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The effect of strontium deficiency in $Pr_{0.6}Sr_{0.4}MnO_3$ perovskite manganites

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ABSTRACT

The structural, magnetic and magnetocaloric properties of the mixed valent manganites $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ ($0 \le x \le 0.2$) with perovskite structure have been investigated. X-ray diffraction (XRD) analysis using Rietveld refinement show that all our samples are single phase and crystallize in the orthorhombic structure with *Pbnm* space group. Strontium vacancy leads to a gradual increase of the unit cell volume. Paramagnetic (PM) to ferromagnetic (FM) transitions have been observed in all our synthesized samples. With increasing Sr-deficient amount, the Curie temperature T_C decreases from 310 K for $x = 0$ to 170 K for $x = 0.2$. From the measured magnetization data of $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ ($0 \le x \le 0.2$) samples as a function of magnetic applied field, the associated magnetic entropy change $\left|\Delta S_M\right|$ close to the Curie temperature T_C has been determined. The $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ compound ($x = 0.05$) exhibits a maximum entropy change $\left|\Delta S_M^{\mathrm{Max}}\right|$ of 4.81 J/(kg K) at 260 K in a magnetic applied field of 5 T. $\left|\Delta S_M^{\mathrm{Max}}\right|$ decreases to 4.17 J kg/K at 175 K for $x = 0.2$ in the same field magnitude. Large relative cooling power (RCP) value of 260.7 J/kg is obtained for $x = 0.05$ sample at a field change of 5 T.

1. Introduction

Mixed-valent manganites with general formula $Ln_{1-x}A_xMnO_3$ (Ln = rare-earth cation, A = alkali-metal or alkaline-earth cation) have been the subject of a considerable interest after the observation of colossal magnetoresistance (CMR) and large magnetocaloric effect in these materials which are represented, respectively, by a change of the electrical resistivity and the magnetic entropy caused by a variation of an external magnetic applied field [1–6]. These oxides present a rich variety of physical properties related to the competing electron–lattice and electron–electron interactions [7–9]. Double exchange interaction (DE) between Mn^{3+}/Mn^{4+} pairs and the lattice distortion have been clarified to play an important role for the properties of these materials [10,11]. The properties of these compounds are significantly influenced by at least three factors which are namely doping level x (the Mn^{4+} amount), average size of the A cation site and cationic disorder [12–14]. Furthermore, depending upon the synthesis method, oxygen excess in $LaMnO_3$ leads to cation vacancies in the lattice structure on both the lanthanum and the manganese sites. In these compounds, the cation vacancy concentration as well as their relative distribution affects the physical properties [15,16].

It was shown by many authors that the presence of vacancies in perovskite manganites can exhibit improved physical properties. Arroyo et al. [17] reported that, as a result of the introduction of cationic vacancies in $La_{0.5}Ca_{0.5}MnO_3$ samples, the system presents an evolution from an anti-ferromagnetic/charge ordered insulating phase towards a ferromagnetic metallic state. Hébert et al. [18] have studied magnetic and transport properties of $LaMn_{1-x}O_3$ and $La_{0.9}Sr_{0.1}Mn_{1-x}O_3$ and they have shown that the creation of Mn site vacancies induces ferromagnetism and lowers the resistivity but prevent the establishment of metallicity for any of their samples. Phan et al. [19] have investigated the magnetocaloric properties of $(La_{1-x})_{0.8}Ca_{0.2}MnO_3$. They found that the maximum magnetic entropy change increased with increasing vacancies content from 3.11 J/(kg K) at 170 K for $x = 0.05$ to 5.46 J/(kg K) at 190 K for $x = 0.2$. Previous study in our group showed that praseodymium deficiency in $Pr_{0.7-x}\square_xSr_{0.3}MnO_3$ and $Pr_{0.8-x}\square_xSr_{0.2}MnO_3$ powder samples leads to an increase of the Curie temperature T_C and consequently to a reinforcing of the ferromagnetic state [20,21]. However, in $Pr_{0.5-x}\square_xSr_{0.5}MnO_3$ compounds vacancy destroys totally the paramagnetic–ferromagnetic transition followed by the ferromagnetic–antiferromagnetic one observed in the $Pr_{0.5}Sr_{0.5}MnO_3$ stoichiometric sample [22]. Studies on the praseodymium deficiency effects in the $Pr_{0.6}Sr_{0.4}MnO_3$ showed that $Pr_{0.6-x}\square_xSr_{0.4}MnO_3$ samples exhibit a ferromagnetic metallic behavior at low temperature and a decrease in the transition temperature with increasing deficiency content [23]. In this

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paper and as a continuing effort, we report the effect of the presence of a cationic vacancy on the A-site on the structural, magnetic and magneto-caloric properties in $Pr_{0.6}Sr_{0.4}MnO_3$ compounds.

