

Materials Science

INFLUENCE OF SUBSTITUTION OF THE MAGNETIC 3d METALS FOR Mn IN PEROVSKITE $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = Fe, Co, Ni) COMPOUNDS

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Abstract. Influence of substitution of 3d metals for Mn on properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{TM}_{0.1}\text{O}_3$ (TM = Fe, Co, Ni) compounds was studied. Ferromagnetic – paramagnetic and metals – insulator transitions were significantly affected by Mn-site substitution. However, no observable difference was found in their crystal structure from X-ray diffraction analysis. At room temperature the structure characterization of these compounds gave the single phase and structure is the distortion orthorhombic cell with space group symmetry Pnma. The magnetoresistance measurement showed that the magnetoresistance ratio MR increases until 17% in magnetic field of 0.4 T, and in low magnetic field region ($\mu_0 H < 0.05$ T), MR = 7.5% at 102 K. The investigations of EPR showed that the intensity of resonance line can be well fitted by the expression: $I(T) = I_0 \exp(E_a/k_B T)$. The values of activation energy have been determined with $E_a = 0.074$ eV, 0.093 eV and 0.086 eV for substituted Fe, Co, Ni samples, respectively. These values are slightly smaller than the value of $E_a = 0.12$ eV for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. We attribute the reason to the reduction of Mn^{3+} content caused by TM substitution for Mn. The dependence transition temperatures and transport properties of all samples are well explained by introducing the SE interaction with considering that the Fe^{3+} , Co^{3+} and Ni^{2+} ions have high-spin configuration, the local DOS near the Fermi level at the TM site $N_x(E_f)$ would decrease from Ni to Co and Fe [1], thus reduces the hopping probability and increases the resistivity in order.

1. INTRODUCTION

LaMnO_3 is the antiferromagnetic insulator, when it is doped with the divalent ions ($\text{La}_{1-x}\text{A}_x\text{MnO}_3$ with $\text{A} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \dots$) it can be driven into a metallic ferromagnetic state due to conversion of proportional number of Mn^{3+} to Mn^{4+} through double exchange (DE) of $\text{Mn}^{3+} - \text{O}^{2-} - \text{Mn}^{4+}$ interaction [1]. The electronic configurations are Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} ($t_{2g}^3 e_g^0$). The mobile e_g electrons produced due to the hole doping DE mediate ferromagnetism and conduction, thus the DE interaction not only controls ferromagnetic state but also influences metal–insulator transition temperature in doped $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ compounds.

The basic structures of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds are ABO_3 -type perovskite, in which A - site cations and oxygen ions form the structures frame. The B - site cation is relatively small sized and resides in an octahedral site. The Mn and O form a basic module of the MnO_6 octahedron, which plays a major role in determining the properties of materials. The various cations in the A site produce different chemical pressures to change the Mn–O–Mn bond angle and bond distance. It is found that the average size of A-site cations and their size distribution have significant effects on properties of manganites [2,3]. However, the influence of substitution on A–site is indirect to the environment of the

MnO₆ octahedron structure. So, it is more interest to study the influence of substitution of B-site (Mn), which rather direct to extend understanding in this system.

Usually, the observations showed that Mn-substitution weakens the double-exchange (DE) interaction, but origin do not explained clearly yet. There are many reasons to be considered upon Mn-substitution, such as structure deformation due to the size difference between Mn-ions and substituting elements, formation of antiferromagnetic clusters by substitution, change of electronic structure of Mn ions, different Mn³⁺/Mn⁴⁺ ratios, and the magnetic nature of substituting element etc [4].

Some investigators have studied the substitution of Fe, Co, Ni for Mn in La_{1-x}Ca_xMn_{1-y}TM_yO₃ compounds [5-7]. It is found that only the Mn e_g band is electronically active, where electron hopping between the Mn³⁺ and Mn⁴⁺ ions is happened. Since TM replaces Mn, it reduces the Mn³⁺/Mn⁴⁺ ratio and reduces the number of available hopping sites. Thus the DE is suppressed, resulting in the reduction of ferromagnetic exchange and metallic conduction. Some authors show that in the low temperature range, the spin - glass type of behaviors and antiferromagnetic clusters occurred [5, 8].

