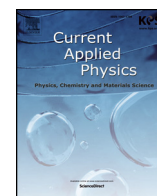




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Magnetic properties and magnetocaloric effect of Sr-doped $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ compounds

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ABSTRACT

In this work, we pointed out that Sr substitution for Ca leads to modify the magnetic and magnetocaloric properties of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds. Analyzing temperature dependence of magnetization, $M(T)$, proves that the Curie temperature (T_C) increased with increasing Sr content (x); T_C value is found to be 130–260 K for $x = 0.0$ – 0.3 , respectively. Using the phenomenological model and $M(T,H)$ data measured at several applied magnetic field, the magnetocaloric effect of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds has been investigated through their temperature and magnetic field dependences of magnetic entropy change $\Delta S_m(T,H)$ and the change of the specific heat change $\Delta C_p(T,H)$. Under an applied magnetic field change of 10 kOe, the maximum value of $-\Delta S_m$ is found to be about 3 J/kg·K, and the maximum and minimum values of $\Delta C_p(T)$ calculated to be about ± 60 J/kg·K for $x = 0.3$ sample. Additionally, the critical behaviors of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds around their T_C have been also analyzed. Results suggested a coexistence of the ferromagnetic short- and long-range interactions in samples. Moreover, Sr-doping favors establishing the short-range interactions.

1. Introduction

Recently, perovskite manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd} \dots$; $\text{A} = \text{Ca}, \text{Sr}, \text{Ba} \dots$; be referred as manganites) have been an interested topic in the solid state physics community due to their rich electrical magnetic properties [1–4]. The close relationship between structural, electrical, and magnetic properties has opened new aspects in studying of manganites in the fundamental and application viewpoints. It has been reported LnMnO_3 as an insulator antiferromagnetic (anti-FM) with Néel temperature to be about 135 K [5]. A partial replacement of Ln^{3+} by A^{2+} introduces numbers of Mn^{3+} ions to be converted to Mn^{4+} ions, leads to a mixed valence state $\text{Mn}^{3+}/\text{Mn}^{4+}$. Therefore, the double-exchange interactions of Mn^{3+} - Mn^{4+} ions appeared. Material thus exhibits the ferromagnetic (FM)-paramagnetic (PM) phase transition taking place at Curie temperature (T_C). Changing the $\text{Ln}^{3+}/\text{A}^{2+}$ ratio, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio will be modified, and affect structural and physical properties of materials [6–8]. Basically, electrical and magnetic properties of manganites can be explained by such mechanisms i) the coexistence and competition of the Mn^{3+} - Mn^{4+} double-exchange interactions and the super-exchange interactions of Mn^{3+} - Mn^{3+} and

Mn^{4+} - Mn^{4+} pairs [6,9], ii) the strong electron-phonon coupling (called the Jahn-Teller effect) [10,11], and iii) the change of the average cationic radius [8,12].

Motivated by the fact that several manganites exhibit a discontinuous variation in the structure and a sharp magnetic phase transition, which is known as the first-order phase transition (FOPT) [13–15]. Among them, $\text{Ln}_{0.7}\text{A}_{0.3}\text{MnO}_3$ systems usually exhibit the strongest physical effects [9,16–18]. However, the FM-PM phase transition in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($\text{Ln} = \text{La}$) single-crystal or polycrystalline bulk is the first-order [12,19–22], whereas, other cases (e.g. $\text{A} = \text{Sr}, \text{Ba}, \text{Pb}$) are the second-order phase transition (SOPT) [12,22–24]. Studies on the critical properties around the FM-PM transition of $\text{La}_{0.7}\text{Ca}_{0.3-x}(\text{Sr},\text{Ba})_x\text{MnO}_3$ have shown that the partial replacement of Ca^{2+} by Sr^{2+} results in the change from the long-to short-range FM order [12]. This is the opposite for the case of Ca^{2+} replacement with Sr^{2+} [12,22,24].

The previous reports have pointed that $\text{Pr}_{1-x}\text{A}_x\text{MnO}_3$ compounds ($\text{Ln} = \text{Pr}$) are interesting systems with a rich phase diagram [25–28]. For $\text{A} = \text{Ca}$, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ exhibits a FM insulator in the range of $x = 0$ – 0.3 and the anti-FM charge-ordering behavior when $x = 0.3$ – 0.5 .