2. Experimental techniques

Powder samples of $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ ($0 \leq x \leq 0.2$) have been synthesized using the standard solid state reaction method at high temperature. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000 °C for 60 h. The obtained powders were then pressed into pellets (of about 1 mm thickness and 13 mm diameter) and sintered at 1300 °C in air for 60 h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction at room temperature. As our samples have been synthesized in air, they are consequently stoichiometric in oxygen [24]. Structural analysis was carried out using the standard Rietveld technique [25,26]. Magnetization measurements versus temperature in the range 20–300 K and versus magnetic applied field up to 8 T were carried out using a vibrating sample magnetometer. MCE were deduced from the magnetization measurements versus magnetic applied field up to 8 T at several temperatures.

3. Results and discussion

The results of the X-ray diffraction (XRD) studies at room temperature of $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ ($0 \leq x \leq 0.2$) compounds indicate that all our samples were found to be single phase and have the same perovskite structure. As the vacancy content increases there is a shift in the intense diffraction peak to the lower angle. This result indicates an increase in the volume of the unit cell as the vacancy content increases. The structural parameters of the samples are refined by Rietveld's profile-fitting method. It has been found that all our samples can be indexed the orthorhombic structure with *Pbnm* space group. Fig. 1 shows typical measured and refined XRD patterns for $x = 0.05$ and 0.1 samples. As seen in Fig. 2a, for $0 \leq x \leq 0.1$, the lattice parameters a, b and $c/\sqrt{2}$ verified the relation $c/\sqrt{2} < a < b$ which indicates that the samples are characterized by the presence of the static Jahn–Teller distortion. With further increasing deficiency amount, the lattice deformation decreases ($c/\sqrt{2} \approx a < b$). The unit cell volume increases with increasing deficient content (Fig. 2b). As a strontium-deficiency induces an increase of the Mn^{4+} content with average ionic radius (0.53 Å) smaller than that of Mn^{3+} (0.65 Å), the increase of the unit cell volume with lacuna content cannot be explained in terms of Mn^{4+} amount, it may rather be related to an average ionic radius $\langle r_A \rangle$ of the A cation site with a vacancy radius $\langle r_V \rangle$ larger than Sr^{2+}.

Fig. 3a shows the temperature dependence of magnetization of $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ ($0.05 \leq x \leq 0.2$) samples at 50 mT. All samples exhibit a paramagnetic to ferromagnetic transition with decreasing temperature. It should be noted that the magnetization decrease at low temperature observed in praseodymium-deficient samples $Pr_{0.6-x}\square_xSr_{0.4}MnO_3$ ($0 \leq x \leq 0.15$) (related to the coexistence, at low temperature, of two phases: an orthorhombic phase with *Pnma* space group and a monoclinic one with *I*2/*a* space group) has not been detected in our strontium deficient compounds [27,28]. Fig. 3b displays the Curie temperature T_C (defined as the temperature at which dM/dT shows a minimum) as a function of Sr-deficient content. It is found that the T_C shifts to lower values from 260 K for $x = 0.05$ to 170 K for $x = 0.2$. According to the double exchange model, the decrease of T_C arises from a strong tilt of the MnO_6 octahedral which reduces the overlap between Mn 3d and O 2p orbital [29]. For all our samples, in the paramagnetic phase ($T > T_C$), the temperature dependence of the magnetic susceptibility follows the Curie–Weiss law, $\chi = C/(T - \theta_P)$, where C is the Curie constant and θ_P is the Curie–Weiss temperature (inset Fig. 3a). The values of θ_P are found to be 257 K, 236 K, 180 K and 177 K for $x = 0.05$, 0.1, 0.15 and 0.2, respectively. The positive θ_P values imply the ferromagnetic nature of the magnetic interactions between Mn ions. For $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ samples, θ_P value agrees with its T_C value, while for $x \leq 0.1$, θ_P values are higher than their corresponding T_C values. This difference indicates a presence of magnetic inhomogeneity in the paramagnetic phase. The Curie constant values calculated from the line slopes of the reciprocal susceptibility versus temperature curve, χ^{-1} (T), have been used to estimate the

