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# STUDY ON PROPERTIES OF THE PEROVSKITE $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ SYSTEM

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## ABSTRACT

In this paper, the electrical and magnetic properties of a perovskite series of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ (with x = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) have been studied, in order to investigate the influence of Co substitution for Mn. From XPD patterns, the crystalline structure of all samples has been investigated carefully. Our experiment results from VSM measurement showed that the ferromagnetic – paramagnetic phase transition temperature decreases with increasing the Co content. The temperature dependence of resistivity is well fitted by the functions of $R(T) = R_o e^{\frac{E_a}{k_B T}}$ in the range of temperature from 150 K to 300 K, in which $E_a$ is activation energy. Also, magnetoresistance in the low magnetic fields of 0 – 0.4T of all samples has been investigated. It is found that the Co content dependence of $E_a$ and $CMR_{max}$ (the maximum of magnetoresistance ratio) of these sample is similar. These results can be explained in terms of double-exchange interaction of $Mn^{3+}$–$O^{2-}$–$Mn^{4+}$ and super-exchange interactions of $Co^{3+}/Co^{4+}$–$O^{2-}$–$Mn^{4+}$.

*Keywords*: crystal structure, Curie temperature, activation energy, competitive interaction, colossal magnetoresistance.

## 1. INTRODUCTION

The manganese perovskite with general formula $R_{1-x}A_xMnO_3$ (where R = rare earth; A = Ca, Ba, Pb) was widely studied [1, 2] because their electrical and magnetic properties are promising for technology applications in the future. In this system, there is coexistence of $Mn^{3+}$ and $Mn^{4+}$ ions. Also, there is coexistence of Double–exchange (DE) and Super-exchange (SE) interactions in these compounds. DE interaction between $Mn^{3+}$ and $Mn^{4+}$ ions leads to metallic ferromagnetism, while SE interaction between $Mn^{3+}$–$Mn^{3+}$ or $Mn^{4+}$–$Mn^{4+}$ results in insulating antiferromagnetism [3, 4]. Therefore, the magnetic and electrical properties of these mixed valence Mn compounds are determined by competition between DE and SE interactions which strongly relates to the ratio of $Mn^{3+}/Mn^{4+}$, which can be controlled by substituting divalent ions such as $Ca^{2+}$ for $La^{3+}$. Recent studies have showed that Curie temperature $T_C$ and magnetoresistance are optimized when ~30% of the $Mn^{3+}$ ($t_{2g}^3 e_g^1$, S = 2) is converted to $Mn^{4+}$ ($t_{2g}^3 e_g^0$, S = 3/2) by substituting $Ca^{2+}$ for $La^{3+}$ [5, 6, 8].

Another way to tailor the ratio of $Mn^{3+}/Mn^{4+}$ is substituting other transitional metal elements for Mn, which exhibits the dissimilar electronic configuration as well as the difference in ionic radius to the Mn site, it shall lead to dramatic change in the electrical and magnetic properties of manganese compounds. Hence, it is interesting to study the effect of substitution by the 3d magnetic elements for Mn-site. In this paper, we focus to study influence of Co substitution on the magnetic and electrical properties of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ compounds ($0.05 \leq x \leq 0.3$). Our experimental results showed that their Curie temperatures are depressed from 248.5 K for the sample with x = 0.05 to 212 K for the sample with x = 0.30. Also, the transport properties of these compounds are significantly changed with variation of x. The results can be explained in terms of DE interaction of $Mn^{3+}–O^{2-}–Mn^{4+}$, the SE interaction of $Co^{3+}/Co^{4+}–O^{2-}–Mn^{4+}$ and competition between them.

## 2. EXPERIMENTAL

The samples with nominal composition of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ ($x$ = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) were prepared by standard solid-state reaction method [12]. Crystal structure of all the samples was examined by X–ray powder diffraction. The properties of our samples have been investigated by scanning electron microscope (SEM), an energy dispersive spectrometer (EDS), a vibrating sample magnetometer (VSM), and resistivity measurements in magnetic fields of 0.0–0.4 T.

