

Effect of Sm^{3+} Ions on the Transport and Sublattice Magnetization of Perovskite System

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PEROVSKITE compounds $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ $0 \leq x \leq 0.14$ were prepared using the double sintering ceramic technique. The measurement of the magnetic susceptibility at different temperatures as a function of the magnetic field intensity showed the change of the state from completely ordered to completely disordered state at T_C which shifts to lower value by increasing Sm content. The tolerance factor decreases with increasing Sm concentration. Resistivity measurements indicate the disappearance of the related peaks with increasing Sm content. The large increase in the resistivity below 530K is related to the spin transition of Mn^{3+} ions from high to low state.

Keywords: Transport phenomena, Magnetic properties, AC resistivity and Perovskite.

The discovery of the colossal magnetoresistance (CMR) in $\text{R}_{1-x}\text{B}_x\text{MnO}_3$ (R=rare earth elements, B= divalent cations) has attracted many researchers in the physics of condensed matter due to their wide range of applications⁽¹⁻⁴⁾. Guo *et al.*⁽⁵⁾ found that the pure compound RMnO_3 are antiferromagnetic (AFM) insulators where Mn^{3+} and Mn^{4+} present simultaneously upon doping R^{3+} by divalent metal ions. The correlation between the magnetic and electrical properties of such compounds has been qualitatively understood on the basis of the double -exchange (DE) model⁽⁶⁻⁸⁾. When replacing La^{3+} ions of larger radius ($r_{\text{La}}=1.15 \text{ \AA}$) by a smaller ions such as Pr, Nd, with radii of 1.09 \AA and 1.08 \AA , respectively, a large distortion of the Mn-O-Mn bond takes place, thus weakening the double exchange (DE) and reducing the transfer interaction of electrons. In manganites the ferromagnetic to metallic (FM) transition temperature (T_C) is raised, and thus the system can be turned between the low and high conductivity phases. One of the very important perovskite compounds to be used as a magnetic sensor is the La-Ca-manganite⁽⁹⁾. For this purpose many parameters should be considered for potential industrial use, such as the processing temperature, the final grain size and the change in the resistance at low magnetic field. These factors can raise the possibility of using La-Ca-manganite in magnetic field sensor and magnetic read-⁽⁹⁾ write heads. Zener⁽¹⁰⁾ found that in the presence of magnetic field, for La-Ca-manganite, the transport between adjacent ferromagnetic regions is enhanced, *i.e.* colossal magneto resistance (CMR) is present owing to the spin alignment as well as the double exchange mechanism⁽¹⁰⁾.

The mismatch between the equilibrium and lengths A-O and M-O of an AMO_3 cubic perovskite is given by the deviation from unity of the tolerance factor⁽¹¹⁾

$t = (A-O) / \sqrt{2} (M-O)$. Preewitt *et al.*⁽¹²⁾ found that if $t < 1$, the M-O bonds are under compression and those of A-O are under tension. These internal stresses are relieved by a cooperative rotation of the MO_6 octahedral that lowers the symmetry of the unit cell from cubic to rhombohedral ($R\bar{3}C$) or orthorhombic (Pbnm). In this case the resultant bending of the M-O-M bond angle from 180° to $(180 - \Phi)$ reduces the δ - bonding nearest neighbor M-O-M resonance integral⁽¹³⁾.

The aim of the present work was to study the effect of variation of A site cation radius when substituting La^{3+} by Sm^{3+} with different concentration on the magnetic properties of Ca^{2+} doped $LaMnO_3$ of the formula $(La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO_3$. Also, the electrical properties in the paramagnetic region were studied as a function of temperature and frequency to spot light on the effect of the dopant radius on such properties.

Experimental

Samples of the general formula $(La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO_3$ were prepared using the double sintering ceramic technique⁽¹⁴⁾ in which pure analar oxides from British Drug House (BDH) were mixed together in stoichiometric ratio and ground in agate mortar for 3hr followed by a further 3hr grounding in an agate electric ball mill. The samples were pressed into pellets form and then calcined at $900^\circ C$ for 10hr in a muffle furnace (Lenton UAF16/5). After that the samples cooled to room temperature with the same rate as that of heating than they were grounded again to very fine powder and sintered at $1000^\circ C$ for 5hr, grinded again and pressed uniaxially at $8 \times 10^5 N/m^2$ into pellets, and sintered at $1150^\circ C$ for 2hr. X-ray diffraction (XRD) using $CuK\alpha$ radiation of wave length 1.5405 \AA was performed to assure the completion of the solid state reaction and formation of the sample in the proper form. IR spectra were also carried out using FTIR (Shimatzu) spectrophotometer model 4000, the FTIR spectra ($600-200 cm^{-1}$) of various compounds were recorded as KBr discs using (Nexus 670) FTIR spectrophotometer, resolution $4 cm^{-1}$ polyethylene detector Nicolet (U. S. A).

