PROPERTIES OF La-DEFICIENT $La_{0.50}Ca_{0.30}MnO_{3-\delta}$ COMPOUND

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Abstract: A La-deficient sample of $La_{0.50}Ca_{0.30}MnO_{3-\delta}$ was prepared by the solid-state reaction method. The crystal structure of the sample is single phase and orthorhombic. Together with M(T) curves, from the χ_{ac}^{-1} curve the Curie temperature of this compound nearly 300K has been determined which is significantly higher than those of the $La_{1-x}Ca_xMnO_{3-\delta}$ system. The magnetic entropy change reaches a maximum value of $-\Delta S_M$ = 5.3J/kg.K at the Curie temperature upon a 5T magnetic field variation. Values of 0.0163 and 0.153 for the oxygen deficiency δ and the ratio of Mn^{3+}:Mn^{4+}, respectively, have been determined. It is suggested that this compound is a suitable candidate for application as a working substance in magnetic refrigeration.

1. Introduction

Magnetic refrigeration has attracted considerable interest due to its advantages over gas refrigeration [1]. Recently, attentions are focused on compounds with a large magnetic entropy change at a high temperature as well as $La_{1-x}Ca_xMnO_{3-\delta}$ compounds [2]. On the other hand, one of the interesting problems of manganese perovskites is the non – stoichiometry of oxygen – the La-deficient compounds. In particular, a giant magnetocaloric effect, and magnetic properties take place in La-deficient compounds. Experimentally, the charge-ordered state (CO) the real-space ordering of charge carriers Mn^{3+}, Mn^{4+} was observed in many of the hole-doped manganese oxides. In this paper, electronic and magnetic properties of La deficient $La_{0.5}Ca_{0.3}MnO_{3-\delta}$ compound have been presented. Especially the charge order state was observed at near antiferromagnetic to paramagnetic transition temperature.

2. Experimental

The sample of non-nominal- stoichiometry compositions of $La_{0.5}Ca_{0.3}MnO_3$ was prepared by the solid state-reaction method, which had reported somewhere [3]. The measurements have been carried out by X – ray powder diffraction (XPD), magnetization M(T), magnetocaloric effect, susceptibility (χ_{ac}) resitivity R(T), oxygen deficiency (δ) and ratio of Mn^{3+}:Mn^{4+}.

3. Results and discussion

The XPD patten reveals that the sample is a single phase orthorhombic - perovskite structure. Lattice parameters of the sample have been determined, which are a = 5.447,

b = 7.713 and C = 5.445 which is identified with the Pnma structure in comparison with the crystal structure of the parent compound $LaMnO_3$ [4]. So it is found that the crystal structure of sample has been distorted by the La deficiency.

By the tritation method, the oxygen concentration in $La_{0.5}Ca_{0.3}MnO_{3-\delta}$ has been determined. With δ = 0.0163. From the oxygen deficiency δ, the ratio of Mn^{3+}: Mn^{4+} was estimated to be 0.153. It can be seem that the large amount of Mn^{3+} became Mn^{4+} in comparison with that of $LaMnO_3$, which contained about 5% Mn^{4+} only [4]. This is the main reason that causes the changes in properties of the sample.

From EDS pattern, the real compositions of the sample has been estimated wish La = 66.475%, Ca = 3.70% and Mn = 29,83%.

Fig. 1 shows the temperature dependence of the magnetization measured up field of 1000 Oe under zero – field (ZFC) and field cooled (FC) conditions. It is found that the magnetic moment curves of the sample in the ZFC coinciding with that is FC. This suggests that the spin order does not depend on external magnetic filed until 1000 Oe. The Curie temperature T_c is determined as 292K on both the temperature dependence of the magnetization and of the susceptibility measurements. From the χ_{ac}^{-1} curve in fig 2, the paramagnetic-ferromagnetic transition at Curie temperature has indicated. The T_c of this sample is relative large than that of $La_{1-x}Ca_xMnO_3$ system. The key mechanism is connected to the charge transfer induced by either stoichiometric defects, such as action vacancies or oxygen content or hole doping by partial substitution on the Mn – site. That means the substitution of Ca^{2+} for La^{+3} in La – deficient case leads to an increase of the Mn^{3+}-Mn^{4+} localized states, accompanying an enhancement of the ferromagnetic double exchange interaction. Therefore, the Curie