## 3. RESULTS AND DISCUSSION

The XRD patterns of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ ($x$ = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) samples indicated that all samples are single phase with orthorhombic perovskite structure, as shown in Figure 1. From data of XRD, the lattice parameters and unit cell volume of these samples were determined and tabulated in Table 1. It is found that the lattice parameters and unit cell volume of samples strongly decreased with increasing x which can be attributed to the smaller ionic radii of Co ions in comparison to Mn ions. We supposed that in the LaCaMnCoO system, it has various ion radius of $Mn^{3+}$, $Mn^{4+}$, $Co^{3+}$, and $Co^{4+}$ with the $Co^{3+}$ ions in the both of the low–spin state, and high–spin state, and $Co^{4+}$ ion in high–spin state only. In other hand $Mn^{3+}$ and $Mn^{4+}$ ions are in high–spin state [7–11]. It leads to the distortion of an octahedral structure in frame of $MnO_6$.

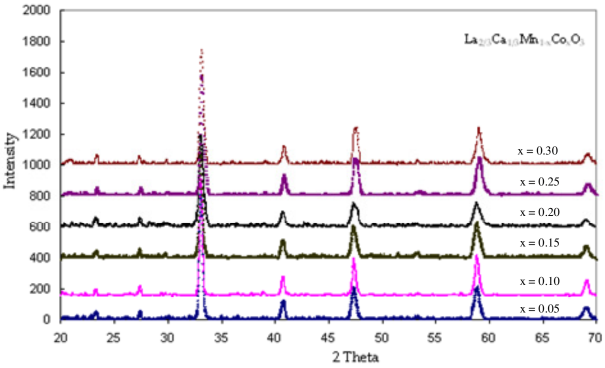

*Figure 1.* X–ray diffraction patterns of the $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ systems.

*Table 1.* The lattice parameters, volume unit cells, the $T_C$ and the ratio of $Mn^{3+}/Mn^{4+}$ for $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ samples.

| Samples | a(Å) | b(Å) | c(Å) | V(Å$^3$) | $T_C$ | $Mn^{3+}/Mn^{4+}$ |
|---|---|---|---|---|---|---|
| x = 0.00 | 5.473 | 7.728 | 5.471 | 231.398 | 260 [12] | 2.00 |
| x = 0.05 | 5.447 | 7.726 | 5.446 | 229.187 | 248.5 | 1.48 |
| x = 0.10 | 5.438 | 7.718 | 5.438 | 228.235 | 235.5 | 1.08 |
| x = 0.15 | 5.433 | 7.712 | 5.436 | 227.765 | 230.0 | 0.76 |
| x = 0.20 | 5.433 | 7.704 | 5.435 | 227.486 | 220.5 | 0.50 |
| x = 0.25 | 5.431 | 7.699 | 5.430 | 227.046 | 215.0 | 0.46 |
| x = 0.30 | 5.430 | 7.694 | 5.429 | 226.815 | 213.0 | 0.39 |

