THE ELECTRIC, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF PEROVSKITES $La_{0.6}(Pb_{0.4-x}Ca_x)MnO_3$ (x = 0.0, 0.2)

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Abstract: In the previous paper we investigated the structure, magnetic, magnetocaloric and magnetoresistance properties of perovskites $La_{1-x}Pb_xMnO_3$. In this work we report the influence of the simultaneous substitution of Pb and Ca on the properties of materials. The studied perovskites were single phase with rhombohedral structure. The microstructure of manganites were examined by SEM and the results show that the sample $N^0$1 has homogeneous grain structure with the size of 0.3 μm while the sample $N^0$2 has inhomogeneous grain structure with the size ranging from 0.4 to 1.2 μm.

The FC and ZFC measurements performed at low field indicated that there is spin glass like state occurring in both compositions. The substitution of Ca for Pb (radius of Ca^{2+} ions is less than of Pb^{2+}) in the sample leading to reduce of $<r_A>$ and yielding decrease of T_C, closing to room temperature. The sharp change of M(T) around FM-PM transition leading to significantly increase of $(\Delta S_m)_{max}$.

1. Introduction

Rare earth manganites $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth) have a subject of intensive study due to their interesting behaviors, such as colossal magnetoresistance (CMR) [1,2], charge ordering, phase separation and their promised for future technological applications. Double exchange (DE) mechanism provides a qualitative explanation for the magnetoresistance properties of these materials. By substituting Ca and Pb for La in $La_{2/3}(PbCa)_{1/3}MnO_3$ single crystal, Young et al [3] found that the maximum magnetic entropy change $|\Delta S_m| \approx 7.5$ J/kg.K at Curie temperature (T_C) 290K and magnetic field variation 7T. Troyanchuk et al. [4] have observed that the $La_{1-x}Pb_xMnO_3$ perovskites (x = 0.4 ÷ 0.6) have a rhombohedral (slightly distorted) cubic structure. Hwang et al. [5] have studied the crystal structure and the magnetic scaling behavior of $La_{1-x}Pb_xMnO_3$ perovskites (x = 0.0 ÷ 0.5) and have show that all the samples crystallize in the rhombohedral structure. In our previous paper, overall investigation of properties of $La_{1-x}Pb_xMnO_3$ (x = 0.0 ÷ 0.5) has been performed [6]. The results show that the symmetry decreases from cubic (x = 0.5) to rhombohedral (x = 0.4) and triclinic (x = 0.3, 0.2, 0.1), moreover the Curie temperature increases from 235 K for x = 0.1 to 310 K for x = 0.2 and then remained almost constant with further increasing x.

In this work, we report on our study of structure, magnetic and magnetocaloric properties of $La_{0.6}(Pb_{0.4-x}Ca_x)MnO_3$ (x = 0.0, 0.2) manganites.

2. Experimental

The samples $La_{0.6}(Pb_{0.4-x}Ca_x)MnO_3$ (x = 0.0, 0.2) were prepared by method of standard solid-state reaction technique. Presintering are twice performed at 800°C and 900°C. The samples are sintered at 920°C (sample $N^0$1) and 950°C (sample $N^0$2).

The structure of the samples was examined in a Bruker D5005 X-ray diffractometer. The microstructure and chemical composition were studied in a 5410 LV Jeol scanning electron microscope (SEM. Magnetic measurements were performed in a vibrating sample magnetometer (VSM) DMS 880 in magnetic field up to 13.5 kOe.

3. Results and discussion

The SEM analysis indicates that the crystallites of the sample N^{0}1 has homogeneous grain structure (Fig.1) with the size of 0.3 μm while the sample N^{0}2 has inhomogeneous grain structure with the grain size ranging from 0.4 to 1.2 μm.

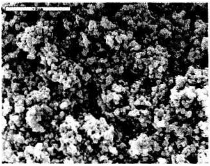

Fig.1. SEM photograph of the surface of sample N^{0}1.

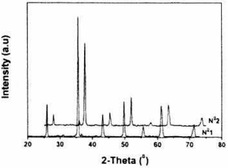

Fig. 2. X-ray diffraction patterns of studied samples.

Fig.2 presents the X-ray diffraction patterns of studied samples. It's clearly that all samples are of single phase with rhombohedral structure. The lattice parameters were determined from X-ray data. The results show that the lattice parameters decrease lightly in sample N^{0}2 with smaller amount of Pb.

