

PHYSICAL PROPERTIES OF PEROVSKITE $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.90}\text{Co}_{0.10}\text{O}_{3.6}$

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Abstract: Ferromagnetic-paramagnetic transition was significantly affected by Mn-site substitution, however no observable changes were found in its crystal structure of the sample. The Curie temperature strongly decreases from 267 K to 160 K for the sample of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.90}\text{Co}_{0.10}\text{O}_{3.6}$, respectively. Especially, it is observed that the charge-ordering appeared at 125 K. The activation energy value (E_a) has been estimated by EPR measurement as 0.093 eV. The anomaly in the thermal evolution of the EPR linewidth has been observed also. This anomaly has been attributed to a Jahn-Teller transition or an electric phase separation. The changes of the physical properties of this sample are successfully explained by introduction the SE and antiferromagnetic order in Co-O-Mn bond.

1. Introduction

La-Ca-Mn-O have an ABO_3 -type perovskite structure, in which Mn and O create a basic module of the MnO_6 octahedron, and that plays a major role in deciding on the properties of material. Within the frame of MnO_6 , various cations in La-site produce different chemical pressures to change the Mn-O-Mn bond angle and bond distance. It has been proved that the average size of La-site cation and their size distribution have significant effect on the properties of manganites. However, the effects of La-site substitution are indirect to the environment of the MnO_6 octahedron. Therefore, it is more interesting to study the effects of Mn-substitution, which is direct to extend our understanding of this compound.

Some authors have been suggested [1,2] that Mn substitution weakens the double exchange (DE) interactions but the origin is not clear yet. On the other hand, can play an important role or not the magnetic nature of doping cations in this compound? We investigated the physical properties of perovskite $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.90}\text{Co}_{0.10}\text{O}_{3.6}$ compound to contribute to solution this question.

2. Experimental

The sample was prepared by solid state reaction method. From mixed high-purity powders of La_2O_3 , CaCO_3 , MnO_2 and CoO_3 we pressed into pellets and then presintered at 1000°C for 2 hours, at 800°C for 24 hours and cooled down by the furnace turning off. After that, the pellets were grounded about 1 hour and palletized again. A multi-step procedure is applied for the heat treatment of the sample. The sample has been investigated by XPD, $M(T)$, $\chi_{ac}(T)$, $R(T)$, EPR and ratio $\text{Mn}^{3+}:\text{Mn}^{4+}$.

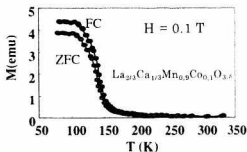


Fig.1. The $M(T)$ curve of the sample

3. Results and discussion

From XRD pattern showed that the sample was single phase and the lattice parameters have been determined with $a = 5.439 \text{ \AA}$, $b = 7.690 \text{ \AA}$, $c = 5.423 \text{ \AA}$. These values are in comparison with those of the 5% at Co-substitution in the $La_{2/3}Ca_{1/3}Mn_{0.95}Co_{0.05}O_3$ [3]. It showed that the lattice parameters in our sample are light smaller. The reason is that the radius of Co^{3+} (0.61 \AA) is smaller than that of Mn^{3+} (0.65 \AA). The oxygen concentration (δ), amount of Mn^{3+} , Mn^{4+} and the ratio of Mn^{3+}/Mn^{4+} have been obtained $\delta = 0.0079$, $Mn^{3+} = 4.4858$, $Mn^{4+} = 0.4142$, and the ratio of $Mn^{3+}/Mn^{4+} \cong 1.173$. This value is smaller than that ratio of Mn^{3+}/Mn^{4+} is $2/3:1/3 = 2$ in $La_{2/3}Ca_{1/3}MnO_{3.5}$ compounds indicating that the Mn^{3+} decreases and Mn^{4+} increases with affects of doping Co. Some results indicated that substituting an ion Co with the higher magnetic moment produces the lower magnetization. This strongly implies that DE model alone cannot explain the effect of the transition metal substitution.

