THE MAGNETIC PROPERTIES AND CHARGE-ORDERING STATE IN $La_{1-x}Ca_xMnO_3$ (x = 0.46; 0.50) COMPOUNDS

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Abstract. The compounds of $La_{1-x}Ca_xMnO_{3-\delta}$ with x=0.46 and 0.50 occupy special positions in the phase diagram of $La_{1-x}Ca_xMnO_{3-\delta}$ system due to their interesting properties and charge-ordering phase transition. The samples were prepared by a solid-state reaction method. The XPD patterns show that the samples are of a single-phase orthorhombic-perovskite structure. The chemical compositions of the samples are investigated by EDS. The concentrations of oxygen and Mn^{3+}; Mn^{4+} ions have been determined by dichromate method. The charge-ordering state have been found below 150 K by magnetic and resistance measurements. This phenomenon relates to metal-insulator transition. The results are discussed in competition between double exchange (DE) and super-exchange (SE) interaction.

1. Introduction

Doped perovskite manganites of the form $La_{1-x}Ca_xMnO_{3-\delta}$ are mixed valence systems containing Mn^{3+} and Mn^{4+} ions. They exhibit colossal magnetoresistance effects (CMR). Such CMR effects originate from a double exchange mechanism (DE) between Mn^{3+} and Mn^{4+} species that induces ferromagnetic correlation. Besides DE, it has been found that the super-exchange interaction (SE) also has an important role to govern the electronic and magnetic properties of these compounds [1, 2].

The compound of $La_{1-x}Ca_xMnO_{3-\delta}$ with $x = 0.50$, where one e_g hole (or one electron) hoping between two Mn sites, shows a peculiar behavior of charge-ordering (CO) transition which takes place when the electrons become localized because of the ordering of cations of different charges on specific lattice sites. The charge-ordering state can be melted by a strongly external magnetic field and also by high pressure. This phenomenon has an origin from competition between the double exchange and antiferromagnetic super-exchange interaction [1, 3]. In present work we investigate the magnetic properties and charge-ordering state of $La_{1-x}Ca_xMnO_{3-\delta}$ (x = 0.46 and 0.50) compounds.

2. Experiments

The samples with nominal composition of $La_{1-x}C_xMnO_{3-\delta}$ (x=0.46 and x=0.50) were prepared by standard solid-state reaction method [4]. The structure of the samples was inspected by X-ray powder diffraction (XPD) using Cu-K_α radiation at room temperature. The chemical composition was checked by Energy Dispersive Spectra (EDS). The magnetization curves were measured with a vibrating sample magnetometer (VSM). The a.c susceptibility measurement was performed in the

range of temperatures from 70 K to 310 K. Resistance versus temperature curves were measured on cooling from 300 K to 77 K without an external magnetic field by four-point probe technique. The magnetocaloric effect measurement was performed in a pulse field.

3. Results and Discussion

The XPD patterns of the $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.46; 0.50) samples indicate in figure 1. It shows the single-phase orthorhombic perovskite structures. The structure parameters of $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.46; 0.5) derived from XPD data collected at room temperature are identified *Pnma* structure. The obtained lattice parameters of the samples with x=0.46 and 0.50 are similar (different about some parts of thousand angstroms, please see table 1). However, these values are smaller than those of the undoped $LaMnO_3$ compounds, due to the fact that the radius of Ca^{2+} (0.99 Å) is smaller than that of La^{3+} (1.016 Å) [3].

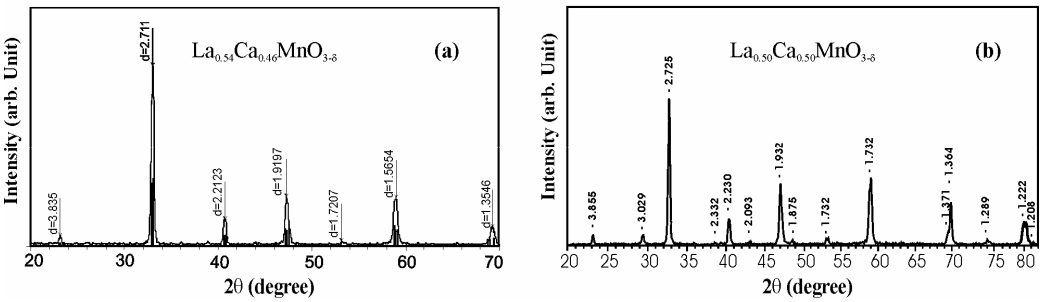

Figure 1a, 1b: XPD patterns of the $La_{1-x}Ca_xMnO_{3-\delta}$ samples (x = 0.46, 0.50).

Table 1: The lattice parameters of the samples $La_{1-x}Ca_xMnO_{3-\delta}$ with x = 0.46 and 0.50.