To prepare the samples for electrical properties measurements, they were accurately polished to assure uniform thickness, coated with silver paste and checked for good conduction. The two-probes method was used for measuring the electrical properties at different temperatures as a function of the applied frequency using LCR high tester HIOKI model 3531 (Japan). The conventional Faraday's method was used for measuring the magnetic susceptibility as a function of temperature from 78K up to 370K at different magnetic field intensities. The temperature of the sample was measured using T-type thermocouple with accuracy $\pm 1^\circ C$.

Results and Discussion

The IR transmission spectra of the perovskite structure of the general formula $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $0 \leq X \leq 0.14$ was represented in Fig. 1. From the figure it is clear that four transmission bands were obtained, three of them are the fundamentals ν_1 , ν_2 , and ν_3 while the fourth one appeared at $\approx 250 \text{ cm}^{-1}$ depending on Sm content. Since the samples under investigation crystallize in orthorhombic structure, then the appearance of more than three bands is obvious and expected. The first one (ν_1) which lies between 588 and 602 cm^{-1} depending on the Sm content is due to Mn-O bond stretching vibration of the MnO_6 octahedra. The second band (ν_2) ranges between $405 - 463 \text{ cm}^{-1}$ was assigned to the bending vibration of the Mn-O bond. The third one (ν_3) in the range ($319-395 \text{ cm}^{-1}$) was assigned to the lattice vibrations.

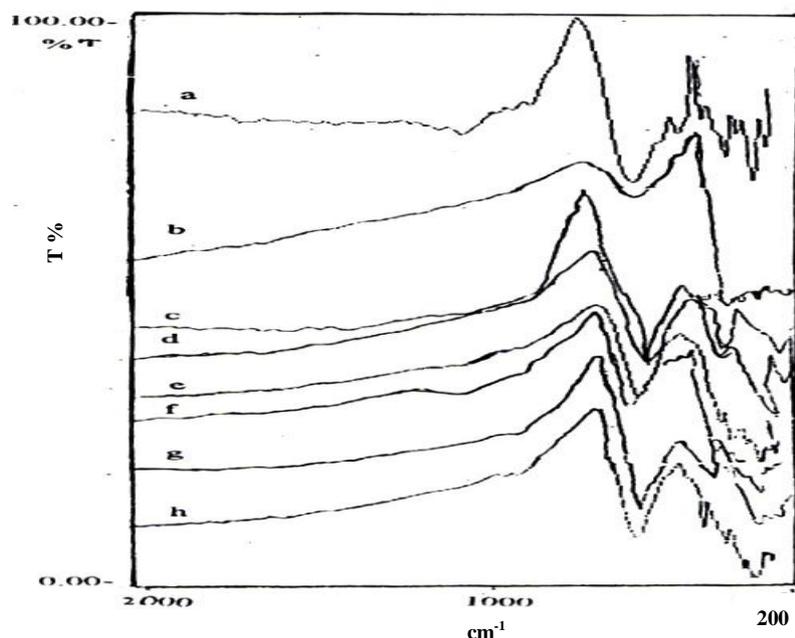


Fig. 1 (a-h). IR transmission spectra for the samples $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. $0 \leq x \leq 0.14$.

Figure 2(a) shows the dependence of ν_1 position on the Sm^{3+} ions ratio. This band shifts toward low value with increasing Sm^{3+} . Nearly, the same trend is obtained for ν_2 and ν_3 (Fig. 2-b) except the small increase after $x=0.1$. This increase is attributed directly to the distortion in the perovskite unit cell and reflects the decrease in the tolerance factor with increasing Sm^{3+} in the compound due to its small ionic radius as compared with that of La^{3+} ions.

