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Effect of Li doping on the magnetic and magnetocaloric properties of $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ $(0 \le x \le 0.3)$

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ABSTRACT

The magnetic properties and magnetocaloric effect have been studied in $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ $(0 \le x \le 0.3)$ prepared by conventional solid-state reaction. Magnetic measurements versus temperature revealed that the Curie temperature (T_C) increased gradually with increasing lithium content $(0.05 \le x \le 0.2)$; T_C values are about 260 and 290 K for $x=0.05$ and 0.2, respectively. But it shows abrupt drop in T_C value for $x=0.3$ ($T_C=235$ K). Meanwhile, the paramagnetic–ferromagnetic (PM–FM) transition is second-order in $x \le 0.2$, it changes into first order for $x=0.3$. However, the magnitude of the isothermal magnetic entropy (ΔS_M) increased gradually. In a magnetic field change of 15.0 kOe, the maximum ΔS_M achieved around T_C are -1.03, -1.05, -1.48, -2.17 and -2.64 J kg^{-1} K^{-1} for $x=0$, 0.05, 0.1, 0.2 and 0.3, respectively. Although ΔS_M for $x=0.2$ is smaller compared to the composition $x=0.3$, the relative cooling capacity (RCP) 59.6 J kg^{-1} is similar compared with the value 59.8 J kg^{-1} for $x=0.3$. Addition of suitable T_C makes it a desirable material for room temperature magnetic refrigeration.

1. Introduction

The magnetocaloric effect (MCE) describes the temperature change of magnetic materials in an adiabatic process in response to an external magnetic field. Since this effect based on intrinsic property of magnetic materials is considered to be more energy efficient and environmentally friendly compared with conventional refrigeration, the refrigeration technology based on this effect is building up with time. Mostly, Laves phases, $La(Fe,Si)_{13}$ intermetallics, gadolinium germanium silicides and heusler alloys show giant magnetic entropy change (ΔS_M) because of their large magnetic moments and an abrupt change in magnetization at the magnetic ordering temperature arising from strong coupling between spin and lattice (a first-order phase transition FOPT) [1]. However, these materials have the thermal and magnetic hysteresis associated with FOPTs, which imply a waste of energy in refrigeration cycle [1,16]. Manganites with low cost of preparation, higher chemical stability and electrical resistivity with low eddy current have been intensively investigated, especially the manganites undergoing second-order phase transition (SOPT) with large MCE and negligible hysteresis are considered as promising candidates for application [2,7,16].

The perovskite $Pr_{1-x}Sr_xMnO_3$ system is an important member in the manganite family with intermediate one electron bandwidth [3]. From the magnetic phase diagram [4], for $0.50 < x < 0.55$ a narrow transition was obtained, which shows the coexistence of two magnetic transitions from PM to FM and FM to A-type AFM. It is found that the competition between double exchange interaction and super exchange interaction is the reason for phase coexistence. Large positive magnetic entropy change have been reported in this A-type anti-ferromagnetic $Pr_{0.5}Sr_{0.5}MnO_3$ ($\Delta S_M = +6.8$ J kg^{-1} K^{-1} for $\Delta H=5$ T) [5]. After that, more researches focus on this system to learn magnetic properties and other physical mechanisms. Biswas et al. [6] found, in $Pr_{1/2}Sr_{1/2}MnO_3$, particle size has significant effect on charge-ordered state (CO), but no effect on the ferromagnetic transition temperature (T_C) which is associated with double change interaction. Phan investigated large magnetic entropy change ($\Delta S_M = -8.52$ J kg^{-1} K^{-1} for $\Delta H=5$ T) in $Pr_{0.63}Sr_{0.37}MnO_3$ single crystal [7], and large positive magnetic entropy change ($\Delta S_M = +9$ J kg^{-1} K^{-1} for $\Delta H=7$ T) was also obtained by Naik et al. [8]. Monovalent elements doped in Lanthanum manganites have been extensively researched [9–11], however, the influence on magnetic properties and the magnetocaloric effect by monovalent elements substituted in $Pr_{1-x}Sr_xMnO_3$ system was scarcely reported so far. So in this paper, we focus on learning the structure change, magnetic property and subsequently magnetocaloric effect variation of the praseodymium manganites doped by small radii monovalent element.