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Besides, this system also reveals a coexistence of the FM and anti-FM interactions, and spin-glass behaviors in samples with low Ca-doping level ($0.0 < x < 0.2$) [27]. A non-monotonic change of Curie temperature has been also observed in the range of $0.2 < x < 0.3$, in which a maximum value of T_C appears at $x = 0.25$ [26]. The complex magnetic properties in this system can be understood via detailed analyses of the critical behaviors. A recent report indicated that the critical exponents (β and γ) of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds are very sensitive to Ca-doping concentration ($\beta = 0.351$ and $\gamma = 1.372$ for $x = 0.25$, $\beta = 0.521$ and $\gamma = 0.912$ for $x = 0.29$) [29]. It suggested that Ca-doping favors establishing the FM long-range order in this system. For $A = \text{Sr}$, Knizek et al. [28] reported that $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ with $0.3 \leq x \leq 0.4$ is a FM conductor at low temperature, whereas $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is a charge-ordered anti-FM. However, using the isothermal magnetization $M(H, T)$ data, Phan et al. [30] indicated a large magnetocaloric effect (MCE) in $\text{Pr}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$ single crystal, which exhibits the negative slopes of the H/M versus M^2 plots. This reflects that $\text{Pr}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$ single crystal is not a conventional ferromagnet, which is known as the FOPT [30]. In our previous report [31], we observed an opposed behavior for $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds with $x = 0.3$ – 0.45 . All compounds in the range of Sr-doping undergo the SOPT with the critical exponent β value decreasing monotonically as Sr concentration increasing [31]. Presently, very few studies regard on the influences of A-site substitution on the MCE and the critical behaviors of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compound. The electrical magnetic properties of Ca and Sr co-doping in $\text{Pr}_{0.65}\text{A}_{0.35}\text{MnO}_3$ compound have been reported by Biswas et al. [32]. They pointed out that $\text{Pr}_{0.65}(\text{Ca}_{0.7}\text{Sr}_{0.3})_{0.35}\text{MnO}_3$ compound has two large MCEs taking place at the charge order transition ($T_{\text{CO}} = 220$ K) and the spontaneous destabilization of charge ordered state ($T_M = 120$ K). In the earlier works, the electronic, magnetic, and thermal properties of $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ compounds have been done [33,34]. Mollah et al. [33,34], reported a phase separate induced significant enhancement of magnetoresistance 10% at 100 Oe and 99% at 5 kOe around the metal-insulator transition. However, detailed analyses related to the magnetic critical region, and the magnetic interactions in these compounds have not been carried out yet and therefore this issue needs a more deep assessment.

To further understand the influences of Ca and Sr co-substitution, we prepared $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.0$ – 0.3 and investigated their critical properties in the vicinity of the magnetic phase transition. Basing on a phenomenological model proposed by Hamad [35] [36], and using magnetization versus temperature $M(T)$ data measured at several applied fields, we have predicted the MCE and the FM orders of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds through their typical parameters, such as the magnetic entropy change (ΔS_m), the relative cooling power (RCP), the variation of the specific heat change (ΔC_p), and the critical exponent β corresponding to the spontaneous magnetization (M_S). The results obtained reveal all the samples undergoing the SOPT together high values of ΔS_m . Further, the FM short-range order in $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds is favored when Sr concentration increases.

2. Experimental

Four compounds of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.0, 0.1, 0.2,$ and 0.3 were prepared by a solid-state reaction method. Firstly, stoichiometric masses of Pr_6O_{11} , CaCO_3 , SrCO_3 and Mn powders with high purity (99.9%) were ground and mixed, and then calcinated at 1200°C in air for 24 h. After that these mixtures were reground and pressed into pellets under a pressure 5000 kg/cm^2 , and then sintered at 1300°C in air for 48 h. X-ray diffraction (XRD) pattern was recorded at room temperature on an X-ray diffractometer Bruker AXS (D8 Discover) using a $\text{Cu-K}\alpha$ radiation. The Win-metric software was used to calculate the lattice parameters. Temperature dependences of magnetization under various magnetic fields ranging $H = 0$ – 10 kOe were measured on a vibrating sample magnetometer (VSM), according to the increasing direction of temperature with an increment of 2 K. T_C value of samples