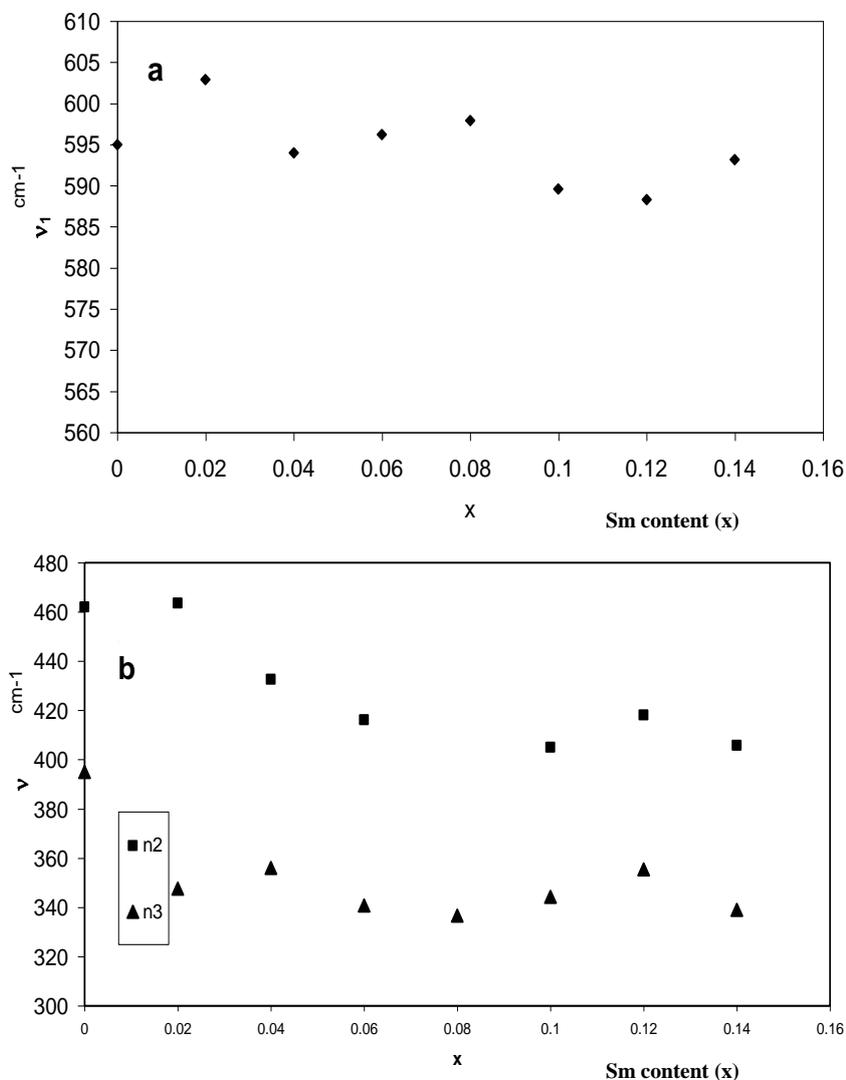


Fig. 2 (a,b). Dependence of the vibrational frequency on the Sm concentration of the investigated samples.

X-ray diffractograms were carried out for the samples with $0.04 \leq x \leq 0.14$ (Fig. 3- a, b). The data are indexed as orthorhombic perovskite of the type [GdFeO₃-type] structure^(15, 16) of space group Pbnm. In this type of structure central Mn atom is octahedrally surrounded by its nearest neighbor six O anions. The ideal octahedron MnO₆ has the symmetry of the point group, which has six vibrating modes two of them are IR active.

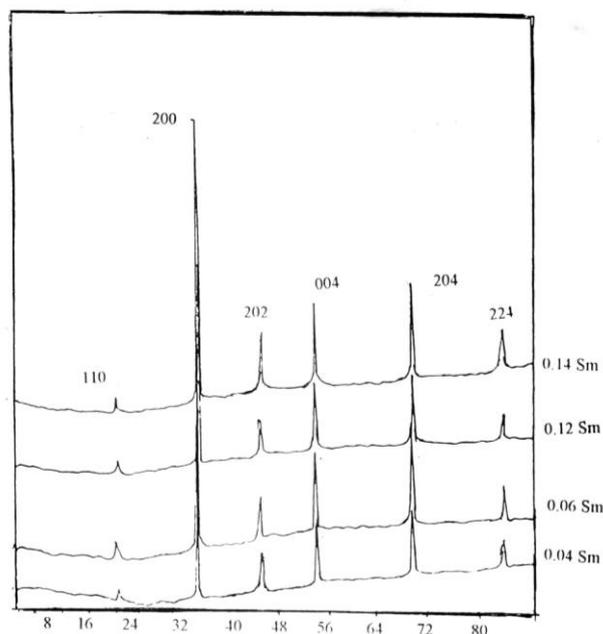


Fig. 3. X-ray diffraction patterns for the sample at different Sm content for $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, $x = 0.04, 0.06, 0.12, 0.14$.

Two states of spin configuration exist for Mn^{3+} ions in the perovskite under investigation, the first one is the high spin in which the 4 unpaired electrons exist ($t_{2g}^3 e_g^1$). In this case the crystal field stabilization energy (CFSE) $10Dq$ is lower than that of low spin configuration. This behavior can be ascribed to the large number of unpaired electrons existing in ($t_{2g}^3 e_g^1$). Though the resistance of the samples was expected to decrease with increasing temperature above room temperature. In the case of low spin configuration, there exist two unpaired electrons distributed in d_{xy}^1, d_{xz}^1 in t_{2g} and e_g^0 . This small number of unpaired electrons gives low probability of conduction rather than the high spin configuration at the same temperature. Therefore, one can guess that the high spin configuration case is the most probable one.

