Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary

Crystal Structures, Magnetic and Electrical Properties of Manganese Perovskites

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The $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ system with $y \leq 0.2$, crystallizes in an orthorhombic type structure having Pnma space group. The $La_{1-x}Pb_xMnO_3$ perovskites with $0.24 \leq x$ 0.40 have a rhombohedral structure of $R\bar{3}c$–type. The $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ samples show a mictomagnetic type behaviour. The analysis of charge compensation mechanism suggests that the number of oxygen vacancies increases with Al content. A semiconducting type behaviour was also shown. The contributions of double exchange mechanism to magnetic ordering in $La_{1-x}Pb_xMnO_3$ increase as the lead content is higher. A nearly ferromagnetic type ordering was shown for the sample with $x=0.4$. The number of Mn^{4+} ions fits well with the Pb^{2+} ones, suggesting that the change in Mn valence state is the dominant mechanism for charge compensation. A transition from metallic to semiconducting type behaviour is shown at temperatures by$\cong$130 K lower than the Curie points. Magnetoresistivities up to $\cong$ 50 % were determined in fields of 60–70 kOe.

Keywords: perovskites, crystal structure, magnetic and electronic properties

The $R_{1-x}A_xMnO_3$–type manganites, where R is a trivalent rare–earth or yttrium and A a divalent element (A=Ca,Sr,Pb,Ba) ,have been subjected to intensive investigations due to their interesting magnetic and electrical properties with possible technical applications [1]. Because of the presence of A^{2+} ions, a fraction of the manganese ions changes their valence states from Mn^{3+} to Mn^{4+}. For an octahedral coordination, the configurations of manganese ions are $t_{2g}^3 e_g^1 (^5E)$ for Mn^{3+} and $t_{2g}^3 (^4A_2)$ for the Mn^{4+}. As function of the composition, the relative content of Mn^{3+} and Mn^{4+} ions can be greatly changed.

The magnetic ordering in $R_{1-x}A_xMnO_3$ perovskites are determined by the presence, in a given sample, both of superexchange and double exchange interactions. The Mn^{3+}–O–Mn^{3+} and Mn^{4+}–O–Mn^{4+} superexchange interactions lead to an antiferromagnetic type ordering. There are also Mn^{3+}–O–Mn^{4+} double exchange interactions. The e_g electrons of Mn^{3+} are mobile charge carriers, interacting with the Mn^{4+} ions. The carrier hopping depends on the relative alignment of the charge spin to the localized Mn^{4+} spin. When the two spins are aligned this leads to a ferromagnetic coupling of manganese moments. In addition, the carriers avoid the strong on–site Hund exchange energy and thus hop easily [2]. In case of $R_{1-x}A_xMnO_3$ compounds, as function of the relative content of Mn^{3+} and Mn^{4+}, there is a competition between antiferromagnetic and ferromagnetic exchange interactions and as a results a complex magnetic behaviour is frequently evidenced. Thus, is of interest to analyse the evolution of the physical properties of perovskite systems when the ratio between the number of manganese ions in the two valence states is continuously modified. For this reason we studied the $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ and $La_{1-x}Pb_xMnO_3$ perovskites. In the first system, a fraction of Mn^{3+} ions is substituted by Al^{3+}, while in the second one, the replacement of La^{3+} by Pb^{2+} leads to the increase of Mn^{4+} content.

Previously, some physical properties of $La_{1-x}Pb_xMnO_3$ were reported [3–9]. These generally were analysed on a limited compositions range. Thus, electrical resistivity [3, 7], neutron diffraction[6], magnetic [5, 8, 9] or electronic structure [4] were studied. Contradictory data were sometimes reported.

Experimental part

The samples were prepared by standard ceramic procedure. The $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ samples with $0 \leq y \leq 0.2$ were obtained from stoichiometric proportions of Y_2O_3, $CaCO_3$, $MnCO_3$ and Al_2O_3, having analytical purities. The starting materials were grounded, mixed together and heated at 1250°C for 48 h. Then, the powders were pressed in pellets and sintered at 1425°C, in air, for 12 h. The $La_{1-x}Pb_xMnO_3$ perovskites were obtained from La_2O_3,PbO and $MnCO_3$ following the same procedure. The pellets were sintered, at 1200°C, during 24 h.

