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Magnetocaloric effect at room temperature in manganese perovskite $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ with double resistivity peaks

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ABSTRACT

Series of polycrystalline manganese perovskite oxides $La_{0.7-x}Nd_xPb_{0.3}MnO_3$ (x=0, 0.05, and 0.1) are prepared by the sol–gel technique, $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ were representatively investigated because the peculiar double resistivity peaks were found; the maximum magnetic entropy change $\Delta S_H = -2.03$ J/kg K and its good refrigerant capacity 71.05 J/kg around room temperature were obtained under 9 kOe magnetic field variation. The expected double peaks of magnetocaloric effect had not occurred since magnetic entropy change originated from the differential coefficient of magnetic moment to temperature; the relatively well refrigerant capacity possibly results from the faint magnetic inhomogeneity mixed in the double exchange strong magnetic signal.

1. Introduction

An intense research effort has recently been devoted to study the interplay between the crystal structure, electrical, magnetic, and thermal properties in the perovskite manganese oxides (ABO_3) $A_{1-x}A'_xMnO_3$ ($A^{3+}=La^{3+}$, Nd^{3+}, Pr^{3+}, Sm^{3+}, etc., $A'=Ca^{2+}$, Sr^{2+}, Ba^{2+}, Pb^{2+}, etc.). As a function of temperature, applied magnetic field, and doping, this system displays a rich phase diagram in the magnetotransport and structural properties, for example, the negative colossal magnetoresistance effect (CMR) and the conventionally insulator–metal transition; the latter is generally accompanied by the ferromagnetic order transition [1–8]. Another important physical diagram, the magnetocaloric effect (MC, i.e. the magnetic entropy change), 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 some advantages over gas refrigeration as, low noise, softer vibration, longer usage time, absence of freon, etc. Perovskite manganites, with the same CMR, MC also is often observed around the ferromagnetic ordering transition temperature (i.e. the Curie temperature between a low temperature, metallic–ferromagnetic state and a high temperature, and insulating–paramagnetic state) [9–11], and this evidently suggests that there exists a certain replacing of definite relation between magnetic entropy change and metal–insulator transition of resistivity.

Based on the newly discovered double metal–insulator peaks of resistivity, the aim of this research paper is to search for the possible broad and large refrigerant capacity of magnetocaloric effect in the manganese perovskite at low magnetic fields and in the vicinity of room temperature.

On one hand, the common perovskite manganese oxides are metallic and ferromagnetic at low temperature, while their conductivity displays insulating or semiconducting behavior at high temperature. There is a transition between a metallic–ferromagnetic state at low temperature and an insulating–paramagnetic state at high temperature. The metal–insulator transition of the resistivity between these two states is strongly coupled with the magnetic ordering transition. On the other hand, when a field is applied in the manganese perovskite materials, the unpaired spins are aligned parallel to the field, which lowers the entropy and causes the sample to heat up, on the contrary, when an applied field is removed from a magnetic sample, the spin tends to become random, which increases the entropy and causes the material to cool off. Therefore, the magnetocaloric effect in this kind of material also always occurs at its magnetic ordering transition temperature (i.e. T_C).

According to the conventionally double exchange interactional mechanism that involves interaction between pairs of Mn^{3+} and Mn^{4+} ions introduced by Zener in [12], the above-mentioned simultaneous occurrence of ferromagnetism and metallic behavior in manganese perovskite could be explained as reason. In the double exchange model, 'e_g' electrons can be transferred easily between

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ions if the manganese spins are in parallel alignment and are coupled in ferromagnetic, and then the resistivity behavior in some perovskite sample showed a single metal–insulator transition peak. However, it was suggested that the double exchange interactional mechanism alone is not sufficient to explain the details of the observed resistivity behavior such as the insulating behavior above Curie temperature T_C, which caused the increase in resistivity as temperature was reduced. The origin of the double metal–insulator transition peaks is still considered an open question and more correlative researches should be carried out to explain this kind of peculiar phenomenon [13–21].

In this paper, we report the magnetocaloric effect of a special perovskite manganite with the double metal–insulator transition peak—$La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ at room temperature ($T_C \sim 293$ K).

2. Experiments

In the study of manganese perovskite, most endeavors have been concentrated on the doping range $x \sim 1/3$ or 0.3, 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 mechanism. Following the considerable manganese perovskite in the optimized electronic doped range, our series of optimal doping manganese perovskite oxides samples $La_{0.7-x}Nd_xPb_{0.3}MnO_3$ ($x=0$, 0.05, and 0.1) were prepared by the sol–gel technique, in addition, by Nd doping, aimed at fine tuning the average A-site cation radius $\langle r_A \rangle$ in this series of manganese perovskite, T_C were successfully modulated toward room temperature for the utility of this magnetocaloric effect [11,22–25]. Citric acid was used as gelling agents for La^{3+}, Nd^{3+}, Pb^{2+}, and $Mn^{3+/4+}$ ions in a sand bath, and the obtained gel was subjected to preparatory replacing of successive heat treatment at 873 K for 2 h. After that, the microcrystalline powder was pelletized, pressed into disks and successive sintered at 1573 K for 5 h in an oxygen flow. The crystal structure of the bulk samples was determined by an X-ray diffractometer (XRD) with Cu $K\alpha$ radiation (RK-D/Max-RA). M–T and M–H curves were measured by a vibrating sample magnetometer (VSM, LakeShore Cryotronics Inc.), with the sample placed inside a polyethylene pipe. Magnetization was measured using a vibrating sample magnetometer with an absolute accuracy of 5×10^{-5} emu. The magnetization of an isothermal regime in the series samples was measured under an applied magnetic field varying from 0 to 9 kOe. The isotherms M versus H measurement was performed around the ferromagnetic ordering transition temperature (T_C) of the samples. In the vicinity of T_C, isothermal M–H curves were obtained by a step of 5 K. The resistivity ρ as a function of temperature was measured by the conventional in-line four-probe technique in a superconducting magnet with an applied field of 0 or 1 T.

