MAGNETIC PROPERTIES AND EXISTENCE OF CHARGE-ORDERING STATE IN $La_{1-X}Ca_XMnO_3$ SYSTEM

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Abstract: Magnetic properties of $La_{1-x}Ca_xMnO_3$ ($x = 0.00 \div 0.70$) system have been investigated. All the samples were single phase and their lattice parameters decreased by Ca-doping concentrations. The Curie temperatures, magnetic entropy changes and ratio of Mn^{3+}:Mn^{4+} in samples have been determined. The real compositions of La, Ca, Mn were estimated by EDS-measurement. Especially, the existence of charge-ordering state have been found in low-doping samples of $x = 0.10$ and 0.30 at $T_{CO} \approx 200$ K and 110 K, respectively.

1. Introduction

The discovery of the magnetoresistive behaviour of the mixed valence manganites $A_{1-x}B_xMnO_3$ (with A = La, B = Ca, Sr, Ba...) in 1993 [1], opened a very interesting field of research from the fundamental as well as from the practical point of view. The hole-doped mixed-valence manganite perovskites can exhibit a magnetic transition at a Curie temperature (T_C), from a paramagnetic state (PM) at high temperature to a ferromagnetic state (FM) at low temperatures. Also, they present a transition from an insulator state to a metallic conducting state, which is companied by a peak in the resistivity at T_p [2]. In addition, the colossal magnetoresistance, the phase separation and the charge ordering effects [3] in different regions of the hole concentration (x) have been found. These interesting properties of the $La_{1-x}Ca_xMnO_3$ system are governed by competing Mn^{3+}-Mn^{3+} superexchange (SE) and Mn^{3+}-Mn^{4+} double exchange (DE) interactions accompanied with local Jahn-Teller distortions and formation of a mobile small-polaron state [4].

This paper investigated the magnetic properties of the $La_{1-x}Ca_xMnO_3$ system, especially, the existence of the charge-ordering state in low doping region ($x = 0.10$ and 0.30) was shown.

2. Experimental

Sample of $La_{1-x}Ca_xMnO_3$ were prepared with high-purity oxides of $CaCO_3$, MnO_2, La_2O_3 by solid state reaction method. The mixtures were presintered at 950°C for 10 hours and then that materials were grounded and pressed into the pillets. After that, the sintering process was carried out at 1340°C for 30 hours and then annealed at 650°C for 48 hours. The samples were cooled in air by the furnace turned off.

3. Results and discussion

The XPD patterns revealed that the samples were a single phase with orthorhombic perovskite structure. From XPD peaks, the lattice parameters (a, b, c) of the samples have been calculated. From obtained results, it can be seen that with increasing of the doping concentration Ca^{2+}, the a and b lattice parameters were reduced. One of the major reasons for this reduce may be radius of ion Ca^{2+} (0.99Å) smaller than that of La^{3+} (1.016 Å). Also because of this reason the volume of cell units decreases by increasing Ca-doping concentrations. Thus, the increase in doping Ca concentration causes the lattice distortion and thus is Jahn-Teller distortion typical. When La^{3+} is substituted by Ca^{2+}, the proportion of Mn^{4+} increases and the orthorhombic distortion decreases. The ratio of Mn^{3+}:Mn^{4+} ions dependences on the doping concentration (x) in system showed in Fig. 1. This curve looked like a fitting hyperbola. The real compositions of La, Ca and Mn were estimated in Ca/La units by EDS measurement more smaller than nominal compositions in all samples (these values are not shown here). The temperature dependence of the magnetization in all samples have been measured in field cooled (FC) and zero-field cooled (ZFC) under an external field of 1.1 kOe. From M(T) curves we extract the T_C values of the samples as the temperature where the curve has its inflexion point. The Curie temperature showed in table 2.