Powder X–ray diffraction patterns were obtained, at ambient temperature, by using a Brucker D8 diffractometer. The Rietveld refinements were performed by using a Topas code. The microstructure and the grain compositions were studied by using an electron microscope. EDX analyses were also made in order to obtain information on the particles homogeneity.

The magnetic properties were studied in the temperature range 4.2 K–400 K with an Oxford Instruments type equipment, in field up to 90 kOe. Above the Curie temperatures, the magnetic susceptibilities were determined, with a Faraday type balance.

The resistivities and magnetoresistivities were determined by four probe method, in field up to 7 T.

Crystal structure and microstructure

The X–rays analyses show that the samples are single phases. In the limit of experimental errors no presence of impurities was evidenced. As examples, the refined X–rays

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spectra for the $Y_{0.67}Ca_{0.33}Mn_{0.9}Al_{0.1}O_3$ and $La_{0.64}Pb_{0.36}MnO_3$ samples are shown in figure 1. There is a good agreement between the computed spectra and those experimentally determined.

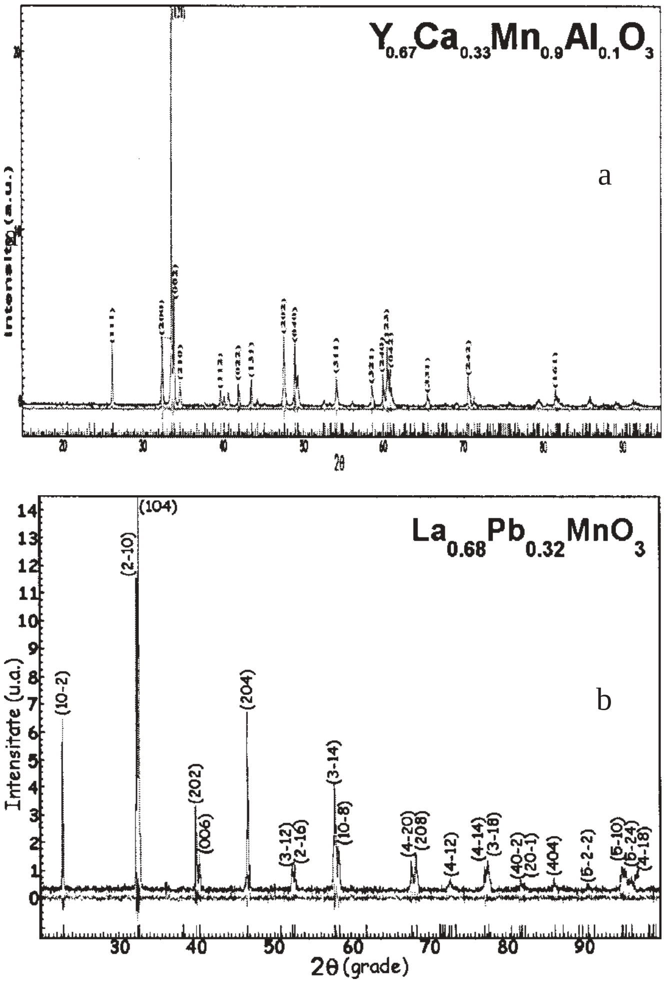

Fig.1.The refined X–rays spectra for $Y_{0.67}Ca_{0.33}Mn_{0.9}Al_{0.1}O_3$ (a) and $La_{0.68}Pb_{0.32}MnO_3$ (b) perovskites

The $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ perovskites with y≤0.2 crystallize in an orthorhombic type structure having Pnma space group. When increasing the aluminum content, the cell volumes decrease, as compared to that of $Y_{0.67}Ca_{0.63}MnO_3$, by 0.13 % (x=0.1) and 0.29 % (x=0.2) [10]. This behaviour can be correlated with the smaller Al^{3+} radius, as compared to either Mn^{3+} or Mn^{4+} ones. The b and c lattice parameters are only little influenced by substitutions, while the a lattice parameters decrease significantly, when aluminum content is higher. The Mn–O1–Mn and Mn–O2–Mn angles increase from 145.9° and 148.1°, for x=0, to 147.9° and 150.1°, respectively in case of $Y_{0.67}Ca_{0.33}Mn_{0.8}Al_{0.2}O_3$ sample.