Figure 4 (a-c) shows the dependence of the molar magnetic susceptibility (χ_M) on the absolute temperature from liquid nitrogen up to near room temperature as a function of the magnetic field intensity for the perovskite samples:

(La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO₃; x=0.02, 0.08 and 0.1. The data in the figure show the same trend with a sudden decrease at the Curie temperature (T_C) where the state of the samples is changed from completely ordered (ferromagnetic) to completely disordered state (paramagnetic). The Curie temperature for the sample without Sm is relatively high \cong 218K and decreases to 190K at x=0.02. Continuous increase of Sm content in the samples decreases the ordered region on the expense of the paramagnetic region because Sm³⁺ ion is highly paramagnetic, with the result of decreasing of the exchange interaction constant in the system. The double exchange interaction is predominant in this system while the weak component appears to reflect the spin canting of the antiferromagnetic exchange interaction. The magnetic constants were calculated from the data and reported in Table 1(a-b). The effective magnetic moment is increased by introducing Sm³⁺ ions in the sample and decreases with further increase in Sm³⁺ content reaching a minimum value at x=0.08 and then increases again, (Fig. 5a). The data in the figure show that, the double exchange interaction resulting from ferromagnetic coupling of Mn³⁺ and Mn⁴⁺ ions was the main source of interaction in the investigated Ca doped La manganite where some Mn⁴⁺ ions were generated to preserve charge neutralization. In other words, doping with Sm³⁺ ions rises the magnetic moment from 3.5 B.M. at x=0 to 14 B.M. at x=0.02 due to the probable coupling between 4f and 3d orbitals of the Sm and Mn ions. The decrease of μ_{eff} from x=0.02 to x=0.08 can be ascribed to the increase in the distortion resulting from the small size of the Sm³⁺ as compared with La³⁺ ions, thereby decreasing the angle Mn-O-Mn as well as the exchange interaction constant. The increase of μ_{eff} above x=0.08 *i.e.*, at high Sm content may be due to the valence change between Sm³⁺ and Sm²⁺ (1.51 B.M., and 3.63 B.M., respectively) which increases μ_{eff} . So, one can consider x=0.08 as a critical Sm content. This behavior is also reflected in the dependence of both t and T_C on x as a break at x=0.08. The values of the tolerance factor

were calculated from $t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$; where r_A, r_B and r_O are the ionic, radius

of the A, B and oxygen ions, respectively. The ionic radii were taken in 12 fold coordination site for the A cation⁽¹⁷⁾. The apparent decrease in both T_C and tolerance factor t, (Fig.5b), with increasing Sm content reflect the dependence of T_C on the distortion occurring in the perovskite by decreasing the radius of the A cation. The Curie temperature was directly proportional to $\cos^2\theta$ ^(18, 19) where θ is the Mn-O-Mn angle. This means that, at θ lower than 180° an increase in the distortion occurred accompanied with a decrease in the tolerance factor.