In this report we show our results of examinations on properties of compounds La_{0.67}Ca_{0.33}Mn_{0.90}TM_{0.10}O₃ (TM = Fe, Co, Ni) to extended understanding the role of substituting elements in the system.

2. EXPERIMENTAL

The samples of La_{0.67}Ca_{0.33}Mn_{0.90}TM_{0.10}O₃ (TM = Fe, Co, Ni) were prepared by solid state reaction method. Starting high-purity compositions of La₂O₃, CaCO₃, MnO and transition metal oxides of CoO₃, Fe₂O₃, NiO were mixed and grounded for 2 hours. The mixed powders were dried at 200⁰C for 2 hours and pressed into pellets. The pellets were first presintered at 100⁰C for 2 hours, at 800⁰C for 24 hours and then cooled down to room temperature by the furnace turning off. After that, the pellets were grounded about one hour to collect particles smaller than 100μm and pelletized again. A multi-steps procedure is applied for the heat treatment of the samples. The samples have been investigated by X-ray powder diffraction (XPD), magnetization, energy dispersive spectrum (EDS), oxygen concentration, resistivity, magnetoresistance and electron paramagnetic resonance (EPR) measurements.

3. RESULTS AND DISCUSSION

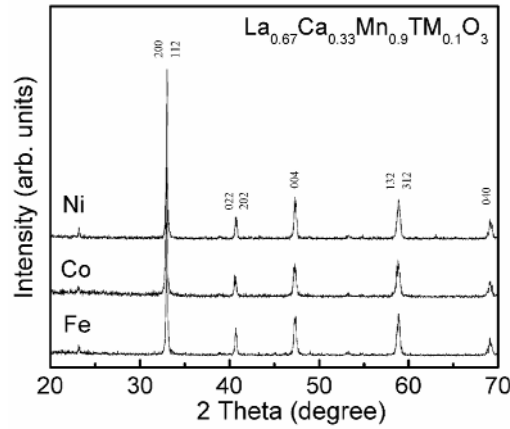
3.1. Crystal structure investigations

The XPD patterns of La_{0.67}Ca_{0.33}Mn_{0.90}TM_{0.10}O₃ (TM = Fe, Co, Ni) in Fig. 1 showed that all samples are single phase with a perovskite structure. All reflections could be indexed on the basis of the distortion orthorhombic cell with space group symmetry Pnma. The values of the lattice parameters and cell unit volume of the samples were shown in Table 1.

It indicated that with amount of substitution of 10% at Fe³⁺, Co³⁺ and Ni²⁺ the lattice parameters and cell unit volume very slightly decreased in comparison with those of the undoped sample. The reason is that the radii of Fe³⁺, Co³⁺, and Ni²⁺ (0.56 Å; 0.61 Å; 0.69 Å, respectively) are close to the radius of Mn³⁺ (0.65 Å). It may be supposed that in range of low doping concentration, the formation of crystal structure of La_{0.67}Ca_{0.33}Mn_{0.90}TM_{0.10}O_{3-δ} (TM = Fe, Co, Ni) is nearly unchanged in comparison

Table 1. Values of the lattice parameters of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_{3-\delta}$ (TM = Fe, Co, Ni)

Samples	a(Å)	b(Å)	c(Å)	V(Å ³)
$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$	5.483	7.728	5.471	231.82
$\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{Fe}_{0.10}\text{O}_{3-\delta}$	5.442	7.696	5.436	227.67
$\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{Co}_{0.10}\text{O}_{3-\delta}$	5.434	7.687	5.425	226.82
$\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{Ni}_{0.10}\text{O}_{3-\delta}$	5.447	7.717	5.438	228.58

**Fig. 1.** The XPD patterns of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = Fe, Co, Ni)

with pristine material $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [9]. The EDS spectra showed that the actual components of the samples as La, Ca, Mn, Fe, Co and Ni were indicated in Figs. 2a, 2b and 2c, respectively. There are no any impurities index in these compounds.