The $La_{1-x}Pb_xMnO_3$ perovskites with $0.24 \le x \le 0.40$ crystallize in a rhombohedral structure, having space group $R\bar{3}c$. The a lattice parameters are only little dependent on composition. The c parameters as well as the Mn–O–Mn angles increase nearly linear, when lead content increases (fig. 2).

The mean dimensions of the grains, determined by XRD measurements, are situated between 170 and 340 nm. These values were confirmed by electron microscope studies (fig. 3). We analysed also the distribution of the elements along the grains. As seen in figure 3, a rather uniform composition inside the grains is shown. In addition, the compositions of the sintered perovskites are close to those expected from starting compositions.

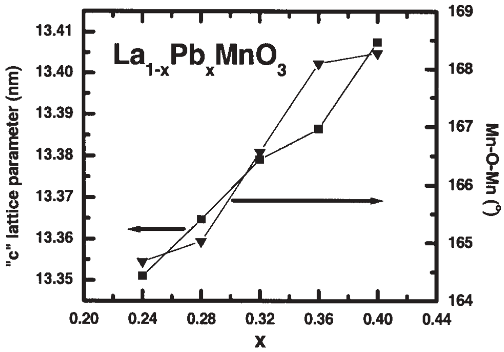

Fig.2.The composition dependences of the “c” lattice parameters as well as of Mn–O–Mn angles for $La_{1-x}Pb_xMnO_3$ perovskites

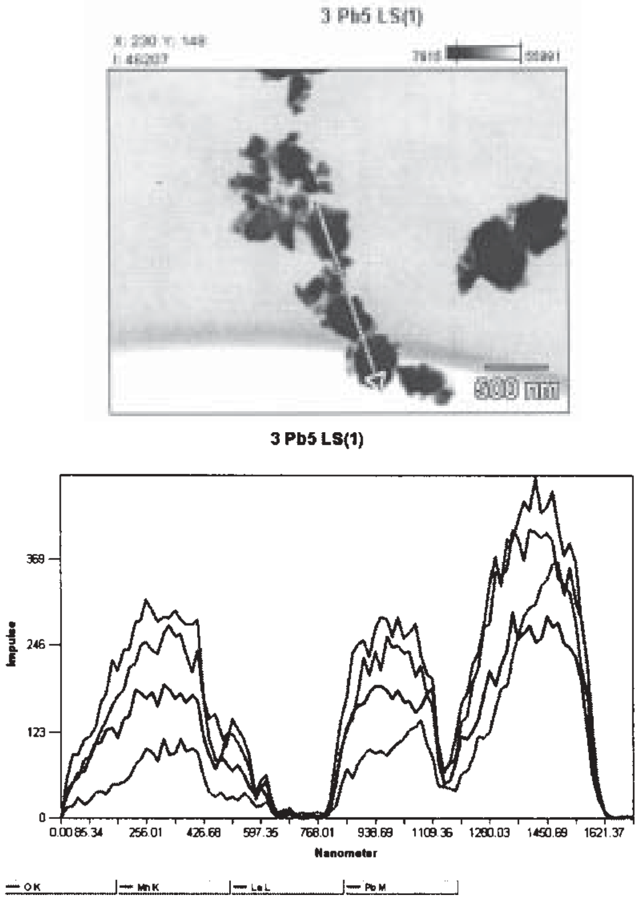

Fig.3.The grain dimensions as well as the distribution of the constituent elements along the $La_{0.6}Pb_{0.4}MnO_3$ grains

Magnetic properties

The magnetization isotherms for $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ samples, at 4.2 K, are plotted in figure 4. The magnetizations are not saturated even in field of 90 kOe. Their linear variations, in fields H≥50 kOe, suggest the presence of a mictomagnetic type behaviour. The above type of ordering is confirmed by the analyses of the temperature dependences of magnetization in samples field cooled (FC) and zero field cooled (ZFC). As evidenced in figure 5, a high irreversibility appears below 60 K. The zero field cooled samples show maxima at T_m in their temperature dependences of the magnetization. The T_m values decrease from T_m=30 K (x=0) to 19 K (x=0.2), suggesting a diminution of the exchange interactions as manganese is replaced by aluminum.