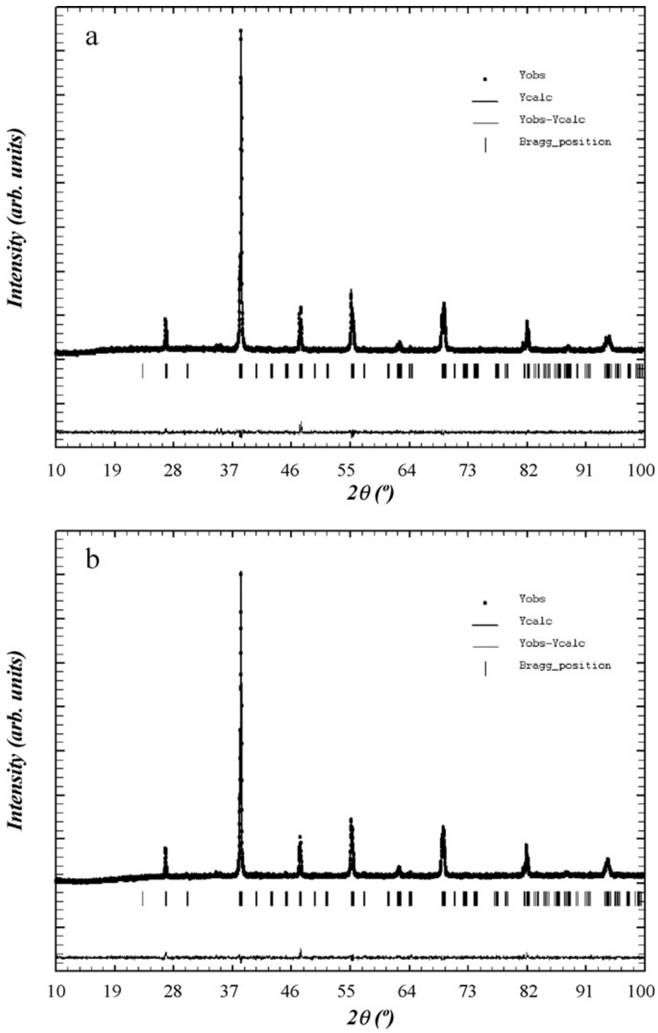

Fig. 1. XRD patterns of (a) $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ and (b) $Pr_{0.6}Sr_{0.3}\square_{0.1}MnO_3$ samples. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

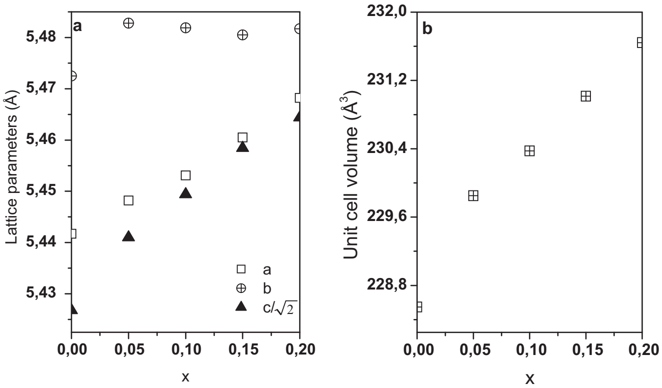

Fig. 2. Evolution as a function of lacuna content of (a) lattice parameters and (b) unit cell volume for $Pr_{0.6}Sr_{0.4-x}\square_xMnO_3$ samples $0 \leq x \leq 0.2$.

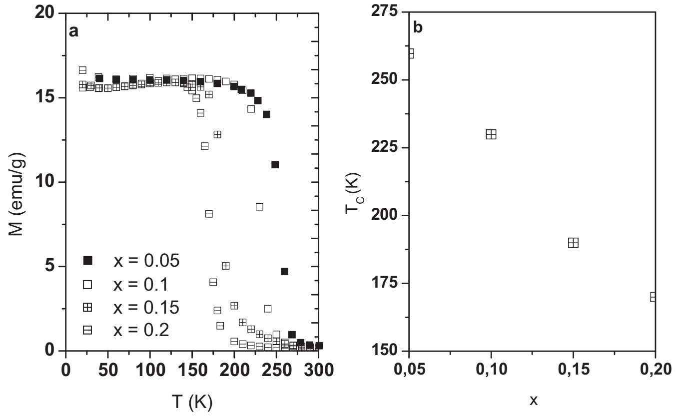

Fig. 3. (a) Temperature dependence of the magnetization at $\mu_0 H = 50$ mT and (b) Curie temperature evolution as a function of Sr-deficient amount for $Pr_{0.6}Sr_{0.4-x}\square_x MnO_3$ samples ($0.05 \leq x \leq 0.2$).

experimental effective paramagnetic moment μ_{eff}^{exp}. We found the μ_{eff}^{exp} value to be 4.8 μ_B, 4.5 μ_B, 3.8 μ_B and 4.7 μ_B for $x = 0.05$, 0.1, 0.15 and 0.2, respectively. These values are higher than the theoretically ones predicted for Mn ions.

