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Magnetic entropy change in perovskite manganites $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ with double metal–insulator peaks

Zhiming Wang [a,c,*], Qingyu Xu [b], Gang Ni [d], He Zhang [a]

[a] Institute of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China
[b] Department of Physics, Southeast University, Nanjing 211189, China
[c] National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
[d] Department of Physics Fudan University, Shanghai 200433, China

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ABSTRACT

Following the double metal–insulator peaks found in series of perovskite manganites $La_{0.7-x}Pr_xPb_{0.3}MnO_3$ (x=0, 0.05, 0.1), the magnetic entropy change of $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ was carefully investigated as a representative. The maximum magnetic entropy change ($\Delta S_H = -1.7$ J/kg K at 300 K) and the expanded refrigerant capacity (about 123.8 J/kg) had been obtained under 10 kOe magnetic field variation, though the double peak of maximum magnetic entropy change had not occurred since the comparative faint magnetic signal from the Pr ions inhomogeneity existed in the octahedral frame submerged in the strong magnetic signal originated from the dominating octahedral frame both in the double exchange mechanism, but the width at half maximum in the magnetic entropy change comparatively broadened.

1. Introduction

Recently, the perovskite manganites $Ln_{1-x}T_xMnO_3$ ($Ln^{3+}=La^{3+}$, Pr^{3+}, Nd^{3+}, Sm^{3+}, Y^{3+}, etc. $T^{2+}=Ca^{2+}$, Sr^{2+}, Ba^{2+}, Pb^{2+}, etc. ABO_3 type) had attracted considerable interest because they exhibit interesting physical effects and had potential applications due to the complex relationship between crystal structure, electrical, magnetic, and thermal properties, for example, the negative colossal magnetoresistance effect (CMR) and the common insulator–metal transition had been observed in the typical CMR material, the later generally accompanied by a Paramagnetic–Ferromagnetic transition [1–5].

Another important physical effect, the magnetocaloric effect, which results from the spin-ordering (i.e. ferromagnetic ordering) and is induced by the variation of the applied magnetic field, is crucial to the technology of magnetic refrigeration with many advantages over gas refrigeration: low noise, softer vibration, longer usage time, and absence of freon, etc. In perovskite manganites, the same with CMR, the magnetocaloric (MC) effect also are often observed around the Paramagnetic–Ferromagnetic transition temperature (i.e. the Curie temperature between a low-temperature, metallic–ferromagnetic state and a high-temperature, insulating–paramagnetic state) and this evidently suggests that there exists a certain of relation between the magnetic entropy change and the resistivity [6–8].

Following the discovered double metal–insulator peaks, the impetus for this paper study was seeking after the possible broad and large refrigerant capacity of the magnetocaloric effect in the perovskite manganites under conveniently low fields and at room temperature.

In the investigation about the perovskite manganites, most efforts had been focused on the doping range $x \sim 0.3$ or 0.33, which is an optimized percentage of Mn^{3+} replaced with Mn^{4+} for the electronic doping and providing potential charge carriers for the electronic conductivity in the double-exchange interaction, for the considerable perovskite manganites in the above-mentioned electronic doping range, these compounds are metallic and ferromagnetic at low temperature, while their conductivity displays the insulating or semiconducting behavior at high temperature. There is a transition between the low-temperature, metallic–ferromagnetic state and the high-temperature, insulating–paramagnetic state in which the magnetic ordering transition is incident with the metal–insulator transition [1–8].

The simultaneous occurrence of ferromagnetism and metallic behavior in perovskite manganites had been explained using the double exchange mechanism (DE), which involves interaction between pairs of Mn^{3+} and Mn^{4+} ions as proposed by Zener [9]. According to the model, e_g electrons could transfer easily between ions if the manganese spins were on the alignments of some frame in the certain of temperature, pressure, applied magnetic field, etc. and then the resistivity behavior showed a metal–insulator (MI)

* Corresponding author at: Institute of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.
Tel.: +86 25 84318429; fax: +86 25 84315694.
E-mail address: zhimingwang@mail.njust.edu.cn (Z. Wang).

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peak in some manganite samples. However, it was suggested that the double exchange mechanism alone was not sufficient to explain the details of the observed resistivity behavior such as the insulating behavior above T_C, here, the origin of the double resistivity peaks was still considered an open question and more investigations had to be carried out to elucidate their nature [10–17,23].

2. Experiments

The doped perovskite manganites $La_{0.7-x}Pr_xPb_{0.3}MnO_3$ (x=0, 0.05, 0.1) were prepared by sol–gel technique. Citric acid was used as a gelling agent for La, Pr, Pb, and Mn ions in a sand bath, and the obtained gel was subjected to successive heat treatment at 873 K for 2 h. After that, the microcrystalline powder was pelletized, pressed into disks and sintered at 1473 K for 24 h in an oxygen flow. The crystal structure of the bulk samples was determined by an X-ray diffractometer (XRD) with CuKα radiation (RK-D/Max-RA). Magnetization was measured using a vibrating sample magnetometer (VSM, LakeShore Cryotronics Inc.) with an absolute accuracy of 5×10^{-5} emu, in which a sample was placed inside a polyethylene pipe. The magnetization of an isothermal regime in the series samples was measured under an applied magnetic field varying from 0 to 10 kOe. The isotherms M vs H measurement were performed from 150 K–350 K run-through the ferromagnetic ordering transition temperature (T_C) of a representative sample $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$, the isothermal M–H curves were obtained by step of 10 K. M–H loops were measured at 160 K, 220 K, 275 K for the sample, respectively.