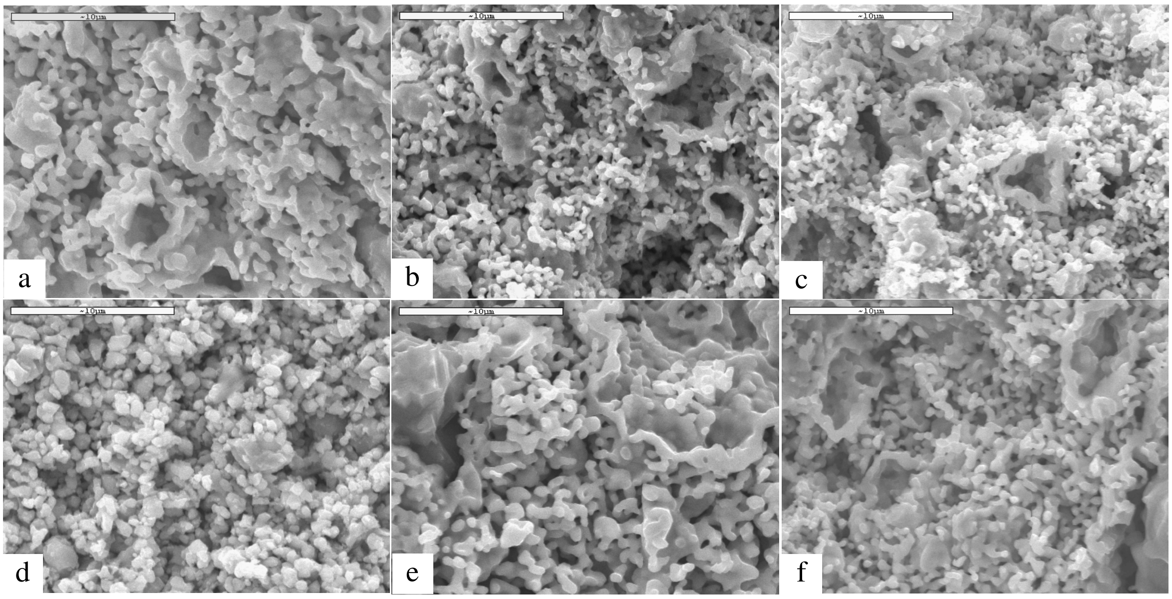

*Figure 2.* The SEM photographs of the surface of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ samples: (a) x = 0,05; (b) x = 0.10; (c) x = 0.15; (d) x = 0.20; (e) x = 0.25 and (f) x = 0.30.

The SEM photographs of all samples have been presented in figure 2. It is showed that the crystallites are homogeneous and sizes of grain have been influenced by the variation of x.

In figure 3 we introduce the EDS spectrum of some representative samples. We can see that all samples have no sign of strange peaks with nominal compositions, this result showed the samples have no impurity.

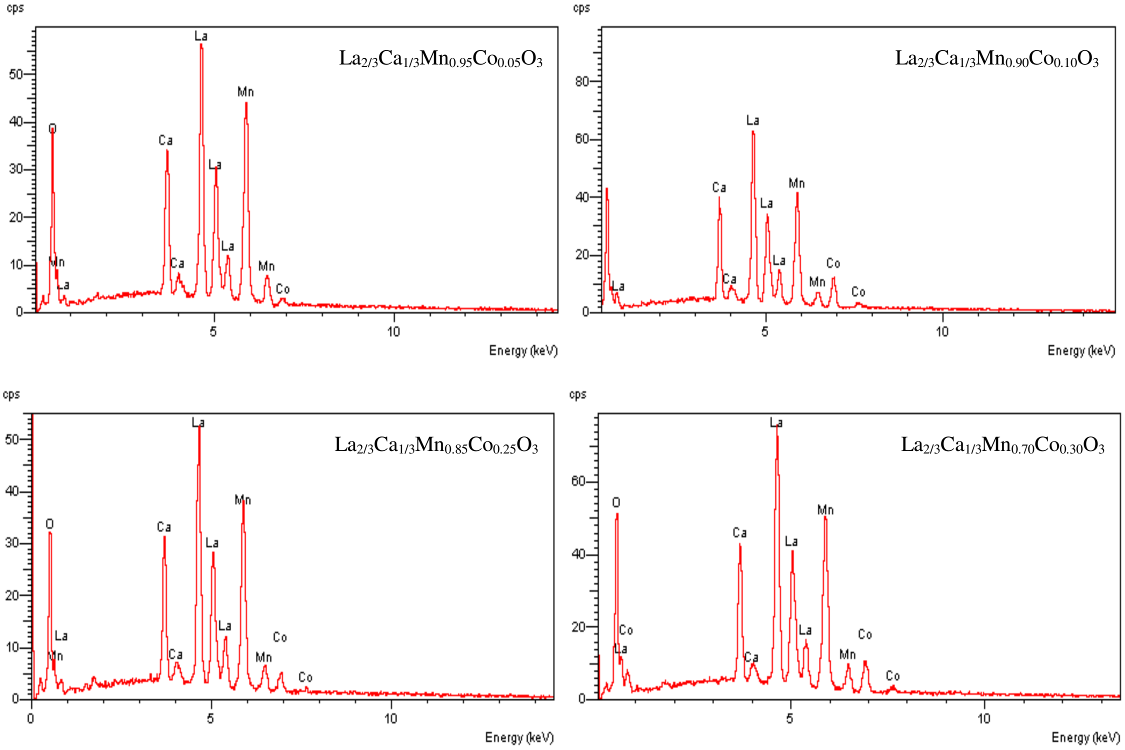

*Figure 3.* Energy dispersion spectrum of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$.