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2. Experimental details

Polycrystalline $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ ($0 \le x \le 0.3$) have been synthesized by using the standard solid state reaction method at high temperature. The starting materials (Pr_6O_{11}, $SrCO_3$, $MnCO_3$, Li_2CO_3,) were mixed in an agate mortar. After ball milling for 2 h, the mixture heated in air up to 1273 K for 24 h. The obtained powders were pressed into pellets about 2 mm thickness and 13 mm diameter and then sintered at 1573 K. Finally, these pellets were slowly cooled down to room temperature. Phase purity and homogeneity were determined by powder X-ray diffraction at room temperature. Magnetization measurements versus temperature in the range of 80–350 K and versus applied magnetic field up to 100 Oe were carried out using a Vibrating Sample Magnetometer (VSM). The MCE was calculated from the magnetization measurements versus applied magnetic field up to 15 kOe at various temperature.

Crystal analysis from room temperature X-ray diffraction has revealed that $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ samples have orthorhombic structure (space group: Pbmn) for $x \le 0.2$, and has small impurity phase $Pr_{0.96}Mn_{0.982}O_3$ for $x=0.3$. A raft of studies suggest that there are many factors that affect magnetic and magnetocaloric properties for A-site substitutions. The average A-site cationic radius $< r_A >$ and A-site cationic size mismatch, which is quantified by variance σ^2 of the ionic radii, strongly affects the structure and magnetic properties of the manganites [4]. Generally, for the same manganese valence, the increase of $< r_A >$ tends to enlarge the Mn–O–Mn angle, increases the bandwidth and subsequently T_C. However, an increase in variance σ^2 always causes weak double exchange interaction or super exchange interaction and destabilizes charge-order state. In addition to the factors mentioned above, carrier nature, concentration and preparation process also have a great impact on the performance of materials.

3. Results

The room temperature powder X-ray patterns of $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ indicate that the distortion degree decreases with an increase when the lithium content is $x \ge 0.1$ as is seen from a decrease in the splitting in pseudocubic reflections (see Fig. 1). The phenomenon resembles as reported in $La_{1-x}K_xMnO_3$ [12]. It is hard to explain the reason of the decrease of the distortion degree; we attribute it to the valence change from Pr^{3+} to Pr^{4+} with large amount increase in lithium content, because of the similar ionic radius Pr^{4+} (0.96 Å) and Li^{1+} (0.92 Å) with eight coordination number [13]. However, for $x \le 0.1$, it may firstly influence the valence of Mn leading to increase of Mn^{4+}.

Fig. 2 shows the temperature dependence of zero field cooled magnetization (ZFC) and field cooled magnetization (FC) under $H=100$ Oe for $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$ ($x=0$, 0.05, 0.1, 0.2 and 0.3). It appears from Fig. 2 that the ferromagnetic (FM) to paramagnetic (PM) phase transition temperature, T_C, slightly decreases with small Li concentration, then this transition shifts towards room temperature on adding more Li content for $x \le 0.2$. However, for $x=0.3$ sample, the T_C reduces greatly showing a striking difference to the others, which is mainly attributed to impurity and large structure change, and is pseudocubic [12] for $x=0.3$ compared to orthorhombic structure for $x \le 0.2$. Consequently, the Curie temperature for each sample, obtained from the critical point in the derivative dM/dT, was found to be 265 K, 260 K, 280 K, 290 K and 235 K for $x=0$, 0.05, 0.1, 0.2 and 0.3, respectively. As compared to the results reported before, no sign of charge-ordered anti-ferromagnetic transition is found for $x=0$ because of different preparation processes, which indicates preparation method producing enormously impacts on the performance of magnetic materials. It is worth mentioning that a bump is found around 160 K for $x=0.1$ in ZFC and FC curves. The bump is a signature of the onset of *A*-type anti-ferromagnetic CO ordering according to early results reported before [5,6,17].