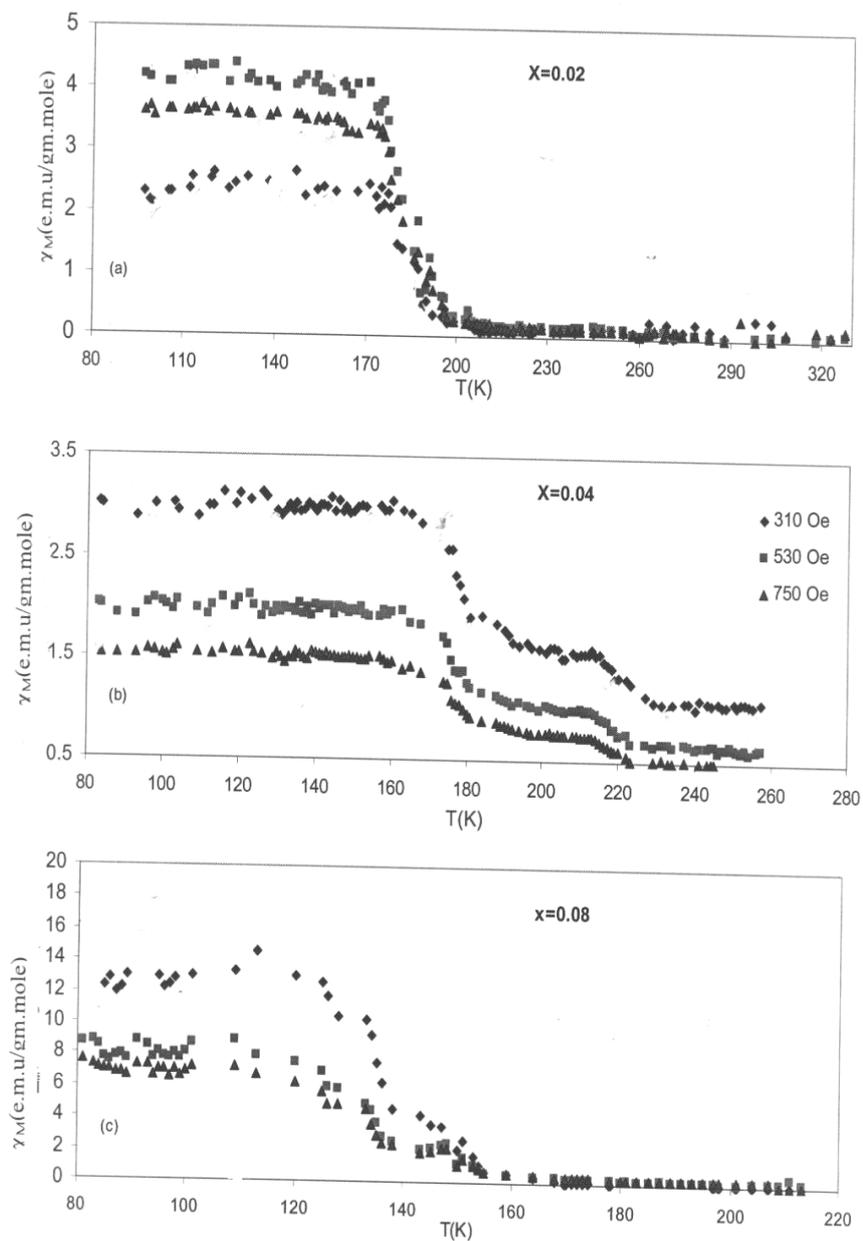


Fig. 4 (a-c). Relation between the molar magnetic susceptibility and absolute temperature for the perovskite $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, a) $x=0.02$, b) $x=0.04$, c) $x=0.08$.

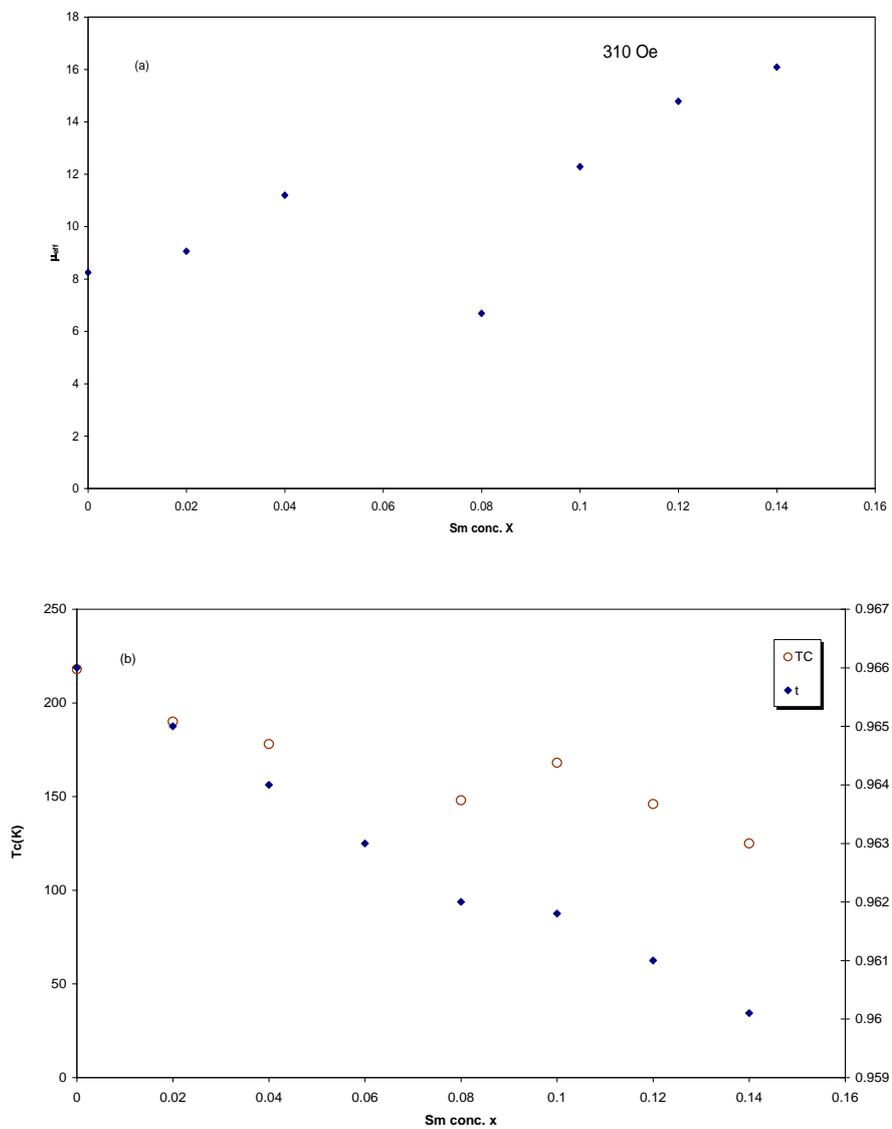


Fig. 5 (a,b). The dependence of the effective magnetic moment m_{eff} , Curie temperature T_C and tolerance factor t on Sm content for $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