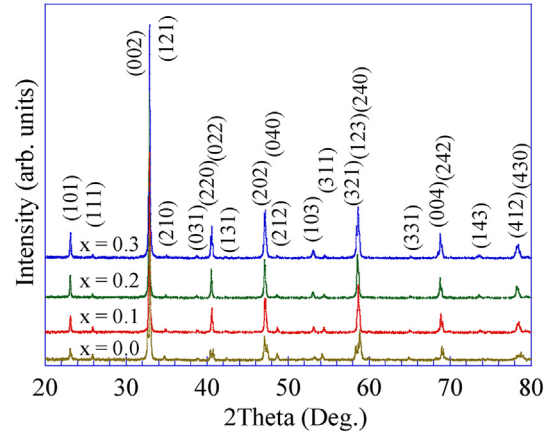


Fig. 1. Room-temperature XRD patterns corresponding to the Miller indices for $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds.

were determined via the second derivative of magnetization versus temperature (d^2M/dT^2 vs. T) [37].

3. Results and discussion

Powder XRD patterns of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds illustrated in Fig. 1 present sharp and intense XRD peaks. These are suitable for a PDF card No. 49–0461 [38] of the XRD standard database. The Miller-indexes of all the XRD peaks belong to an orthorhombic structure with space group $Pbmn$. This suggests that all samples are single phase, without any trace of secondary phase. The lattice parameters (a , b , c , and V) were calculated and presented in Table 1. It shows that the lattice parameters slightly increase with Sr-doping concentration. The variation of the lattice parameters could be associated to a substitution of Sr^{2+} ion with a larger ionic radius ($r_{\text{Sr}^{2+}} = 1.44 \text{ \AA}$) for $\text{Pr}^{3+}/\text{Ca}^{2+}$ ions with the smaller ionic radii ($r_{\text{Pr}^{3+}} = 1.179 \text{ \AA}$ and $r_{\text{Ca}^{2+}} = 1.34 \text{ \AA}$) located at A-site in ABO_3 structure. This also affects the average ionic radius at A-site ($\langle r_A \rangle$), the dispersion of A-cation radius ($\sigma^2 = \sum y_i r_i^2 - \langle r_A \rangle^2$), and the Goldsmith tolerance factor ($\tau_G = (\langle r_A + r_O \rangle / \sqrt{2}(r_B + r_O))$, with r_A , r_B , and r_O are the ionic radii located at A-, B-, and O-sites in ABO_3 structure, respectively). It is also known that if τ_G value is in the range of $0.75 < \tau_G < 1$, ABO_3 compounds has a perovskite structure. These compounds will belong to an orthorhombic structure if $\tau_G < 0.969$. And in an ideal case, their structure is a cubic system corresponding to $\tau_G = 1$ [39]. For our case, the values of $\langle r_A \rangle$, σ^2 , and τ_G were calculated and listed in Table 1. Once can see that these parameters gradually increase with Sr concentration. Among these, the value of τ_G increase from 0.924 for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($x = 0.0$) to 0.935 for $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.3$), suggesting that the distortion in the structure of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ decreases with increasing Sr content.

The field-cooled magnetization versus temperature curves, $M(T)$, measured at 100 Oe of samples are performed in Fig. 2(a). A magnetic phase transition from FM state at low temperature region to PM state at

Table 1
Lattice parameters and T_C of $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ compounds.

Parameters	$x = 0.0$	$x = 0.1$	$x = 0.2$	$x = 0.3$
a (Å)	5.367	5.397	5.423	5.456
b (Å)	5.401	5.428	5.449	5.467
c (Å)	7.719	7.723	7.731	7.739
V (Å ³)	223.752	226.245	228.450	230.839
$\langle r_A \rangle$ (Å)	1.227	1.237	1.247	1.257
σ^2 ($\times 10^{-2} \text{ \AA}^2$)	0.544	0.860	1.155	1.431
τ_G	0.924	0.928	0.931	0.935
T_C (K)	132	145	204	268

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