When Mn ions are substituted by Co ions, it should be consider existence of metal-oxygen bonding, Co-O-Mn and Co-O-Co, but the number of Co ions/Mn ions should be statistically greater than 17% to find the Co-O-Co bond. In this compound, the amount of Co ion is a 10% atom and the probability of a Co-O-Co bond is low. Thus, it may assume that the Co-O-Mn bond is the disturbance only. This is made that Co and Mn ion interact by way of the super exchange (SE) mechanism. This is plausible, because more Mn^{3+} become Mn^{4+} in Co-substituted compound. The competition between DE and SE mechanism is leading that SE rather than DE and SE is dominant in the Co-O-Mn bond interaction, therefore the ferrimagnetic configuration has been formed.

From magnetization curve (Fig. 1), the Curie temperature has been determined as about 160 K. This value can compare with those of some authors [1,2,3].

The comparison indicated that with substitution of Co for Mn the Curie-transition temperature strongly decreases by increasing Co-concentration. As known that the ion Co with the higher magnetic moment produces the lower T_C -temperature due to competition of SE by DE when the Mn^{4+} ions increase in compound. This strongly implies that the effect of the magnetic transition-metal-substitution is existence in $La_{2/3}Ca_{1/3}MnO_3$ compounds.

In general, the substitution lowers the Curie temperature (T_C) and the paramagnetic insulating behavior extends to a lower temperature. The reason is that the atomic number of Co is replaced to Mn and it has the most similar characteristics to Mn among the substituting elements. This implies that the properties of the $LaCaMnCoO$ compound are strongly dependent on the substituting element and DE model is not enough to explain for change in resistivity. Perhaps, the assumes of the SE effect and ferrimagnetic configuration above may be satisfied to discuss for change characteristics of Co-substituted sample. Especially, it is observed that the charge-ordering appeared at 125 K. This behavior must be continued to investigate in next study by systematics.

Line of EPR measured at temperature above $1.1 T_C$ for the sample is shown in fig. 2. It is found that the symmetric EPR lines were occurred at temperatures much higher than T_C . The symmetric EPR signals are believed to be due only to Mn ions in paramagnetic state. The temperature dependences of the peak to peak EPR linewidth, ΔH_{pp} in fig. 3. It

can be seen the temperature dependence of linewidth undergoes two minima. This behavior is probably caused by Jahn-Teller transition which has been observed in LaMnO_3 . Another possibility is that a ferromagnetic phase appears at $T > T_C$ (electronic phase separation). It is worth to note that electronic configuration of Co is very complicated due to the existence of several possible spin state.

EPR line intensity as a function of temperature $I(T)$ is determined by double integration of the experimental derivative absorption curve measured at different temperature. The fitted $I(T)$ by the expression of $I(T) = I_0 \exp(E_a/k_B T)$ is shown in fig. 4. Where E_a is activation energy for polaron hopping. The value of $E_a = 0.093$ eV derived from this fitted line. This value is slightly smaller than that of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ as $E_a = 0.12$ eV. The activity energy has been described by the polaron formation across the ferromagnetic-paramagnetic phase transition. We attributed the observation of lower value of E_a in the sample to the reduction of Mn^{3+} content caused by the Co substitution for Mn.

In conclusion, the changes of physical properties in $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.90}\text{Co}_{0.10}\text{O}_{3.1}$ are successfully explained by introducing the SE and antiferromagnetic order in Co-O-Mn bond. The obtained results showed that the magnetic nature of doping elements must be taken account in understanding the properties of this compound. EPR linewidth curve has two minima. It is concerning to complicated electronic configuration of Co. The activation energy E_a has been determined describing the polaron formation across the ferromagnetic-paramagnetic phase transition.

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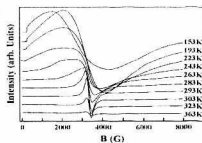


Fig.2. Selected EPR spectra for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$ sample

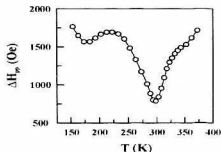


Fig.3. EPR line-width, ΔH_{pp} , for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$ sample

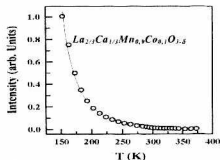


Fig.4. Observed and fitting curve of temperature dependence of the EPR line intensity for sample $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_{3.1}$