The surface structure of the samples obtained by SEM measurement is shown in Fig. 3a, 3b, 3c. It is found that the size, shape and distribution of the grains on the surface of the samples are homogeneous. The grain size and distribution of the grains are not so much changed. It may be seen a little difference between grains of the Fe, Co and the Ni samples. We can suggest the reason is that the ion radii of Fe^{3+} , Co^{3+} are similar to that of Mn^{3+} but that of Ni^{2+} is smaller. This means the crystal structure of all the samples nearly unchanged.

The oxygen deficiency (δ) in these compounds has been determined by Dicromat method. From obtained oxygen concentration, the ions of Mn^{3+} and Mn^{4+} as the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ were estimated (see Table 2).

In this case it can be expected free ion values of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{TM}_{0.1}\text{O}_{3-\delta}$ (TM = Fe, Co, Ni) are 58% of Mn^{3+} ; 31% of Mn^{4+} ; 10% of Fe^{3+} for TM = Fe 48% of Mn^{3+} ; 42% of Mn^{4+} ; 10% of Co^{3+} for Co and 49% of Mn^{3+} ; 40% of Mn^{4+} and 10% of Ni^{2+} for x = Ni, respectively. While the free ion values are 67% of Mn^{3+} and 33% of Mn^{4+} in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$.

Thus, the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in the doped Fe, Co, Ni sample is smaller than that of undoped samples. It strongly implies that DE model alone cannot explain the effect of the transition metal substitution. When Mn ions are substituted by TM (TM = Fe, Co,

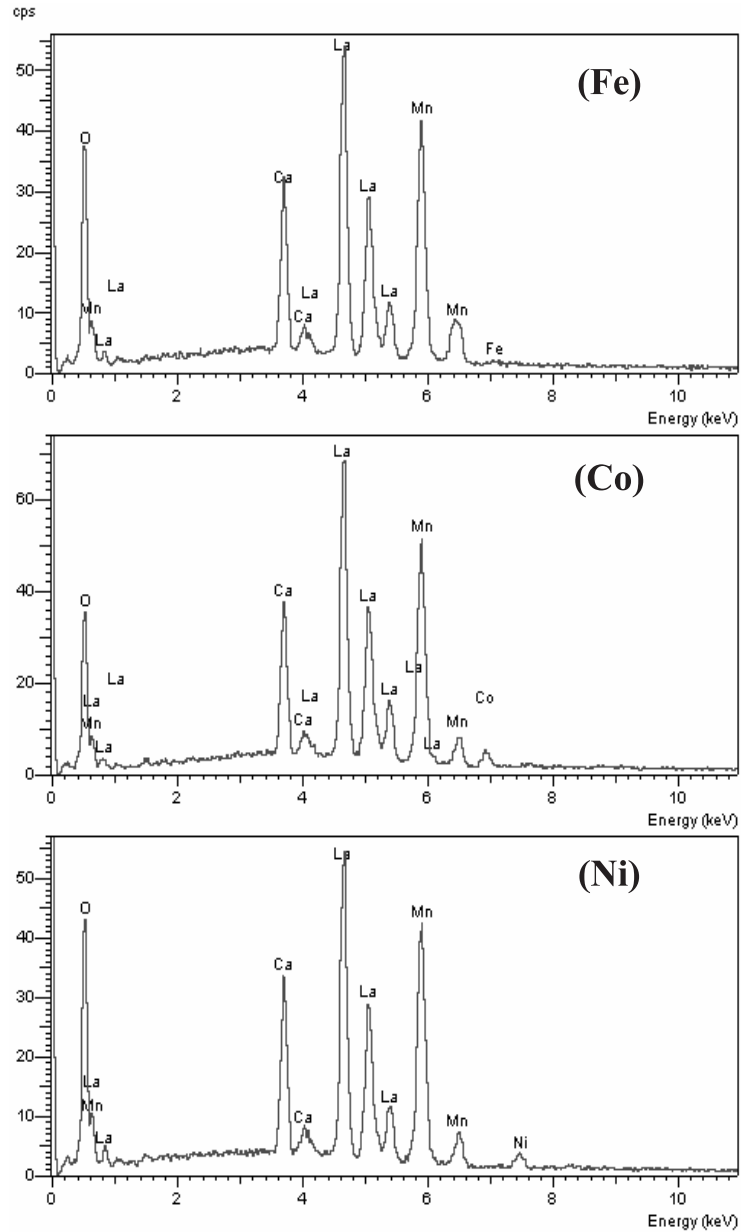
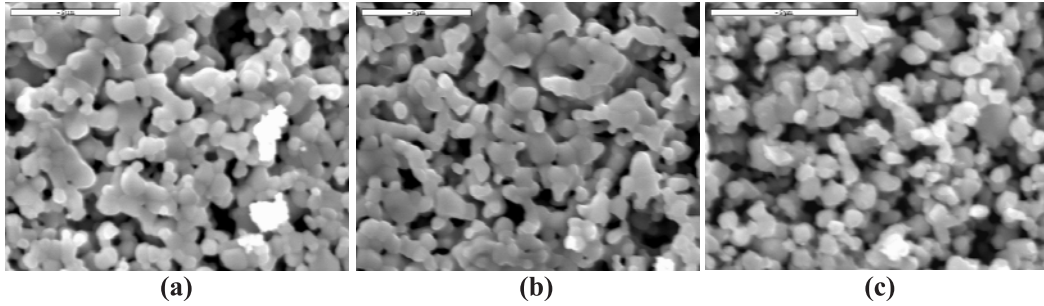


