INFLUENCE OF THE SUBSTITUTION OF Mn-SITE ON THE PROPERTIES OF THE $La_{0.67}Ca_{0.33}Mn_{0.9}A_{0.1}O_3$ (A = Ni, Al, Cu) COMPOUNDS

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Abstract: The influence of the Mn-site substitution (10%) by Ni, Al and Cu on the magnetotransport properties of $La_{0.67}Ca_{0.33}MnO_3$ compound have been investigated. Ferromagnetic-paramagnetic and metal-insulator transitions were significantly affected by Mn-site substitution although no observable differences were found in their crystal structures. The Curie temperature T_C is lowermost for Ni-doped sample. However, magnetic-field-induced resistivity of the Ni-doped sample more strongly changes than that of the other samples. The maximum magnetoresistance ratio (CMR = (R(0)-R(H))/R(0)) reached 17% in the Ni-doped sample at a low-magnetic field of 0.4 T. These results clearly indicated that double exchange (DE) and super exchange (SE) interactions play very important role in CMR for these compounds.

1. Introduction

In recently years, a great deal of work has been devoted to the mixed-valence manganites $R_{1-y}A_yMnO_3$ (R = Rare Earth elements, A = Ca, Sr, Ba, Pb) exhibiting colossal magnetoresistance (CMR) due to its significance both for fundamental research and for practical application in magnetoelectronics [1-2]. It was shown that two factors govern essentially the colossal magnetoresistance (CMR) properties of these compounds, the size of the interpolated cation and the hole carrier density characterized by the mixed valence Mn(III) : Mn(IV). Many issue of this system have focused to revolving of the principal factors to determine the Curie temperature and the magnetoresistance. Some of them have shown that T_C and magnetoresistance are optimized when about 30% Mn^{3+} ion is converted to Mn^{4+} by substitution of strange elements [3]. For the case of doping hole, there are large variations in the observed T_C and in the magnitude of the magnetoresistance in this system. These discrepancies have been ascribed to chemical disorder, oxyen deficienties, grain boundary effects, lattice constant effects, etc.

It is more interest to study the effects of Mn-site substitution, which is direct subtitution of a strange element for Mn in an octahedral structure frame. This may provide clues for both exploring novel CMR materials and concerning the mechanism of CMR. For this reason, we study the magnetic and magnetotransport properties of the $La_{0.67}Ca_{0.33}Mn_{0.9}A_{0.1}O_3$ (with A = Ni, Al and Cu) compounds.

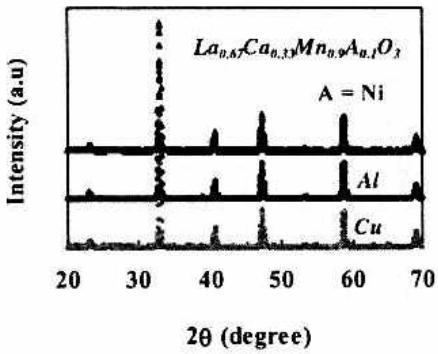

Fig.1. XRD patterns of samples

2. Experimental

Samples with the nominal compositions of $La_{0.67}Ca_{0.33}Mn_{0.9}A_{0.1}O_3$ (A = Ni, Al and Cu) were prepared by using the solid-state reaction method. The crystal structures of samples were checked by powder X-ray diffraction. The magnetic and electronic properties of the samples have been inveatigated by the magnetization and resistivity measurements.

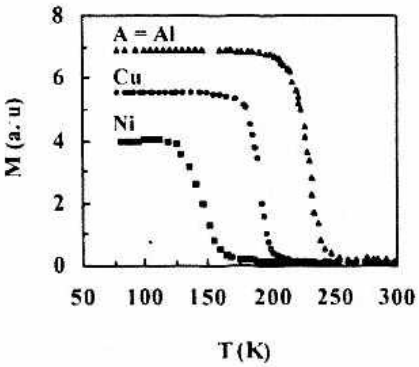

Fig.2. M(T) curves of samples $La_{0.67}Ca_{0.33}Mn_{0.9}A_{0.1}O_3$ (A = Ni, Al, Cu)

3. Results and discussion

Fig. 1, XPD pattern prove that all samples were single phase with orthorhombic perovskite structure.

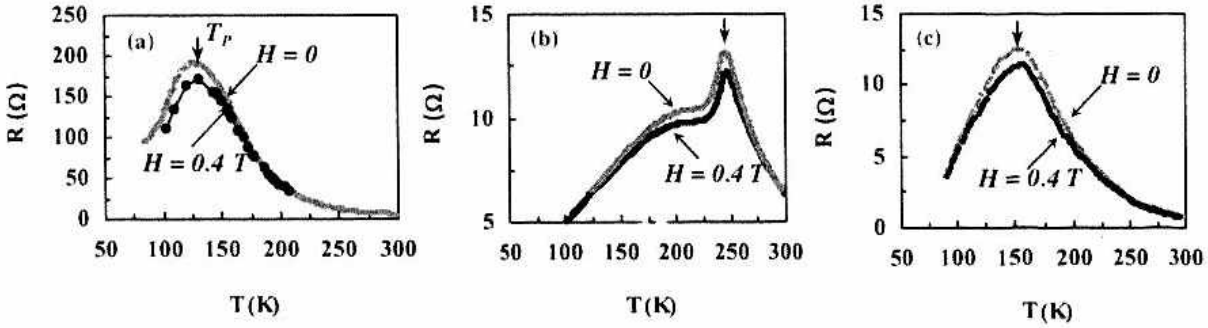

Fig.3. R(T) curves of samples at H = 0 and 0.4 T (a) A = Ni, (b) A = Al and (c) A = Cu