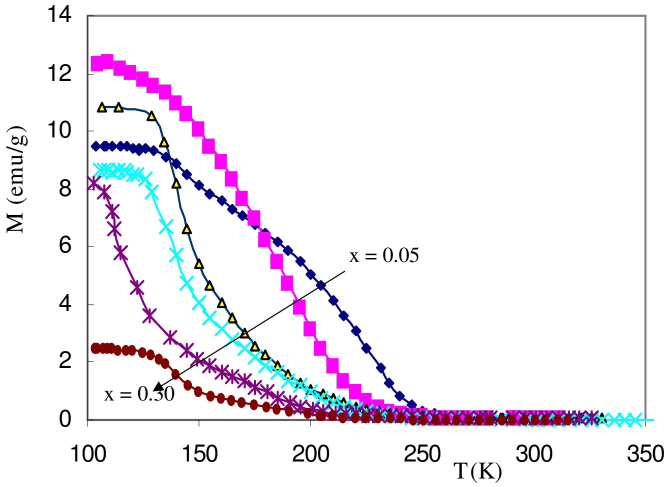

*Figure 4.* The temperature dependence of magnetization of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ (x = 0.05–0.30) samples.

The temperature dependence of magnetization in range of temperature from 100 K to 350 K of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ (x = 0.05–0.30) is plotted in Figure 4. The M(T) curves showed the phase transition from ferromagnetic to paramagnetic state in all samples. Their Curie temperature ($T_C$) and ratio of $Mn^{3+}/Mn^{4+}$ have been determined and tabulated in Table 1. It is found that the $T_C$ decreased with increasing Co content. This can be attributed to the reduction of the ferromagnetism in these samples due to decrease in the ratio of $Mn^{3+}/Mn^{4+}$. Indeed, our calculated results showed that the ratio of $Mn^{3+}/Mn^{4+}$ decreased from 1.48 for the sample with x = 0.05 to 0.39 for the sample with x = 0.30. This decrease in ratio of $Mn^{3+}/Mn^{4+}$ weakens DE interactions, while it enhances SE interactions in the samples leading to the reduction in $T_C$.

By this way of direct replacement of Mn by Co, we should take notice another kind of metal–oxygen bonding, Co–O–Mn and Co–O–Co. However, in the Co-doping compounds, if the amount of Co is small, then the probability of the Co–O–Co bond is the very low. Thus, it may suggest that the Co–O–Mn bond is the only disturbance. A further Co–increasing is made that the Co ion and Mn ion interact with each other by way of SE mechanism, than the competitive interaction between DE and SE mechanism strongly appeared. This competition leads to the ferromagnetic interaction of $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ would be replaced by antiferromagnetic super-exchange of $Co^{3+}$-$O^{2-}$-$Mn^{4+}$ and $Co^{4+}$-$O^{2-}$-$Mn^{4+}$, so that made decrease of $T_C$.

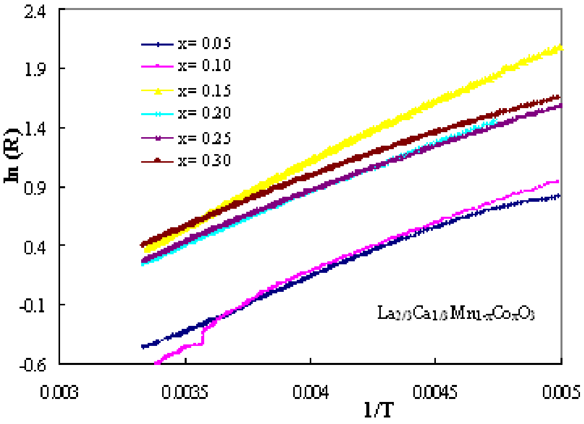

*Figure 5.* The variation of ln(R) as a function of 1/T for $La_{2/3}Ca_{1/3}Mn_{1-x}Mn_xO_3$ samples in zero magnetic field.