By conventional in-line four-probe technique, resistivity ρ was measured as a function of temperature in a superconducting magnet with a maximum applied field of 1 T.

The MR was calculated according to the equation given below:

$$MR(\%)=\frac{\rho(0,T)-\rho(H,T)}{\rho(0,T)}\times 100\%$$

where $\rho(0,T)$ was the zero field resistivity and $\rho(H,T)$ was the resistivity under external magnetic field.

3. Results and discussions

Fig. 1 presented an X-ray pattern of sample $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ and indicated that single-phase perovskite manganites, and the peak corresponding to MnO, MnO_2, and Mn_3O_4 had not been observed [PDF number: 22-1123 wavelength 1.5418 Å]. Fig. 2 showed the electrical resistivity as a function of temperature for the $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ sample under 0 kOe and 10 kOe, respectively. Under

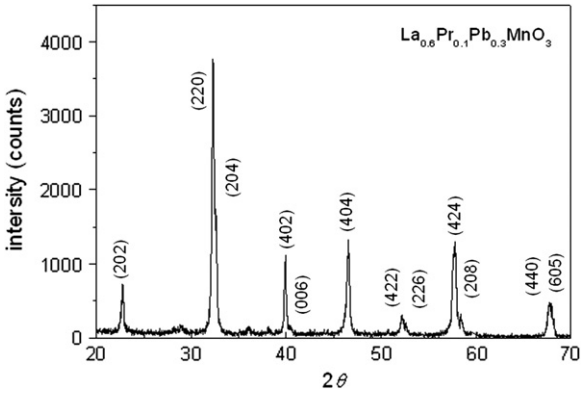

Fig. 1. Electrical resistivity as a function of temperature for the $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ sample under 0 kOe and 10 kOe, respectively. The inset showed the resistivity of $La_{0.7-x}Pr_xPb_{0.3}MnO_3$ (x=0, 0.05) samples under 0 kOe as a function of temperature.

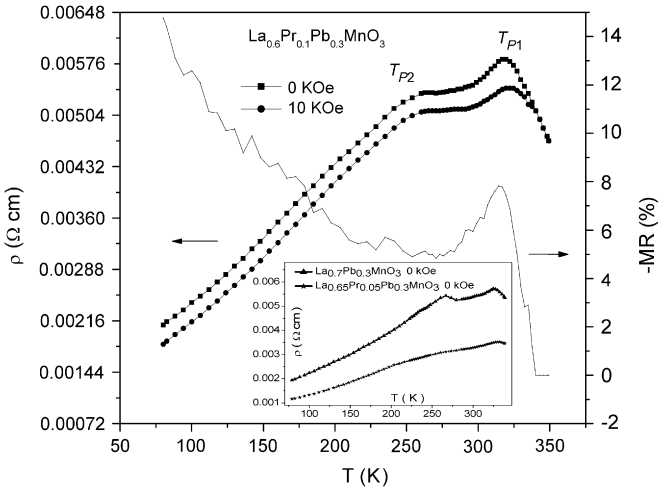

Fig. 2. X-ray diffraction pattern for the sample $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$.

0 kOe, the $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ sample showed the double metal–insulator transition peaks where the first peak at 322 K is defined as T_{p1} and the second peak, T_{p2} at around 258 K. Under 10 kOe magnetic field, there was suppressed resistivity behavior in the sample $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$, which is typical CMR behavior. The inset showed the resistivity of $La_{0.7-x}Pr_xPb_{0.3}MnO_3$ (x=0, 0.05) samples under 0 kOe as a function of temperature. Double metal–insulator peaks also occurred to these samples in the series.

With double M–I transition peaks T_{p1} and T_{p2}, the perovskite samples was rather attractive to improve the magnetocaloric effect, in which double magnetic entropy change peaks or broaden magnetic entropy change were expected.

The shifting of T_{p1} to slightly higher temperatures in the presence of external magnetic field (Fig. 2) might be due to increased alignment of magnetic moments causing delocalization of e_g electrons and enhancement of DE interaction between Mn^{3+} and Mn^{4+}. The delocalization was suggested to contribute to reduction of the T_{p1} resistivity peak. In addition, the fact that the MR peak was present in the vicinity of T_{p1} for x=0.1 $La_{0.6}Pr_{0.1}Pb_{0.3}MnO_3$ (Fig. 2) also indicated that the origin of both MR and T_{p1} peaks were related to the same mechanism, which was based on the double exchange interactions.

However, the fact that the T_{p2} peak did not shift in position upon application of external magnetic field indicated that the origin of this peak was different from that of the T_{p1} peak. A previous study suggested that the secondary T_{p2} peak originates from oxygen vacancies, valence states, ionic radii, external pressure, or magnetic inhomogeneity [18–23].

Uehara et al. [24] reported for the resistivity vs temperature at several Pr compositions of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ using electron microscopy techniques in 1999, that the rapid reduction with increasing y of the temperature at which the peak occurs, which correlated with the Curie temperature, had been interpreted as the evidence of two-phase coexistence, involving a stable ferromagnetic state at small y, and a stable charge ordered (CO) state in the large y PrCaMnO compound. Uehara et al. [24] finally substantiated their claims of phase separation, the direct evidence of the two-phase coexistence was provided by their Dark-field Images of electron microscopy. Using scanning tunneling spectroscopy, Fath et al. [25] had observed a clear phase-separated state in manganites $La_{1-x}Ca_xMnO_3$ and had reported the coexistence of metallic and insulating cluster clouds, based on the different spectroscopic signatures in the insulating (paramagnetic) and metallic (ferromagnetic) phases.