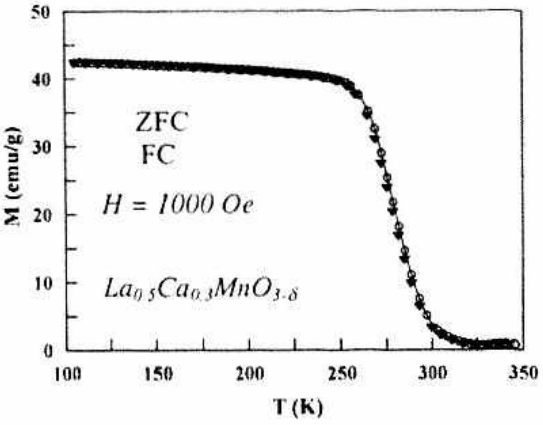

Fig.1. The magnetization curves of FC and ZFC conditions

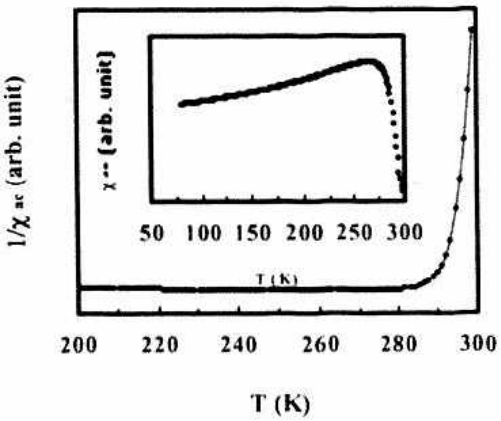

Fig.2. The χ_{ac}(T) curve of the sample (insert is the χac^{-1}(T) curve)

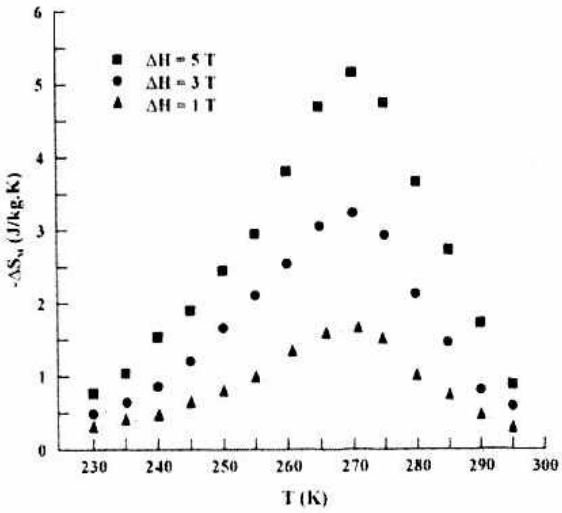

Fig.3. The magnetic entropy change in various fields

temperature has increased. From the M(H) curves of magnetization in the dependence on applied field up to 5 T, the magnetic – entropy change ΔS_{mag} can be approximately calculated and the obtained value as 5.3 J/kg.K (fig. 3). This large value originated from the considerable change of the magnetization near T_C. Another possible reason is that higher magnetic field, the magnetic moments are oriented better than at lower magnetic field and when the ratio of Mn^{3+}/Mn^{4+} was reduced, the competition between DE and SE interaction increased, this SE interaction will be dominated.

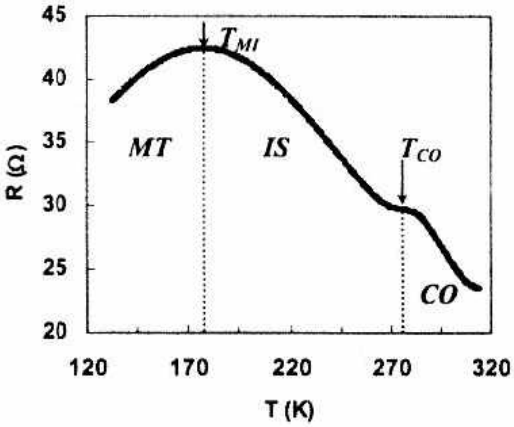

Fig.4. The R(T) curve of $La_{0.5}Ca_{0.3}MnO_{3-\delta}$ sample

The resistivity curve of the sample in fig 4 showed the maximum value at T_{MI} = 185 K where the insulator – metal transition occurs. The nature of the I–M generally transition can be understood that the Jahn – Teller distortion due to the Mn^{3+} ions plays a key role in manganese. The creation of Mn^{3+} ions removes the distortion leading to move cubic structures. Therefore, across the I- M transition appearing at T_{IM}, the J-T distortion decreases [5], and the distortion becomes more prominent in insulating phase. Especially, on the rensitivity curve, we found an anomalous point at about 285 K. The resistivity is strongly dropped from this point toward to higher temperatures. It is suggested that may be this point the charge – ordering, because of charge ordering can also possible occurs around Curie –temperature transiton (292 K).

4. Conclusions

The obtained results revealed intrinsic processes in this compound. It is found that the transition from ferromagnetism to paramagnetic showed at Curie temperature $T_c \approx$ 292K, which is near room temperature, and insulator – metal transition occurs in low temperature region at 185K and large magnetic entropy changes around T_c.

Especially, it is observed the anomalous point at 285K, which we suggested the change ordering around Curie temperature.

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