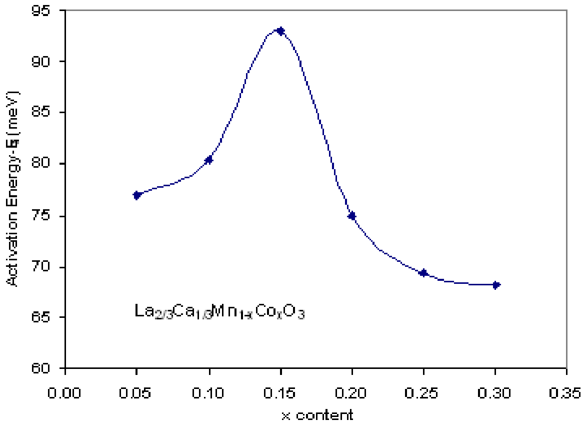

*Figure 6.* The x content dependence of activation energy of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ (x = 0.05–0.30) samples in zero magnetic field.

The temperature dependence of resistance of all samples at the applied magnetic fields of zero and 0.4T have been investigated (their graphs were not shown here). We found that the R(T) curve of the sample with x = 0.05 shows phase transition from metal to semiconductor/insulator. The transition temperature ($T_P$) of this sample is 113K at zero magnetic field and 120 K at magnetic field of 0.4 T, respectively. The R(T) curves for the samples of x = 0.10–0.30 have semiconducting behaviors. The variation of ln(R) as a function 1/T for $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ samples in zero magnetic field with the range of temperature from 150 K to 300 K are displayed in Figure 5. It indicated that all curves have nearly linear behavior. To calculate the activation energy, we find that the temperature dependence of resistance R(T) can be fitted very well by the functions of $R = R_o e^{\frac{E_a}{k_B T}}$, where $k_B$ is the Boltzmann constant and the $E_a$ is activation energy. From the curves of lnR–1/T, we found that the values of $E_a$ are 76.93, 80.40, 93.14, 74.90, 69.29 and 68.21 meV for samples with x = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30, respectively, which can be plotted in Figure 6. These results show that the $E_a$ increases with x up to x = 0.15, and then decreases with increasing of Co–content. It can be explained by the reduction of $Mn^{3+}$ as well as the ratio of $Mn^{3+}/Mn^{4+}$. However, with increasing Co concentration from x = 0.15 to x = 0.30, we assume that the $Co^{3+}$–$O^{2-}$–$Mn^{4+}$, and $Co^{4+}$–$O^{2-}$–$Mn^{4+}$ bonds in LaCaMnCoO compound strongly influences on the hopping of $e_g$-electrons.

The temperature dependence of magnetoresistance curves of the samples at the applied magnetic fields of 0.0T to 0.4T have been measured. The colossal magnetoresistance (CMR) have been determined by using formula, $\mathrm{CMR(T,H=0.4T)} = \frac{\mathrm{R(T,H=0.0T)} - \mathrm{R(T,H=0.4T)}}{\mathrm{R(T,H=0.4T)}} \times 100\%$, which are displayed in Figure 7. Our results showed that the maximum of CMR(T, H = 0.4T) curves of the samples strongly increased with x until x = 0.15, and then decreased with increasing of x. The maximum of CMR(T, H = 0.4T) curve of the sample with x = 0.15 reaches 28.9% at T = 104.5 K, as showed in the inset on Figure 7. In the perovskite manganite, the resistivity depends on the hopping probability of $e_g$-electrons between $Mn^{3+}$ and $Mn^{4+}$ ions, between $Co^{3+}$ and $Mn^{4+}$ ions, and between $Co^{4+}$ and $Mn^{4+}$ ions. These processes related with the variation of activation energy ($E_a$) at different Co-concentration in samples. Thus, the both of maximum value of magnetoresistance and $E_a$ values dependence on Co-doping concentration in our investigated $La_{2.3}Ca_{1/3}Mn_{1-x}Co_xO_3$ compounds.