Fig. 2. The EDS spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = Fe, Co, Ni)

Ni) we should consider the existence of metal–oxygen bonding TM–O–Mn and TM–O–TM but the number of TM ions/ Mn ions should be statistically greater than 17% to find the TM–O–TM bond [5]. In these compounds, the amount of TM ions is only 10% at and the probability of the TM–O–TM bond is low. Thus, it may assume that the TM–O–Mn bond is the disturbance only. This is made that TM and Mn ions interact by way of the superexchange (SE) mechanism. This is supposed that, because more Mn^{3+} became Mn^{4+} in TM- substituted compounds, the competition between DE and SE mechanism

Table 2. The oxygen deficiency (δ), concentration and the ratio of Mn^{3+} and Mn^{4+} ions

Samples	δ	Mn^{3+}	Mn^{4+}	$\text{Mn}^{3+}/\text{Mn}^{4+}$
Undoped LCMO		0.67	0.33	2.00
Doped-Fe	0.0106	5.879	0.3121	1.88
Doped-Co	0.0079	0.4825	0.4175	1.16
Doped-Ni	0.0140	0.4947	0.4053	1.22

**Fig. 3.** The SEM images of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = (a)Fe, (b) Co, (c) Ni).

more strongly leading that SE rather strong than DE in substituted transition metal system. Thus the SE-mechanism will dominant in TM-O-Mn bond interaction when ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ decreases, therefore the ferromagnetic configuration has been formed.

3.2. Magnetization and resistivity

The magnetization versus temperature is shown in Fig. 4. From these curves, the Curie temperature has been determined. Our obtained results are 270 K, 135 K, 160 K and 165 K for LCMO, LCMFeO, LCMCoO and LCMNiO, respectively.

This clearly showed that with substitution of Fe, Co, Ni for Mn in the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ the Curie temperatures (T_C) strongly decrease. It agrees with results of the authors [5] for example.

If the substitution of Fe, Co, Ni for Mn with only 5% at, the Curie temperature decreases from 271K for LCMO to 181K, 214K and 226K for LCMFeO, LCMCoO and LCMNiO, respectively. It can be suggested that when increasing substituted content at% of TM-metal, the Curie temperature more strongly depressed than that of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$.

The resistivity measurements have been carried out on these samples in zero and 0.4T magnetic fields. In case substitution of Fe and Co, the maximum in resistance curves are disappeared and resistance curves increased with decreasing temperature (Fig. 5).