In order to investigate the magnetic behavior at low temperatures, we have carried out magnetization measurements versus magnetic applied field up to 8 T at several temperatures. For all samples we observe a typical behavior of ferromagnetic samples, the magnetization below T_C increases sharply up to 1 T and then saturates. Fig. 4a shows the Arrott plots (M^2 versus H/M) obtained from magnetization isotherms for $x = 0.05$ sample. As can be seen, Arrott plots above T_C display a positive slope which indicates that a second order magnetic transition occurs [30]. Fig. 4b shows the temperature dependence of the spontaneous magnetization and the inverse of the susceptibility deduced from Arrott plots for $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ sample. The estimated value of the critical exponent, associated with the spontaneous magnetization, is found to be 0.2.

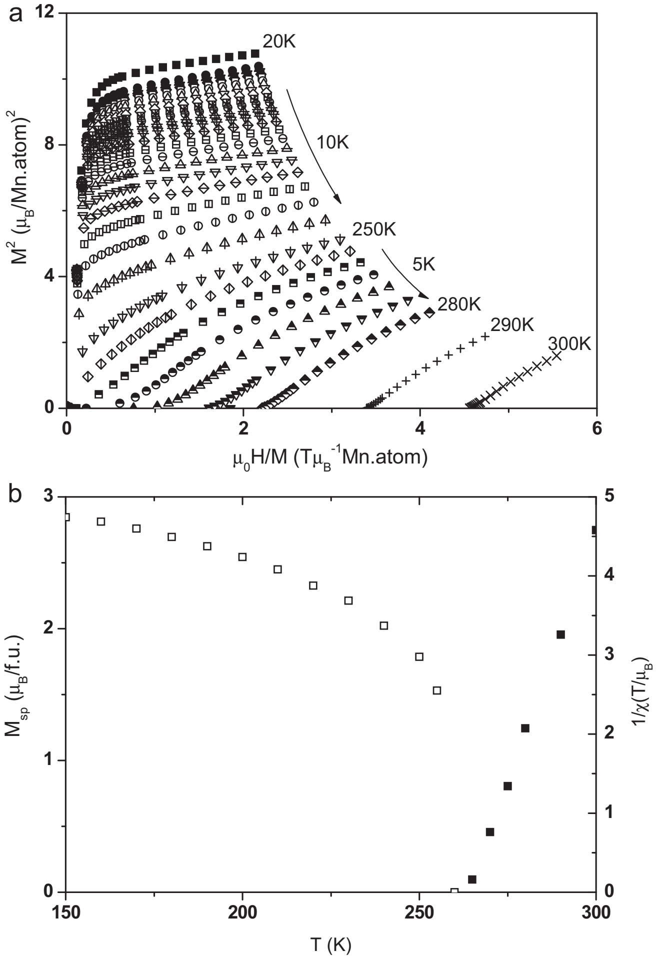

Fig. 4. (a) M^2 versus H/M isotherms and (b) the spontaneous magnetization (M_{sp}) and inverse of susceptibility $1/\chi$ as a function of temperature for $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ compound.