3. Results and discussion

Fig. 1 shows the electrical resistivity and a colossal magnetoresistance as a function of temperature for the $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ sample at 0 and 1 T. Under 1 T magnetic field, there is suppressed resistivity behavior in the $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$, which is a typical CMR behavior. The magnetoresistance was calculated according to the equation given below:

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

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

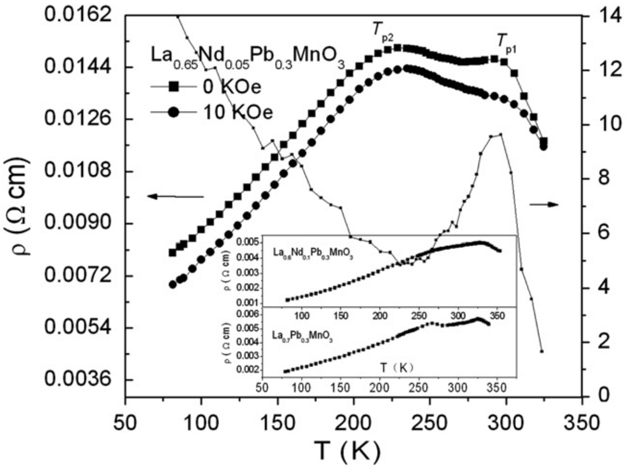

Fig. 1. Electrical resistivity as a function of temperature for the $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ sample under 0and 1 T and the its magnetoresistance calculated out. The inset shows the resistivity of $La_{0.7-x}Nd_xPb_{0.3}MnO_3$ ($x=0$ and 0.05) samples under 0 T as a function of temperature.

At $H=0$ T, the $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ sample showed the obvious double metal–insulator transition peaks where the first peak is at about 295 K defined as T_{p1} and the second peak T_{p2} is at around 225 K, and the maximum scale in the resistivity peaks T_{p2} is larger than maximum scale in the resistivity peaks T_{p1}. These insets show the resistivity of $La_{0.7-x}Nd_xPb_{0.3}MnO_3$ ($x=0$ and 0.05) samples under 0 T as a function of temperature. Double metal–insulator peaks also occurred to these samples in the series.

Since the double metal–insulator transition peaks T_{p1} and T_{p2} occurred, double magnetic entropy change peaks or broaden magnetic entropy change in the manganese perovskite samples were expected in reason, which is rather attractive to improve the magnetocaloric effect and the magnetic refrigeration technology.

On one hand, the shifting of T_{p1} to slightly higher temperatures in the presence of external magnetic field (Fig. 1) may be due to increased alignment of magnetic moments causing delocalization of 'e_g' electrons and the enhancement of double exchange interaction between Mn^{3+} and Mn^{4+}. The delocalization is suggested to contribute to the reduction of T_{p1} resistivity peak. In addition, the fact that the negative colossal magnetoresistance peak was present in the vicinity of T_{p1} for $x=0.05$ $La_{0.65}Nd_{0.05}Pb_{0.3}MnO_3$ (the right coordinate in Fig. 1) also indicates that the origin of both the negative colossal magnetoresistance and T_{p1} peaks are related to the same mechanism, which is based on the double exchange interactions [26–29].

On the other hand, T_{p2} peak does not shift on the resistivity curve plots along with the applied external magnetic field, which indicates that the origin of this peak is different from that of T_{p1} peak. A previous study on $La_{2/3}Ca_{2/3}Mn_{1-x}Co_xO3$ suggested that the secondary T_{p2} peak originates from oxygen vacancies due to substitution of trivalent Co^{3+} in the place of Mn^{4+} [28]. Mazaheri and Akhavan [26] suggested that the secondary T_{p2} peak observed for $(La_{1-y}K_y)_{0.7}Ca_{0.3}MnO_3$ is related to large differences in the valence states and ionic radii of La, Ca, and K ions. Ibrahim suggested that secondary T_{p2} peak observed for $La_{0.85-x}Sm_xAg_{0.15}MnO_3$ may possibly originate from the existence of mixed phases consisting of ferromagnetic and antiferromagnetic phases by increase of magnetic inhomogeneity as a result of double exchange interaction [21].

In a general way, the modification of La vacancies in the divalent alkali ions injection of $LaMnO_3$ stoichiometry phase, which is characterized by a long-range A-type antiferromagnetic order, is linked to superexchange between the Mn^{3+} pairs with the