Fig. 2 shows the temperature dependence of magnetization of all the samples. These curves M(T) show that there exist a magnetic ordering transition from a paramagnetism to ferromagnetism as T decreases. The Curie temperature T_C is 160, 245 and 200 K for A = Ni, Al and Cu, respectively. These values are lower than that of un-doped sample (about 260 K) and T_C is lowermost for Ni-doped sample. This is due to substituting Ni, Al and Cu for Mn dilutes Mn sub-lattice causes decreasing intensity of double-exchange (DE) interaction between Mn^{3+} and Mn^{4+}. However, substituting an ion with the highest magnetic moment (Ni) produces the lowest T_C. This strongly implies that a super exchange-like interaction could take place through Mn^{3+}/Mn^{4+}-O-Ni^{2+} [4].

The temperature dependence of resistance curves under zero and 0.4 T magnetic field are demonstrated in Fig. 3. From these curves, we have determined the transition from a ferromagnetic metallic (FMM) state to a paramagnetic semiconducting (PMS) state as T increases. This transition occurs at temperature about T_p = 125, 242 and 153 K for dopants of Ni, Al and Cu, respectively. Under magnetic field of 0.4 T, T_p displaces toward higher temperature, from 125, 242 and 153 K to 131, 245 and 157 K for Ni, Al and Cu-doping samples, respectively. Displacing to higher temperature the metal-semiconductor (M-SC) transition causes the high magnetoresistance ratio in the vicinity of this M-SC transition as shown in fig. 4. In cases of A = Al or Cu, maxima of CMR in our samples are about 10% at magnetic field of 0.4 T. This value is not smaller than those of un-doped samples, however,

it is significantly lower than those of A = Ni (CMR = 17% at 100 K), although, T_C in case of A = Al and Cu are higher than those of Ni sample. These results prove more that magnitude of CMR closely concerns to SE interactions.

One another hand, in case of A = Ni, CMR response is greatly broadened toward low temperature. This may be result from the cluster glass nature of $La_{0.67}Ca_{0.33}Mn_{0.9}Ni_{0.1}O_3$. Ni substitution induces AFM interaction between Ni^{2+}-O-Mn^{3+}/Mn^{4+} and promotes the proportion of Mn^{4+}-O-Mn^{4+} AFM interaction. The random distribution of FM and AFM exchange interaction would favor the formation of cluster glass, as evidenced in the temperature dependence of magnetization of the sample at low magnetic field [5]. Due to the formation of FM clusters and their randomly frozen moment as well as the large spin fluctuation, there should be severe spatial magnetic disorder that may play a key role in electron localization and lead to high resistivity state at low temperature. When applied magnetic field, the whole moment of the frozen FM clusters expand and their orientation are forced to align uniformly so that the spatial magnetic disorder is reduced, which favors the electron delocalization and consequently results in a significant drop of the low temperature resistivity. This may be the reason that a low temperature CMR effect is usually observed in a cluster glass state.

In conclusion, the suppression of T_C and a large variation of magnetoresistance have related to the effects of Ni, Al and Cu-substitution (10% at) for Mn in $La_{2/3}Ca_{1/3}MnO_3$ compound. The responsible for this case may be there is not only by the decline of DE interaction results from diluted Mn-sublattice but also competition between double exchange and superexchange interactions, especially, the Ni-O-Mn bond and influence of magnetic moment of Ni ions is taken account. Therefore, the magnetic nature of substituting elements cannot be neglected in understanding the properties of LaCaMnAO systems.

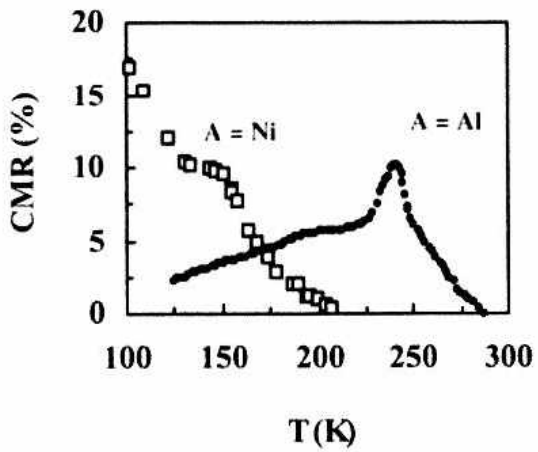

Fig.4. The CMR(T) curves of samples $La_{0.67}Ca_{0.33}Mn_{0.9}A_{0.1}O_3$ (A = Ni,Al, Cu)

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