Above the Curie points, the temperature dependences of the magnetic susceptibilities follow a Curie–Weiss law: $\chi = C(T-\theta)^{-1}$. We denoted by C the Curie constant and θ is the paramagnetic Curie temperature. Starting from the Curie constants we determined the relative content of

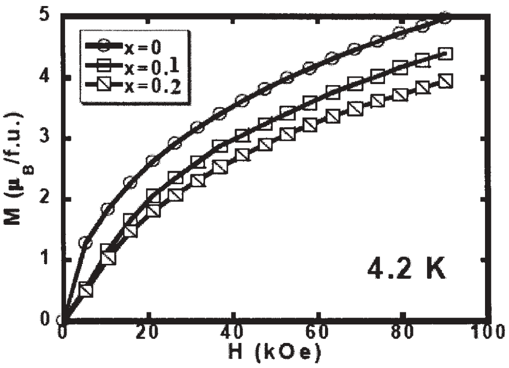

Fig.4.Magnetization isotherms for $Y_{0.67}Ca_{0.33}Mn_{-1-y}Al_yO_3$ perovskites, at 4.2 K

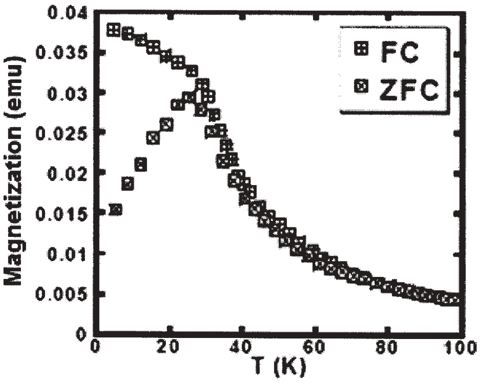

Fig.5.The magnetizations of zero field cooled (ZFC) and field cooled (FC) $Y_{0.67}Ca_{0.33}Mn_{-0.9}Al_{0.1}O_3$ sample in field of 500 Oe

manganese ions in the two valence states. As seen from table 1a, as the aluminum content increase, the relative fraction of Mn^{4+} ions, is greater.

The aluminum is in +3 valence state and thus can substitute only Mn^{3+} ions. The ratio, r, between the number of Mn^{3+} and Mn^{4+} ions for the composition x=0, is nearly 2, suggesting that the dominant mechanism for charge compensation is the change of manganese valence from +3 to +4, corresponding to the fraction of Ca^{2+} ions present in lattice. The ratio between the total number of +3 ions, to those having +4 valence, increases to 2.19 for y=0.1 and to 2.24 for y=0.2. The deviation from the r=2 value can be correlated with the presence of oxygen vacancies in lattice. Their number increases when aluminum content is higher.

From the analysis of experimental data, can be concluded that the superexchange mechanism has a dominant contribution to magnetic ordering, although the double exchange is also present. The substitution of Mn^{3+} by nonmagnetic Al^{3+} diminishes the strength of exchange interactions, the superexchange or double exchange paths being interrupted. This is equivalent to a magnetic dilution and leads to the decrease of Curie temperatures.

The magnetization isotherms of $La_{1-x}Pb_xMnO_3$ samples, at 4.2 K, are plotted in figure 6. The magnetizations are nearly saturated in fields higher than ≅30 kOe. The magnetizations increase when increasing the lead content. A small irreversibility was shown in the magnetizations of samples field cooled and zero field cooled. This irreversibility decreases when the lead content is higher [11]. The Curie temperatures, T_C, increase linearly from 285 K for x=0.24 to 348 K at x=0.40. No fluctuations along the linear variation were shown, as previously reported [9].