Magnetoresistance

The application of a magnetic field of 0.4 T displaces the resistance maximum toward higher temperature from 125 K at $H = 0$ to 131 K at $H = 0.4$ T for Ni-substitution, as shown in Fig. 6. We supposed that displacing to higher temperature the metal-semiconductor (M-SC) transition is due to with increasing field near the ferromagnetic-paramagnetic transition, ferromagnetism is favored over paramagnetism. Consequently,

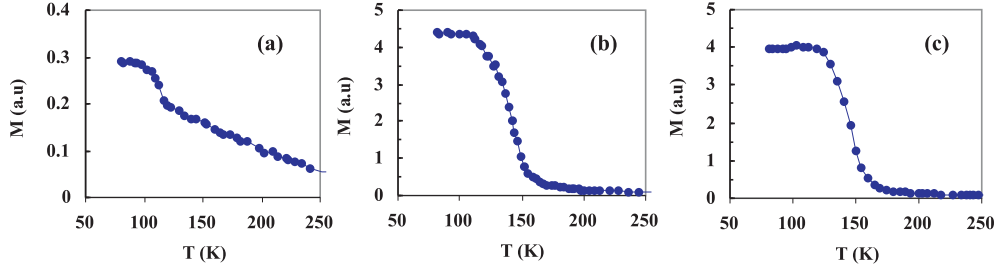


Fig. 4. The $M(T)$ curves of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = (a)Fe, (b)Co, (c)Ni).

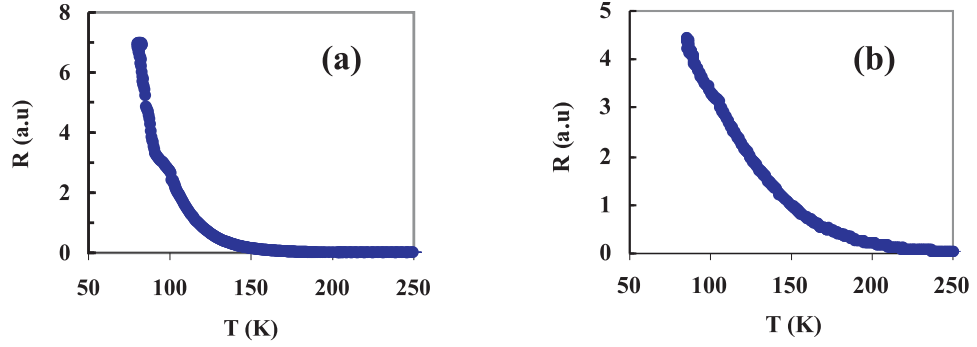


Fig. 5. The $R(T)$ curves of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{TM}_{0.10}\text{O}_3$ (TM = (a)Fe, (b)Co).

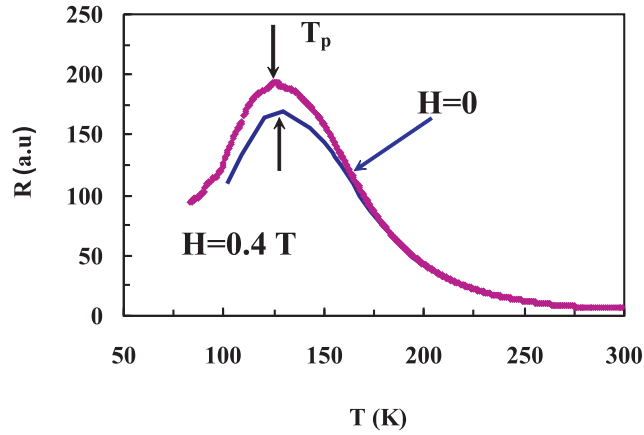


Fig. 6. The $R(T)$ curves of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.90}\text{Ni}_{0.10}\text{O}_3$ at $H=0$ and $H=0.4\text{T}$

the magnetoresistance ratio (MR) increases with decreasing temperature as shown in Fig. 7. Figure 8(a) showed the magnetoresistance curves versus a magnetic field of Ni sample at various temperatures of 102 K, 109 K and 121 K. It is found that the magnetoresistance ratio in their sample reaches 17% at 102 K in a magnetic field of 0.4 T. This value is remarkable large in manganite family of $\text{La}_{1-x}\text{Ca}_x(\text{Mn},\text{TM})\text{O}_{3-\delta}$ with TM are

transition metals. This result has suggested that an existence of doping hole concentration in manganite oxides has been related to magnetoresistance.

