)$ curves reveals the presence

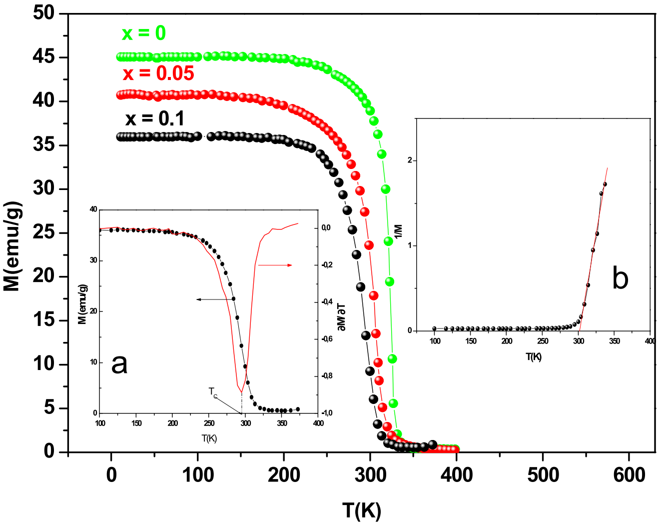

Fig. 2. Field-cooled magnetization of the samples of LNSCMFe$_x$ as a function of temperature at applied field of 500 Oe. The a-inset shows the magnetization derivative as a function of temperature and the b-inset shows the corresponding $1/M$ vs T.