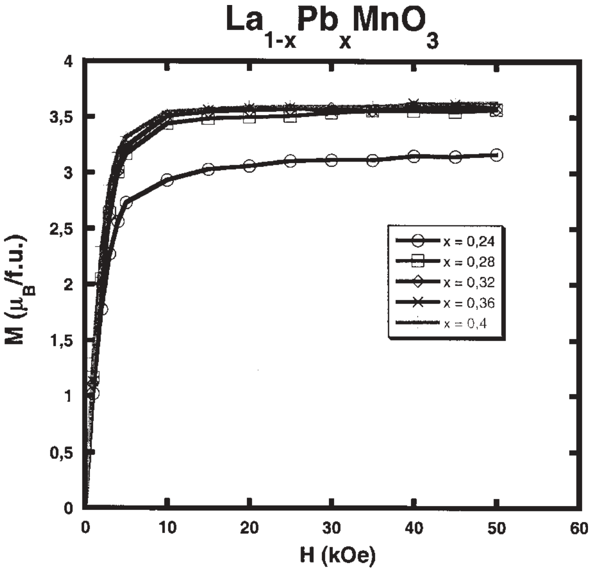

Fig.6.Magnetization isotherms, at 4.2 K, for $La_{1-x}Pb_xMnO_3$ perovskites

Above T_C values, the reciprocal magnetic susceptibilities follow a linear dependence, as described by a Curie–Weiss law. The paramagnetic Curie temperatures are by ≅14 K higher than the ferromagnetic ones. From Curie constants we determined the relative number of manganese ions in the +3 and +4 valence states. As can see from table 1b, the number Mn^{4+} ions fits well with the Pb^{2+} content, suggesting that the change in manganese valence is the dominant mechanism for charge compensation.

Starting from the number Mn^{3+} and Mn^{4+} ions, we evaluated the contributions of Mn^{3+}–O–Mn^{4+} double exchange as well as of superexchange type interactions to magnetic ordering. The increase of the lead content increase the number of Mn^{4+} ions, and as result, the contribution of the double exchange mechanism to the magnetic ordering. This is shown by the increase of saturation magnetizations, as the La is substituted by Pb. Thus, for compositions x=0.40, the magnetization is close to that expected if all the Mn^{3+} and Mn^{4+} are paralelly

Table 1
THE MANGANESE VALENCE STATES

a) $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ system

	y=0	y=0.1	y=0.2
Mn^{3+}(%)	66.4	65.6	60.5
Mn^{4+}(%)	33.6	34.4	39.5

b) $La_{1-x}Pb_xMnO_3$ system

	x=0.24	x=0.28	x=0.32	x=0.36	x=0.40
Mn^{3+}(%)	75.6	71.5	68.1	63.8	60.4
Mn^{4+}(%)	24.4	28.5	31.9	36.2	39.6

aligned. There is also an increase of the strength of exchange interactions due to the increase of Mn–O–Mn angles, when the lead content is higher.

Resistivity studies

The $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ samples are semiconducting. Since of high resistivities, the measurements were performed only at temperatures higher than ≅ 220 K (fig. 7a). The magnetoresistivities, at temperatures close to ambient one, were rather small, of the order of –6%, in field of 60 kOe (fig. 7b). We note that, in the studied temperature range, the samples are paramagnetic.

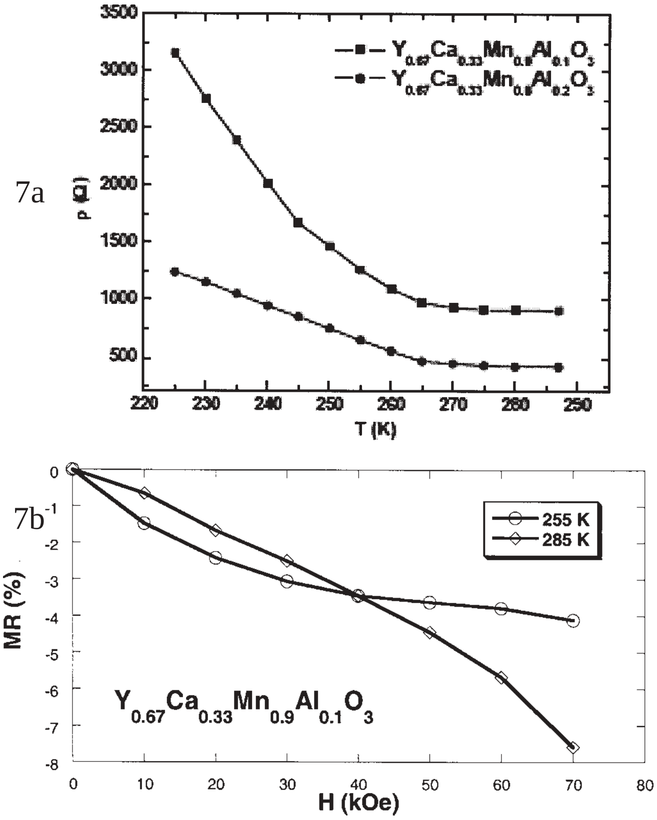

Fig.7.Temperature dependences of the resistivities for $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ samples (a), as well the magnetoresitivities of sample with x=0.1, at 255 K and 285 K (b)