The magnetoresistance curves in low magnetic field region were shown in Fig. 8(b). This indicated the magnetoresistance curves are nearly linear dependence in low magnetic field. Furthermore, MR curves show a significant increasing at low magnetic field of $\mu_0 H < 0.05$ T. Low-field MR has achieved value as high as 7.5 % at 102 K.

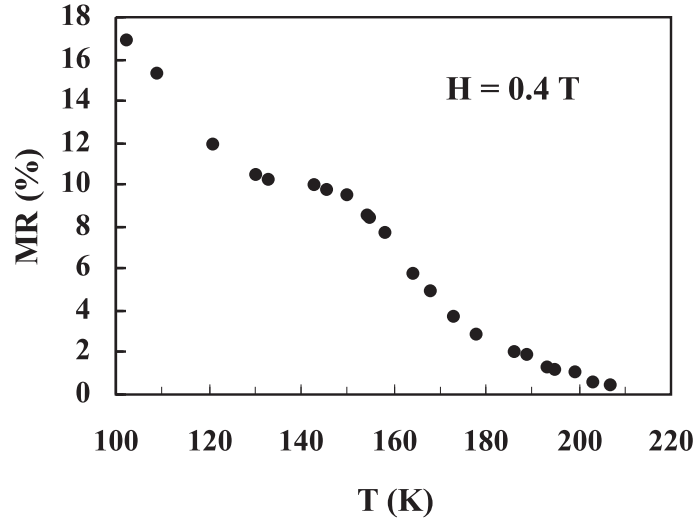


Fig. 7. MR ratio of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$

The dependence of transition temperature of the samples are well explained by introducing the SE–interaction as mentioned above. In the substituted transition metal system of LCMTMO, the e_g electrons of Mn^{3+} ions near Fermi level have to make the hop to nearly Mn^{4+} ions to realize the DE interaction. The probability of hopping would be lower if the DOS at the Fermi level is lower. Considering Fe^{3+} , Co^{3+} and Ni^{2+} ions with high–spin configurations, the local DOS near the Fermi level at the TM site, $N_x(E_F)$ would decrease from Ni to Co and Fe. Thus reduces the hopping probability and increases the resistivity in order.

3.3. EPR studies

Some EPR lines of the investigated samples measured at selected temperature above $1.1 T_C$ are shown in Fig. 9 (a, b, c). For the cases of Fe and Ni-doped the lines are really symmetry with a line shape very close to Lorentzian, whereas for Co-doped sample this behavior only occurs at the temperatures much higher than T_C . The symmetry EPR signals are believed only to be due to Mn ions in paramagnetic state. The resonance field corresponds to a g value of 2.0 and does not depend on temperature. The temperature dependences of the peak-to-peak EPR line-width, ΔH_{pp} , are shown in Fig. 10(a). For TM = Fe and Ni, the line-width decreases linearly as temperature decreasing, passing through a minimum and then increases abruptly near T_C . This behavior of line-width as a function of temperature has been observed and explained in many cases of manganite perovskite. The linear temperature dependence of $\Delta H_{pp}(T)$ in the paramagnetic region