The expected formation of Mn⁴⁺ ions plays a significant role in double exchange mechanism because it varies the ratio Mn⁴⁺/Mn³⁺ where Mn-O-Mn interaction strength decreases by decreasing the tolerance factor as a result of increasing Sm content. This means that Mn-O bond length occurs at the transition point T_c^(20, 21). After T_c, we expect that the Jahn-Teller effect plays a role in the disordered region where this distortion takes about 70% of the Mn³⁺ sites and the other ~ 30% takes Mn⁴⁺ to prevent the formation of a long range cooperatively distorted structures such as the one found in LaMnO₃⁽²²⁾. Generally, it was found that in the ideal AMnO₃ perovskite structure each O atom is coordinated octahedrally by 4A and 2Mn³⁺. In the disordered region, one expect that the A cation gives rise to O displacements perpendicular to the Mn-O-Mn axis which affect directly on the magnetization of the system as well as the effective magnetic moment. The presence of Sm³⁺ ions (1.04A⁰) will initiate Jahn-Teller distortion where Mn ions show mixed valence of Mn⁴⁺/Mn³⁺ as mentioned before. At certain doping ratio, the Mn⁴⁺/Mn³⁺ reaches values at which the sample shows insulator – metal and paramagnetic – ferromagnetic transitions at a temperature designated as T_p. Millis *et al.*⁽²³⁾ found that, Jahn-Teller effect coupled with the double exchange mechanism to play a significant role on the resistance value of the samples.

Figure 6 (a-b) is a typical curve clarifying the dependence of $\chi_M \cdot T$ on the absolute temperature at different magnetic field intensity of (1190, 1410 and 1610 Oe) for the samples (La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO₃ with concentrations 0.02 and 0.08, respectively. The data in the figure shows the same trend for the two concentrations where the values of $\chi_M \cdot T$ vs T increases until reaching the maximum value (transition temperature) which varies depending on the Sm content. After that $\chi_M \cdot T$ decreases suddenly until reaching nearly stable values. The obtained behavior is similar to that of the antiferromagnetic materials ($\chi_M \cdot T$ increases with T at low temperature region). This behavior is similar to that of a typical antiferromagnetic materials where $\chi_m \cdot T$ increases with T. This was expected because the interaction between the different lattice sites is mainly antiferromagnetic. The values of the magnetic constant reported in Table 1a enhances our expectation.