Sample	Lattice parameters			Volume of cell unit
	a (Å)	b (Å)	c (Å)	($Å^3$)
$La_{0.54}Ca_{0.46}MnO_{3-\delta}$	5.457	5.466	7.799	232.628
$La_{0.50}Ca_{0.50}MnO_{3-\delta}$	5.453	5.461	7.801	232.304
$LaMnO_3$	5.532	5.742	7.728	244.500

Base on the oxygen deficiencies (δ) determined by dichromate method, the contents of Mn^{3+}, Mn^{4+} ions and the ratios of Mn^{3+}/Mn^{4+} have been estimated and showed in Tab. 2.

Table 2: Obtained oxygen deficiencies, determined contents of Mn^{3+}, Mn^{4+} ions and Mn^{3+}/Mn^{4+} ratios.

Sample	δ	Mn^{3+}	Mn^{4+}	Mn^{4+}/Mn^{3+}
$La_{0.54}Ca_{0.46}MnO_{3-\delta}$	0.0179	0.5738	0.4242	0.7393
$La_{0.50}Ca_{0.50}MnO_{3-\delta}$	0.0184	0.5368	0.4632	0.8629

Fig. 2a and 2b show the temperature dependences of magnetization for x=0.46 and 0.50, respectively, in both field cooled (FC) and zero-field cooled (ZFC) modes under an external field of 200 Oe. Both field cooled (FC) and zero–field cooled (ZFC) curves show a phase transition from the paramagnetic to ferromagnetic state at Curie temperature T_C=273 K for x=0.46 and T_C=275 K for x=0.50. These values are about 50 K higher than those obtained by other authors [5]. This feature is most probably caused by the different sintering condition in sample preparation, resulting a difference in actual content of Mn^{3+} and Mn^{4+}. According to *Chen* et al. [6], the decreasing of La-content causes significant effects on enhancement of the Curie temperature.

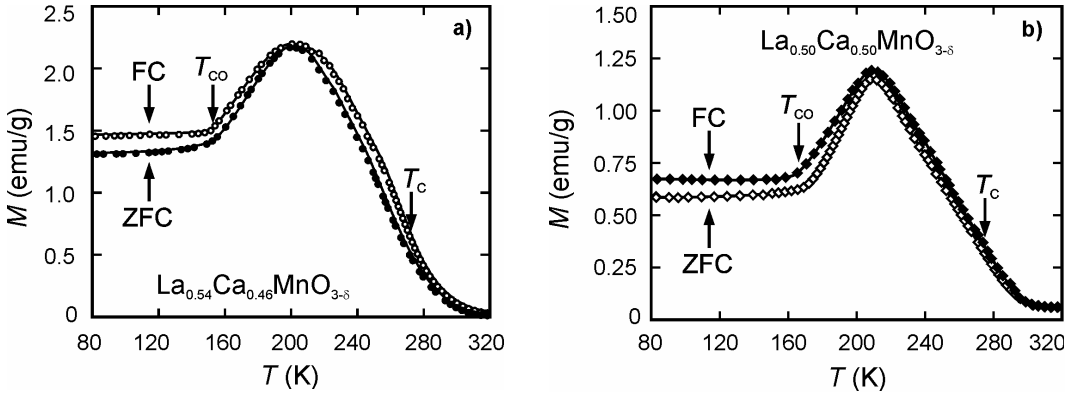

Figure 2a, 2b: Temperature dependences of magnetization for $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.46, 0.50), in both field cooled (FC) and zero-field cooled (ZFC) modes under an external field of 200 Oe.

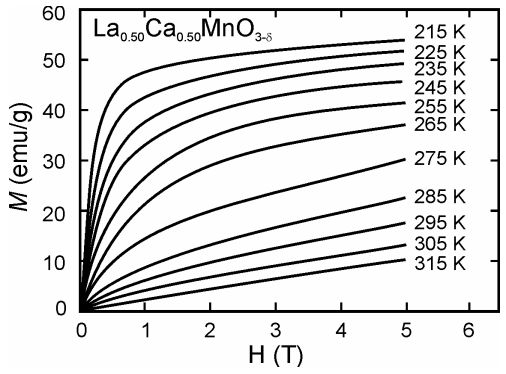

Figure 3: Isothermal magnetization curves for the $La_{0.50}Ca_{0.50}MnO_{3-\delta}$ sample measured up to 5T.

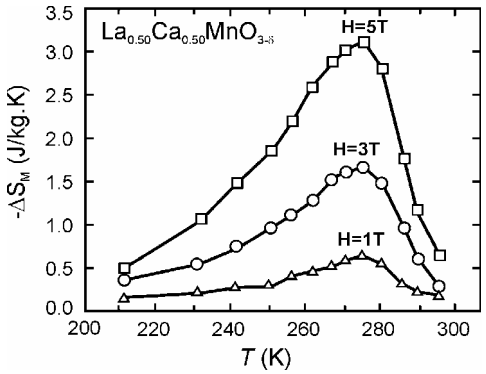

Figure 4: Entropy change as a function of temperature for $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.50) sample under field variations.