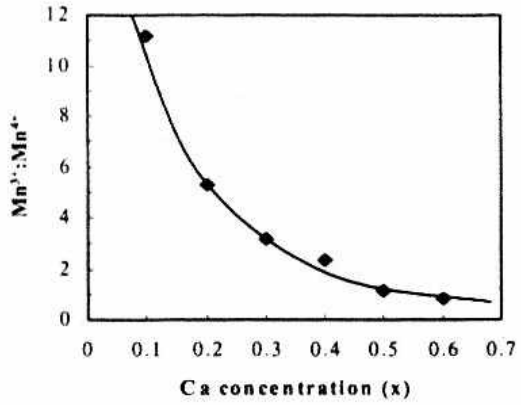

Fig.1. Ratio of Mn^{3+}:Mn^{4+} dependences on doping concentrations

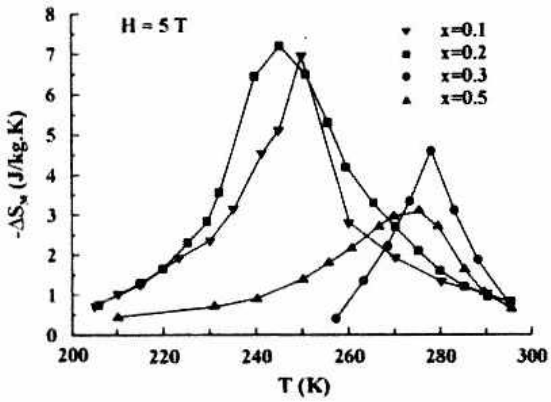

Fig.2. The temperature dependence of ΔS_{mag} of $La_{1-x}Ca_xMnO_3$

The measurement of the magnetization dependence on the various field have been performed up to 5 T, in various temperature ranging from 200 K to 300 K. From these curves, the obtained magnetic entropy change ΔS_{mag} as a function of temperature and their values for each sample was showed in Fig. 2. It is clear that the large magnetic entropy changes in this system originate from the considerable change of magnetization near T_C. The temperature dependence on the susceptibility of the samples has been measured (which are not shown here). From these curves, the Curie-transition temperature has been obtained at peaks of susceptibility curves. The values of the transition temperatures are corresponding to the same obtained those from magnetization curves, which showed transition from ferromagnetism to paramagnetism.

The temperature dependence of the resistivity curves in the samples have indicated that the samples of x = 0.20, 0.40 and 0.60 have a metal-semiconductor like transition at

maximum on resistivity curves. These transition temperatures (T_p) have been determined 251 K, 265 K and 257 K, respectively, which are nearly the T_C temperatures. The resistivity curves showed the charge-ordering state in other samples. Apart from the charge-ordering in sample of x = 0.50, it is found that the existence of charge-ordering state in samples of x=0.10 and 0.30. Fig. 3a and 3b demonstrated the existence of charge-ordering in suddenes of drop on resistivity curves of the samples with x =0.10 and 0.30. This observation is special case because according to the phase diagram of $La_{1-x}Ca_xMnO_{3-\delta}$ have been reported by Shiffer et. al [3], the CO-appeared at x = 0.51. While, Kumar et. Al [8] had found the CO-state in region of 0.63 < x < 0.67. Hyroyuki et. Al [9] observed CO at x < 0.20. This our result contributed to clear that the charge-ordering not only occurred in high-doping concentration with x > 0.50, but there is a very fair possibility of CO-existent in the lower doping concentration of x < 0.50 in $La_{1-x}Ca_xMnO_{3-\delta}$ system, also.

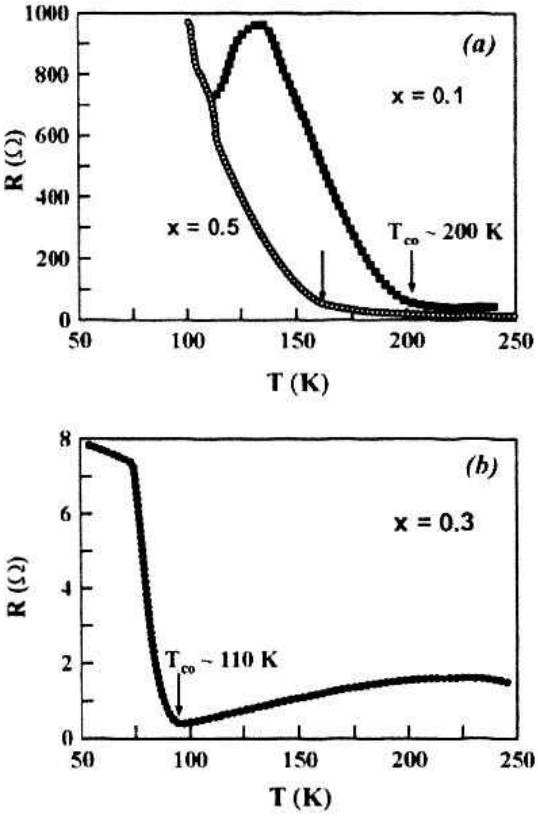

Fig.3. Plots of resistivity versus temperature on $La_{1-x}Ca_xMnO_3$

4. Conclusions

Ca^{2+} substitution for La^{3+} causes the increasing of Mn^{4+} and decreasing of orthorhombic distortion in crystal structure of samples. The values of magnetic entropy change indicated in table 2 are relative large in this system. Especially, the existence of CO-state in low-doping concentration of Ca with x = 0.10 and 0.30 had invented in this system.

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References

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