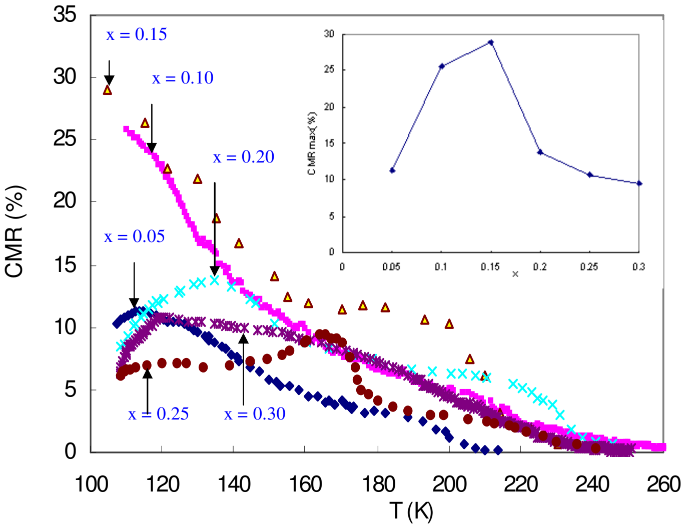

*Figure 7*. The temperature dependence of the magnetoresistance value for $La_{2/3}Ca_{1/3}Mn_{1-x}Mn_xO_3$ samples.

## 4. CONCLUSIONS

We have presented a systematic investigation of the electric and magnetic behavior in the $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ compounds. Our results showed that, all samples are single phase with orthorhombic crystal structure. The substitution of Co for Mn strongly influences on the electric and magnetic properties. It is found that $T_C$ is strongly reduced by increasing Co for Mn. The observed maximum on resistivity curve of x = 0.05, are disappeared for samples of x = 0.10–0.30 in range of investigated temperature. The $E_a$ and the maximum of CMR(T, H = 0.4 T) of the samples strongly increased with x until x = 0.15, and then decreased with increasing of Co concentration. It can be explained by depletion in ratio of $Mn^{3+}/Mn^{+4}$ leads to decrease ferromagnetic $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ bonds. Consequently, it weakens the DE interaction. The ferromagnetic $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ bonds would be replaced by antiferromagnetic super-exchange (SE) of $Co^{3+}$-$O^{2-}$-$Mn^{4+}$ and $Co^{4+}$-$O^{2-}$-$Mn^{4+}$ with increasing Co content in $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ compounds.

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## TÓM TẮT

### NGHIÊN CỨU MỘT SỐ TÍNH CHẤT CỦA VẬT LIỆU PEROVSKITE $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$

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Tính chất điện và từ của hệ hợp chất $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ (x = 0,05; 0,10; 0,15; 0,20; 0,25 và 0,30) đã được nghiên cứu bằng sự khảo sát ảnh hưởng của sự thay thế Co cho Mn. Từ các giản đồ nhiễu xạ bột rơnghen, cấu trúc tinh thể các mẫu đã được khảo sát chi tiết. Kết quả thực nghiệm VSM cho thấy nhiệt độ chuyển pha sắt – thuận từ giảm theo sự gia tăng nồng độ Co. Sự phụ thuộc của điện trở vào nhiệt độ được làm khớp theo hàm $R(T) = R_o e^{\frac{E_a}{k_B T}}$ trong vùng nhiệt độ từ 150 K – 300 K theo năng lượng kích hoạt $E_a$. Từ trở trong vùng từ trường H = 0,0 - 0,4 T của tất cả các mẫu đã được nghiên cứu. Kết quả chỉ ra rằng: Qui luật thay đổi của giá trị từ trở cực đại ($CMR_{max}$) phụ thuộc vào nồng độ Co tương tự với sự thay đổi của năng lượng kích hoạt ($E_a$). Các kết quả được giải thích do sự cạnh tranh giữa tương các tác trao đổi kép (DE) của $Mn^{3+}–O^{2-}–Mn^{4+}$, tương tác siêu trao đổi (SE) của $Co^{3+}/Co^{4+}–O^{2-}–Mn^{4+}$.

*Từ khoá:* cấu trúc tinh thể, nhiệt độ Curie, năng lượng kích hoạt, cạnh tranh tương tác, từ trở khổng lồ.