Fig. 3 shows the magnetization as a function of the applied field up to 5 T measured at various temperatures around the Curie point for $La_{0.50}Ca_{0.50}MnO_{3-\delta}$ sample. From these curves with various temperature intervals, the magnetic

entropy change, $\Delta S_{mag,}$ can be approximately calculated using isothermal magnetization measurements [7]. Fig. 4 presents the magnetic entropy change as a function of temperature for x=0.50 sample. We obtained a peak of magnetic entropy change at T_C. The maximum entropy change corresponding to a magnetic field change of 5 T is 3.25 J/kg.K.

The charge ordering state is found in the temperature dependence of magnetization. As we can see in Fig.5, this phenomenon coincides with the observation of the jumps at T_{CO}=156 K and 150 K on the a.c susceptibility versus temperature plots for the x=0.46 and 0.50 samples, respectively.

Fig. 6 shows the temperature dependences of the resistance of the samples. We can see clearly an abrupt drops at temperature of 156 K and 150 K for x=0.46 and 0.50, respectively, that should also relate to a charge ordering transition. Our result is fairly consistent with the value of 160 K for $La_{0.50}Ca_{0.50}MnO_{3-\delta}$ obtained by Radaelli et al. [8].

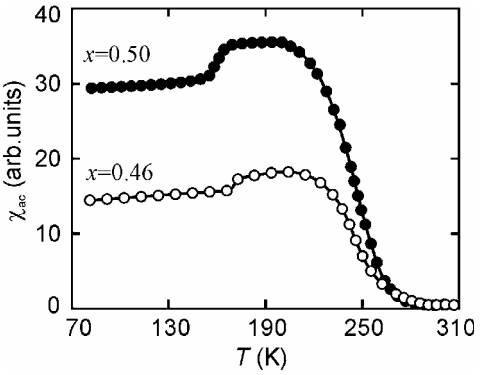

Figure 5: A.c susceptibility versus temperature plots for $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.46, 0.50) samples.

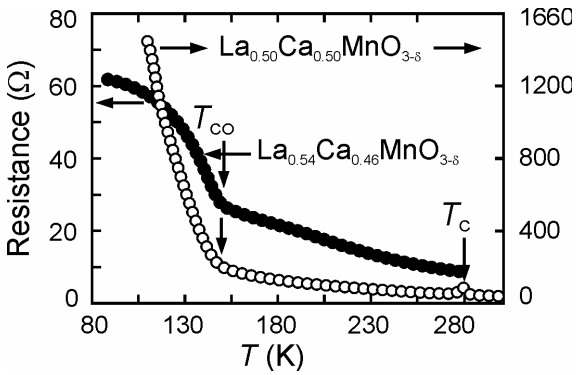

Figure 6: Temperature dependences of the resistance for $La_{1-x}Ca_xMnO_{3-\delta}$ (x=0.46, 0.50) samples.

It has been shown that most of the CO states in $Re_{1-x}A_xMnO_3$ compounds have a CE-type AFM order. In terms of the model proposed by Goodenough [9], Mn^{3+} and Mn^{4+} are arranged like a checkerboard and Mn^{3+} sites have a Jahn-Teller distortion. The charge-ordering state will occur when this distortion becoming stable. Furthermore, the exchange coupling between Mn^{3+} and Mn^{4+} ions depends on the type of e_g orbital occupied at the Mn^{3+} site, leading to the following charge/orbital pattern: along the a-axis, the same in-plane arrangement of Mn^{3+} and Mn^{4+} is stacked and the neighboured planes are antiferromagnetically coupled via super-exchange interaction. On the other hand, charge-ordering phenomenon is mutually exclusive with ferromagnetism in double-exchange (DE) mechanism, which requires a charge-carrier hopping from Mn^{3+} ion across an intervening O^{2-} ion to an adjacent Mn^{4+}. It is very intriguing that charge-ordering state coexists with ferromagnetism in a narrow temperature region in $La_{0.5}Ca_{0.5}MnO_{3-\delta}$, because it is very useful for applications of the micro-technology nowadays.

In conclusions, for present samples, the Mn^{3+}/Mn^{4+} ratio has been modulated mainly by oxygen deficiency. It reveals that the large increase of Mn^{4+} content plays a crucial role in variations of magnetic properties of the samples. We found that the charge-ordering state coexists with a antiferromagnetic state at temperatures below 150 K. The competition between the double exchange (DE) and super-exchange (SE) is believed to be responsible for this peculiar behavior. The observed magnetocaloric effect in $La_{0.5}Ca_{0.5}MnO_{3-\delta}$ sample is remarkable at high magnetic field variation.

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