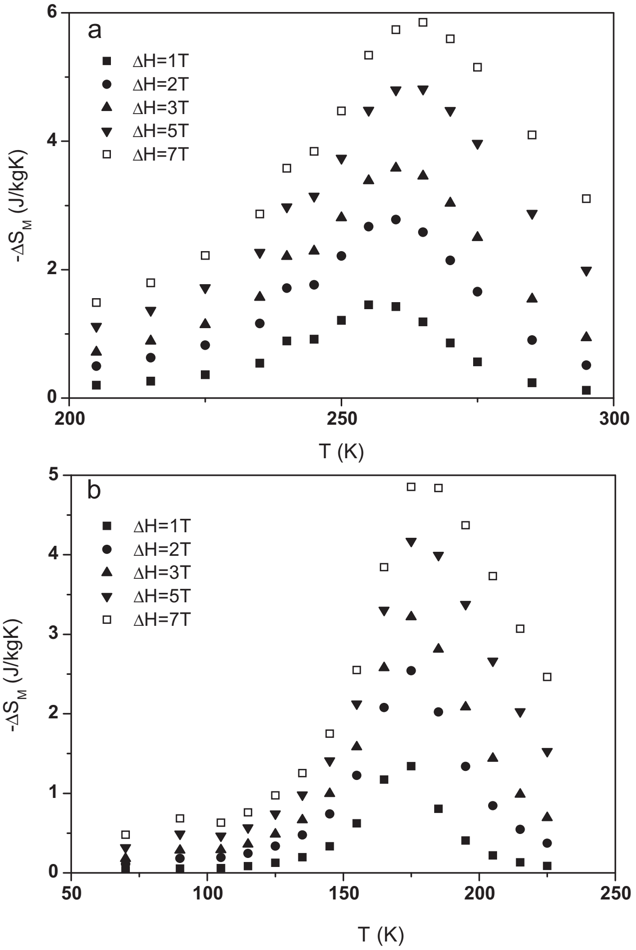

Fig. 5. Magnetic entropy change, $\left|\Delta S_M\right|$, versus temperature around the Curie temperature T_C for (a) $Pr_{0.6}Sr_{0.35}\square_{0.05}MnO_3$ and (b) $Pr_{0.6}Sr_{0.2}\square_{0.2}MnO_3$ samples.

The magnetic entropy change, ΔS_M, induced by the magnetic field change can be calculated according to the classical thermodynamic theory based on Maxwell's relations using the following equation $\left|\Delta S_M\right| = \sum_i (M_i - M_{i+1})/(T_{i+1} - T_i)\Delta H_i$ where M_i and M_{i+1} are the experimental values of magnetization measured at temperatures T_i and T_{i+1}, respectively, under magnetic applied field H_i [31]. Fig. 5a and b shows the behavior of the magnetic entropy change $\left|\Delta S_M\right|$ with external magnetic applied field as a function of temperature for $x = 0.05$ and 0.2 samples. Both samples exhibit large MCE effect around T_C and the magnitude of $\left|\Delta S_M\right|$ increases with increasing the magnetic applied field. For $x = 0.05$ sample, the values of the maximum entropy change, $\left|\Delta S_M^{Max}\right|$, are, respectively, 1.42, 2.78, 3.58, 4.81 and 5.85 J/(kg K) under magnetic applied field changes of 1, 2, 3, 5 and 7 T. With increasing Sr-deficiency amount, $\left|\Delta S_M^{Max}\right|$ shifts to lower value of 4.84 J/(kg K) for $x = 0.2$ upon a magnetic field change of 7 T. Although 5% of strontium lacuna reduces the T_C value compared to the stoichiometric $Pr_{0.6}Sr_{0.4}MnO_3$ sample, it improves the magnetocaloric properties [32]. In magnetic refrigeration, it is important that the magnetocaloric effect extends over a large temperature range. We evaluate the relative cooling power (RCP) as $\mathrm{RCP} = -\Delta S_M(T, H) \times \delta T_{\mathrm{FWHM}}$ where δT_{FWHM} is the full-width at half-maximum of $\left|\Delta S_M\right|$ versus temperature [33]. Upon a magnetic field change of 5 T, the RCP value is decreased with Sr deficiency amount from 260.7 J/kg for $x = 0.05$ to 249.9 J/kg for $x = 0.2$. Compared to the pure Gd which is considered as a typical magnetic refrigerant around room temperature, the RCP value for $\mathrm{Pr}_{0.6}\mathrm{Sr}_{0.35}\square_{0.05}\mathrm{MnO}_3$ sample is about 63% of that exhibited in pure Gd (410 J/kg at 294 K [34]).

4. Conclusion

The strontium-deficient $\mathrm{Pr}_{0.6}\mathrm{Sr}_{0.4-x}\square_x\mathrm{MnO}_3$ powder samples were synthesized using the solid state reaction at high temperature. All our samples are single phase and crystallize in the orthorhombic structure with *Pbnm* space group. The unit cell volume increases with Sr-deficient amount. All our compounds are ferromagnetic at low temperatures with a Curie temperature T_C decreasing with deficiency amount. A large magnetocaloric effect is observed in our samples with RCP value of 260.7 J/kg upon a magnetic applied field change of 5 T for $x = 0.05$ sample making our compounds potential candidates for magnetic refrigeration.

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