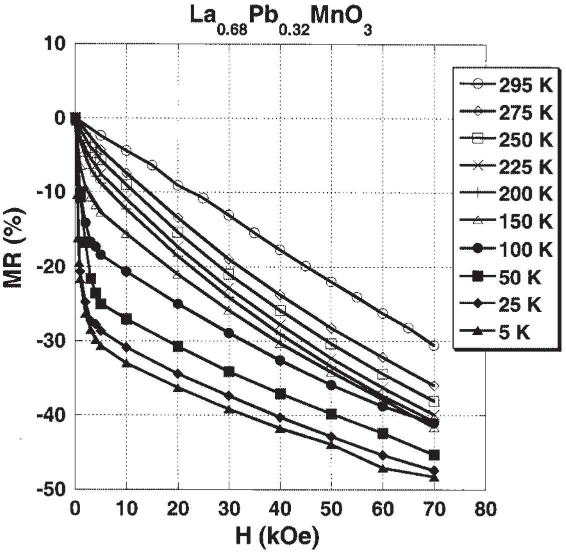

Fig.8.Field dependences of the magnetoresistivites, at various temperatures, for $La_{0.68}Pb_{0.32}MnO_3$ perovskite

The resistivities, ρ, in $La_{1-x}Pb_xMnO_3$ system, increase up to a temperature, T_{max}, which is situated between 180 K (x=0.24) and ≅250 K (x=0.40). In this temperature range the samples are metallic. Above the mentioned temperatures, semiconducting type behaviour is shown. We note that the temperature, T_{max} at which a change in conductivity mechanism appears is smaller than the Curie temperatures. The magnetoresistivities, MR, determined in $La_{0.68}Pb_{0.32}MnO_3$ sample are plotted in figure 8. The MR values are negative and increase in absolute magnitude when increasing the external field or decreasing temperature. The absolute values of magnetoresistivities are nearly linearly dependent on temperature (fig. 9). Rather high MR values, of the order–50%, were determined at low temperatures. At ambient temperature, MR values of –30 % were obtained in field of 60–70 kOe.

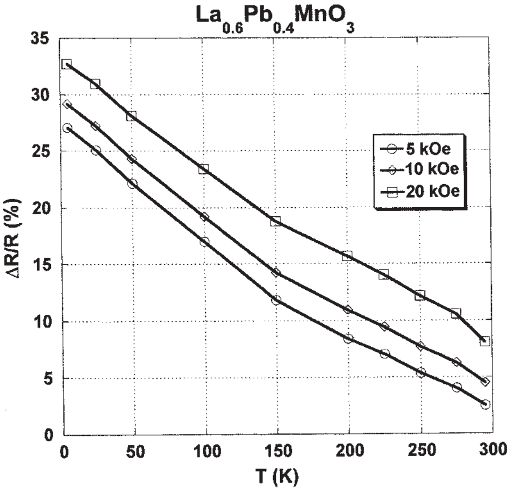

Fig.9.Temperature dependences of the magnetoresitivities for $La_{0.6}Pb_{0.4}MnO_3$ in fields of 5, 10 and 20 kOe

Conclusions

The physical properties of manganese based perovskites are strongly related to the manganese valence states. In $Y_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ system, the Al^{3+} ions substitute the manganese ones having the same valence. The total number of +3 ions is higher than expected by the replacement of Y^{3+} by Ca^{2+} ions. This behaviour can be correlated with the increase of the number of oxygen vacancies as the aluminum content is higher. The presence of Al^{3+} ions break the exchange interactions paths with manganese ions situated in their environments. This fact diminishes the strength of exchange interactions and as a result, there is a decrease of the Curie temperatures.

The increase of Mn^{4+} ions as the Pb^{2+} content is higher, in $La_{1-x}Pb_xMnO_3$ system, leads to the increase of the contributions of double exchange mechanism to the exchange interactions. As a result, there is a gradual change of the magnetic ordering from a mictomagnetic type behaviour to a nearly ferromagnetic one, for x=0.40. A change in transport properties from metallic type conduction to a semiconducting one was shown at temperatures lower by ≅ 130 K, than the Curie points. The semiconducting behaviour at $T<T_C$ cannot be correlated with the mobility reduction by spin disorder. This behaviour can be the attributed to the disappearance of density of state at the Fermi energy, as suggested previously [6].

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