To evaluate the magnetocaloric effect of the samples, a serious magnetic field dependence of magnetization curves (M–H) was recorded around transition temperature for each sample. Fig. 3 shows the representative isothermal curves for (a) $x=0.2$ and (b) $x=0.3$. We have not shown the M–H data for $x=0$, 0.05 and 0.11 since they are similar to $x=0.2$. The rapid increase in magnetization with field $H \le 0.5$ kOe is expected for a ferromagnetic material. It is found that metamagnetic behavior is not clearly emerging, which indicates all the samples undergoing second-order phase transition. To confirm this assessment, we perform H/M versus M^2 (Arrott plots) curves as shown in Fig. 3(c) $x=0.2$ and (d) $x=0.3$ based on the M–H data according to the Banerjee criterion [15]. A positive slope of Arrott plots in the whole temperature for $x=0.2$ is clearly shown; a similar feature has been found for $x<0.2$ indicating that they are all undergoing second-order phase transition. However, a small negative slope is observed at low temperature for $x=0.3$, it is a typical feature of first-order phase transition [14]. A more sensitive method is used

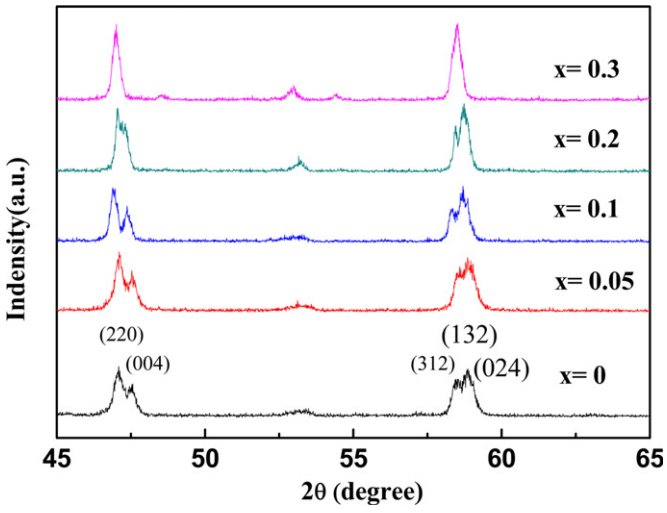

Fig. 1. XRD pattern of the samples.

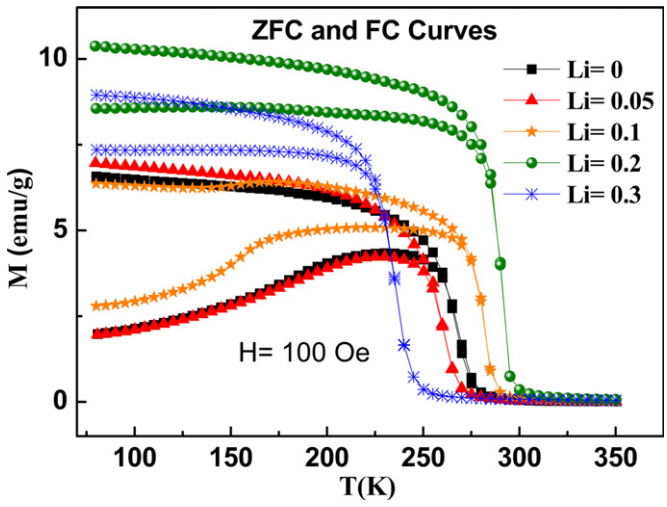

Fig. 2. Temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetization curves measured at 100 Oe for $Pr_{0.5}Sr_{0.5-x}Li_xMnO_3$.