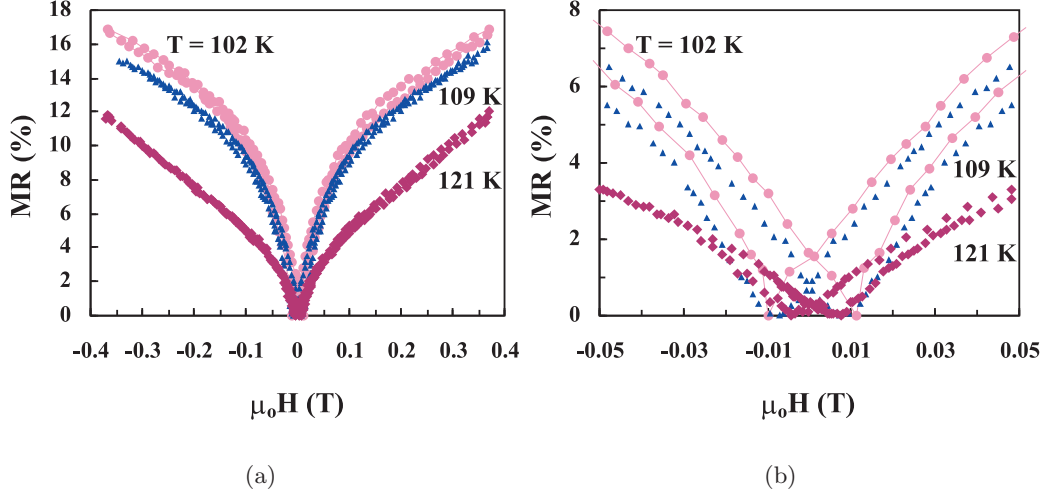


Fig. 8. (a): Magnetoresistance curves of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$. (b): Low-field MR curves of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$

is a manifestation of the one-phonon relaxation process [10]. The values of b (b is the slope of $\Delta H_{pp}(T)$) are 3.1 Oe/K and 4.0 Oe/K for Fe and Ni, respectively, somewhat higher than the value of 2.86 Oe/K obtained for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [11]. This feature could be associated with a little increase in lattice distortion when TM is substituted for Mn. This effect is not really distinct so that we can't observe by XRD technique. In case of Co substitution the temperature dependence of line-width undergoes two minimums. This phenomenon is probably caused by a Jahn-Teller distortion as has been observed in LaMnO_3 by Causa *et al.* [12]. Another possibility, a ferromagnetic phase appears above T_C (electronic phase separation) can be also considered. It is worth to note that the electronic configuration of Co is very complicated due to the existence of several possible spin states.

EPR line intensity as a function of temperature, $I(T)$, is determined by double integration of experimental derivative absorption curve measured at different temperatures. The $I(T)$ dependence shown in Fig. 11(b). It decreases exponentially with T . For T above T_C , we find that the intensity of the resonance line can be well fit by the expression:

$$I(T) = I_0 \exp(E_a/k_B T)$$

Where k_B is Boltzmann constant and E_a is activation energy for polaron hopping, i.e., potential barrier which the polarons must surmount in order to hop into the next sites. Some expressions describing the parameters of CMR materials are considered as the assumption to lead to this expression. This assumption has been reported in [13]. The value of $E_a = 0.074$ eV, 0.093 eV and 0.086 eV derived from this fit for TM = Fe, Co and Ni, respectively, are slightly smaller than the value of $E_a = 0.12$ eV for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [11]. The exponential law of the temperature dependence of EPR intensity where the activity energy is derived from has been described by the polaron formation across the ferromagnetic-paramagnetic phase transition. We attribute the observation of lower values