Zero-field-cooled (ZFC) and field cooled (FC) magnetization measurements were performed in a magnetic field of 20 Oe. Fig. 3 shows that the FC and ZFC curves of samples are separated from each other at low temperatures. It is suggested that spin-glass like state exists in our samples at low temperatures. The competition between ferromagnetic and antiferromagnetic phase plays an important role in this case. The Curie temperature (T_C) of two samples were determined from these thermomagnetic curves. The T_C decrease with decreasing Pb content in sample N^{0}2 from x = 0 (T_C = 360 K) to x = 0.2 (T_C = 305 K). The substitution of Ca for Pb (radius of Ca^{2+} ion is less than of Pb^{2+}) in the sample N^{0}2 leading to reduce of $<r_A>$ and yielding decrease of T_C, closing to room temperature.

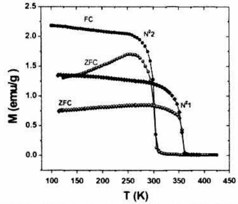

Fig.3. Thermomagnetic field-cooled (FC) and zero-field-cooled (ZFC) curves of samples measured at 20 Oe.

Isothermal magnetization curves M(H) have been measured at various temperature around the Curie temperature, in magnetic field up to 13.5 kOe. In order to evaluate the magnetocaloric effect of the studied samples, we calculated the changes of the magnetic entropy (ΔS_m) caused by the application of internal magnetic fields by using the following expression (1):

$$\Delta S(T,H) = S(T,0) - S(T,H) = \int_0^{H_{max}} \{\partial M(T,H)/\partial T\}_H dH \qquad (1)$$

Where, S(T,0) and S(T,H) represent the entropy without and with applied magnetic field, respectively.

Fig.4 shows the magnetic entropy change of samples as a function of temperature. Clearly that a sharp peak in $|\Delta S_m|$ is occurred around T_C and the maximum value is 0.87 J/kg.K and 1.79 J/kg.K for sample N⁰1 and N⁰2, respectively. The $|\Delta S_m|_{max}$ of sample N⁰2 is higher than those investigated in our previous reports for $La_{1-x}Sr_xCoO_3$ [7], for $La_{1-x}Pb_xMnO_3$ [6] but less than value for $La_{0.7}Sr_{0.3}MnO_3$ [8] with small substitution of Cu for Mn and for $La_{0.7}Sr_{0.3}MnO_3$ with small substitution of Ni for Mn [9].

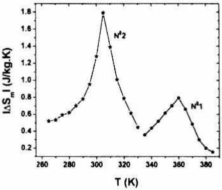

Fig.4. Magnetic entropy change versus temperature, of studied samples.

4. Conclusions

Magnetic and magnetocaloric properties of rhombohedral manganites $La_{0.6}(Pb_{0.4-x}Ca_x)MnO_3$ (x = 0.0, 0.2) were studied. Spin-glass like state exists in both our samples at low temperature. Sample N⁰2 with 1.79 J/kg.K may be considered as magnetic refrigerant materials operating at room temperature.

Acknowledgments:

This work was supported by the National Fundamental Research Program for Natural Science (Project 421004).

References

1. R.Von. Helmolt, J. Wecker, D. Holzapfel, L. Schultz, K. Samwer, *Phys. Rev. Lett.* **71**(1993) 2331.
2. J.M.D. Coey, M. Viret, S. M. Molnar, *Adv. Phys.* **48**(1999) 167.
3. Young Sun, M.B. Salamon, S.H. Chun, *J. Appl. Phys.* **92**(2002) 3235.
4. I.O. Troyanchuk, D.D. Khalyavin, H. Szymczak, *Mater. Sci. Bull.* **32**(1997) 1637.
5. T.S. Hwang, C.H. Chen, M.F. Tai, *Mater. Res. Soc. Symp. Proc.* **674**(2001) U 3.4.1.
6. Nguyen Chau, Hoang Nam Nhat, Nguyen Hoang Luong, Dang Le Minh, Nguyen Duc Tho, Nguyen Ngoc Chau, *Physica B* **327**(2003) 270.
7. N.H. Luong, N. Chau, P.M. Huong, D.L. Minh, N.N. Chau, B.T. Cong, M. Kurisu, *J. Magn. Magn. Mater.* **242-245**(2002) 760.
8. Nguyen Chau, Pham Quang Niem, Hoang Nam Nhat, Nguyen Hoang Luong, Nguyen Duc Tho, *Physica B* **327**(2003) 214.
9. Md.A. Choudhury, J.A. Akhter, D.L. Minh, N.D. Tho, N. Chau, *J. Magn. Magn. Mater.* **272-276**(2004) 1295.