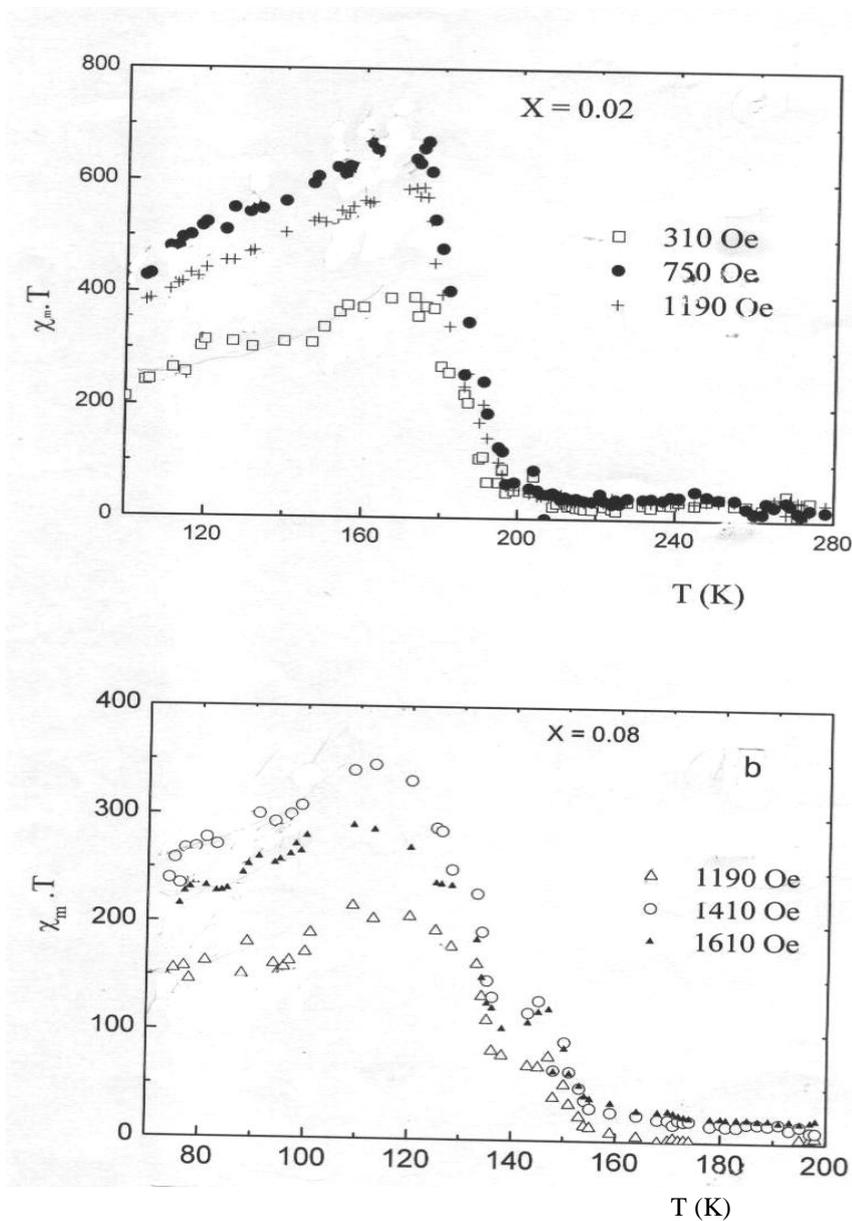


Fig. 6 (a, b). Relation between $\chi_M \cdot T$ vs T for the samples $(La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO_3$, a) $x=0.02$, b) $x=0.08$ at different magnetic field intensities.

TABLE 1a. Values of the effective magnetic moment (μ_{eff}) at different magnetic field intensity for the samples $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ $0 \leq x \leq 0.14$.

x	μ_{eff}		
	310 Oe	750 Oe	1190 Oe
0.00	3.50	7.46	7.369
0.02	14.24	16.98	15.68
0.04	11.20	16.30	19.47
0.08	9.91	5.87	9.91
0.10	12.29	12.07	13.66
0.12	14.78	13.76	13.76
0.14	16.09	17.69	20.28

TABLE 1b. Values of the tolerance factor (t) and Curie temperature (T_c) for the samples $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ $0 \leq x \leq 0.14$.

x	t	T_c
0.00	0.9660	218
0.02	0.9650	190
0.04	0.9640	176
0.08	0.9620	148
0.10	0.9618	168
0.12	0.9610	146
0.14	0.9601	125

Figure 7(a, b) shows the dependence of the resistivity ρ on the absolute temperature $T(\text{K})$ for the investigated samples of $0.04 \leq x \leq 0.14$ at two fixed frequencies 200kHz and 1MHz. At low Sm concentration three peaks appeared at about 410, 550, and 640 K, respectively. By increasing the Sm concentration these peaks seem to disappear. These three transitions which were expected to be due to the, Jahn-Teller distortion, are the polaronic charge carrier at which the system is changed from disordered to ordered state once time again and the change from orthorhombic to pseudo cubic (high temperature orthorhombic)⁽²⁴⁾, respectively. The temperature dependence of resistivity shows a metallic like behavior above $\approx 640\text{K}$ and rather shallow temperature dependence with a broad hump at $\sim 430\text{K}$. The dramatic increase in the resistivity below 530K might be related to the spin state transition of Mn^{3+} ions from high to low state. The sample with $x=0.08$ exhibits the critical behavior in the resistivity measurements

which agree well with the results obtained for the μ_{eff} vs Sm content. The Sm^{3+} ions captured the electrons from the $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + e^-$ double exchange giving rise to some Sm^{2+} ions, thereby increasing the resistivity values above $x = 0.08$.