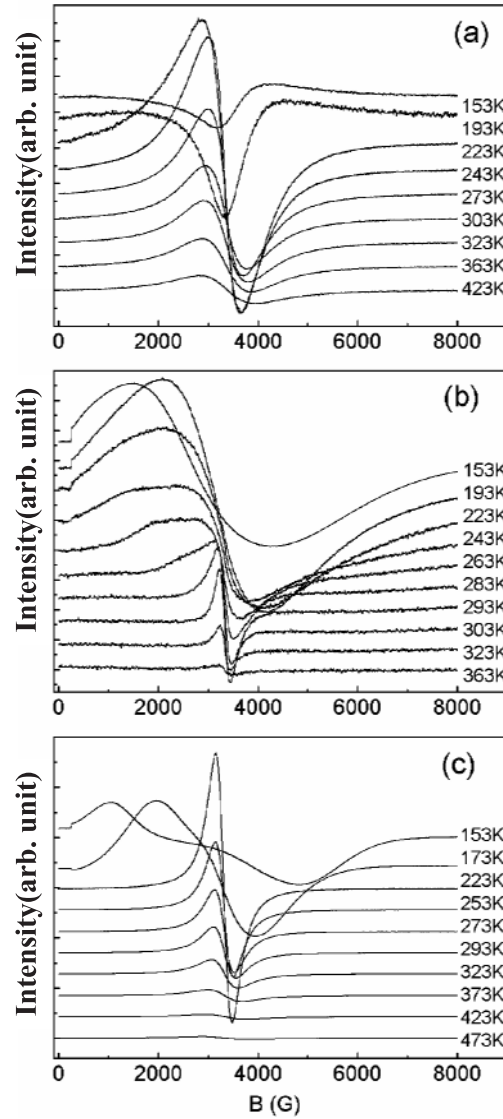


Fig. 9. Selected EPR spectra for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{TM}_{0.1}\text{O}_3$ samples: (a) TM = Fe; (b) TM = Co; (c) TM = Ni.

of E_a in present samples to the reduction of Mn^{3+} content caused by the TM substitution. Our explanation is that the strong decrease in activation energy responsible for the conduction in the paramagnetic state as the Mn^{3+} content is decreased. This is agreement with conclusion of de Teresa *et al.* [14].

4. SUMMARY AND CONCLUSION

When the substitution of TM with 10% at in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, there is no observable change found in its crystal structure of the samples.

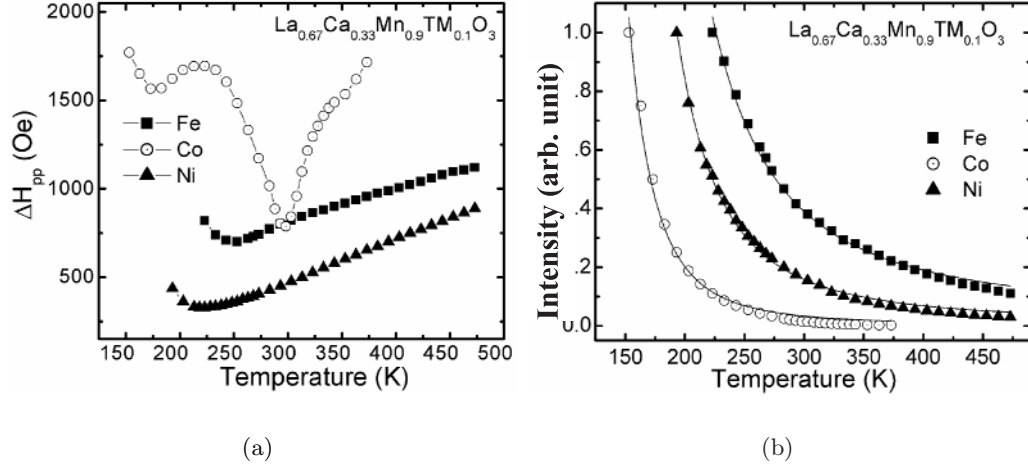


Fig. 10. (a): The temperature dependence of the peak-to-peak EPR line-width, ΔH_{pp} , for studied samples. (b): Observed and fitting curve of temperature dependence of the EPR line intensity for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{TM}_{0.1}\text{O}_3$ samples.

The Curie temperatures strongly decreased with increasing substituted Fe, Co and Ni concentrations.

The maximum of the resistivity curve is obtained at 125 K in zero and 131 K in 0.4 T magnetic fields for the case of Ni substitution and resistivity curves for cases of Fe and Co substitutions increased with decreasing temperature.

The magnetoresistance ratio (MR) increased with decreasing temperatures and the values reached 17% in magnetic field of 0.4 T at 102 K and 7.5% in low magnetic field of $\mu_0 H < 0.05$ T for Ni – doped sample.

The EPR investigation showed that the doping TM in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ diminished the number of ions participating into the DE mechanism. The activation energy is reduced.

With introducing SE dominant in TM substituted compounds, there are well explained some properties mentioned above.

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