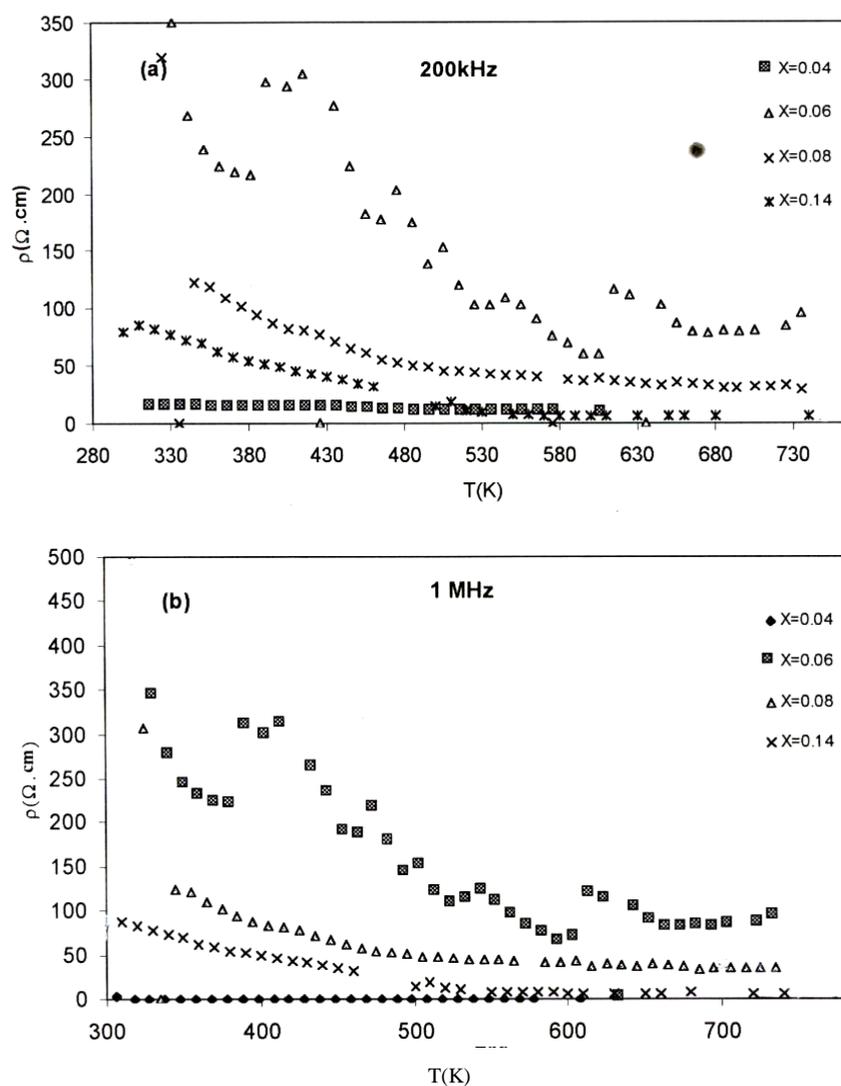


Fig. 7 (a,b). Relation between the resistivity r and absolute temperature at different Sm content for $(\text{La}_{1-x}\text{Sm}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. a) At 200 kHz b) At 1 MHz.

Conclusions

The Curie temperature (T_c) of the sample without Sm is relatively high $\approx 218\text{K}$ and decreases to 190K at $x=0.02$. Continuous increase of the Sm content in the samples decreases the ordered region on the expense of the paramagnetic region. The effective magnetic moment increases by introducing Sm³⁺ ions in the sample and then decreases with further increase in Sm³⁺ content reaching a minimum value at $x=0.08$. Doping with Sm³⁺ ions increases the magnetic moment due to the probable coupling between 4f and 3d orbital of the Sm and Mn ions. The decrease of μ_{eff} can be ascribed to the increase in the distortion resulting from the small size of the Sm³⁺ as compared with La³⁺ ions, thereby decrease the angle Mn-O-Mn as well as the exchange interaction constant. The apparent decrease in both T_c and tolerance factor t , with increasing Sm content reflects the dependence of T_c on the distortion occurring in the perovskite by decreasing the radius of A cation.

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تأثير ايونات Sm³⁺ على النقل و تمغنت الشبكة الجزيئية للنظام البيروفسكيت

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تم تحضير مركبات البيروفسكيت $(La_{1-x}Sm_x)_{0.7}Ca_{0.3}MnO_3$ $0 \leq X \leq 0.14$ باستخدام تقنية مزدوجة تلبد السيراميك . ولقد اظهر قياس القابلية المغناطيسية عند درجات حرارة مختلفة بوصفها وظيفة من شدة المجال.

وأظهر قياس القابلية مغناطيسية عند درجات حرارة مختلفة بوصفها وظيفة من شدة المجال المغناطيسي لتغيير الحالة من أمر منتظم تماما الى حالة غير منتظمة تماما عند Tc والتي حدث لها ازاحة الى قيمة منخفضة وذلك بزيادة محتوى Sm بالمركب . كما وجد ان عامل التولارنس يقل بزيادة تركيز Sm واشارت ايضا قياسات المقاومة الى اختفاء القمم ذات الصلة مع زيادة محتوى Sm.

الزيادة الكبيرة في المقاومة تحت 530 K هذا راجع الى انتقال حالة الغزل للايون Mn³⁺ من عالى الى منخفض الغزل.