Magnetic, Electrical Properties and Spin-Glass Effect of Substitution of Ca for Pr in $Ca_{2-x}Pr_xMnO_4$ Compounds

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Abstract: $Ca_{2-x}Pr_xMnO_4$ (*x = 0.000 to 0.200*) manganites were synthesized by a sol-gel method and then characterized by X-ray diffraction (XRD) at room temperature. Rietveld refinement technique shows that all samples can be indexed in orthorhombic system except for Ca_2MnO_4 (*x = 0.000*) which can be indexed in the tetragonal system. Magnetic and electrical measurements show that magnetization and resistivity have a large dependence of the fractional composition *x* and temperature. The applied magnetic field has also a large influence on magnetization level. Spin-glass behavior was detected at low temperature for the samples with *x≥0.175*. For all *x-values*, all compounds exhibit semiconductor behavior and the ferromagnetic (FM) transition temperature T_C (Curie temperature) is around *105 K*, whatever the applied field.

Keywords: Manganites, perovskite, ferromagnetic, spin-glass.

1. INTRODUCTION

Besides the perovskite family, the Ruddlesden–Popper manganites, which consist of a regular intergrowth of single rock-salt with multiple perovskite layers, were studied most extensively. The crystal chemistry of these oxides shown in numerous studies, are complex and subject to controversy [1-14]. The $Ca_{2-x}Ln_xMnO_4$ compounds (Ln = Pr, Sm, Gd, Ho) are good examples of Ruddlesden-Popper manganites. These compounds display diverse magnetic and electronic phases such as antiferromagnetic (AFM)-insulating, ferromagnetic (FM)-conductor, paramagnetic (PM)-insulating [15], spin-glass [16-26] and charge-ordering [27]. On the other hand, these Ruddlesden-Popper manganites display interesting magnetic properties, depending on the materials-doping, multiple phase transitions, saturation and no-saturation magnetization. The Ln-doped manganites of Ca_2MnO_4 compound induces a mixed valence state (Mn^{3+}/Mn^{4+}) and enhances magnetic behavior transition; which can be explained by the double exchange interaction between Mn^{3+} and Mn^{4+} ions [28]. It has been shown that $Ca_{2-x}Ln_xMnO_4$ (Ln = Pr, Sm, Gd, Ho) compounds, which despite their pure bidimensional character, submit a spin-glass transition at low temperatures. For the praseodymium phases $Ca_{2-x}Pr_xMnO_4$, all compounds exhibit semiconductor behavior. In this paper, we report the effect of Pr doping on the magnetic and electrical properties of $Ca_{2-x}Pr_xMnO_4$ compounds. A detailed experimental study of the dependence of magnetization and resistivity with temperature and composition *x* is reported.

2. EXPERIMENTAL SECTION

$Ca_{2-x}Pr_xMnO_4$ compounds (*x = 0.000* to *0.200*) were synthesized by a sol-gel method. The reaction starts from a stoichiometric mixture of high purity materials: *Ca $(NO_3)_24H_2O$ (98%)*, *MnO_6 (99%)* and *Pr_6O_{11} (99.9%)*. The samples were subjected to five cycles of sintering for *48 h* at *500 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C* and a last cycle at *900 °C* for two weeks. Before every cycle, the samples were grinded and pressed with less than *2 tons*, into a disc shape of *8 mm* diameter. Samples were characterized at room temperature by a Siemens D5000 X-ray powder diffractometer (XRD) with a graphite monochromatized CuKα radiation (*λ = 1.54056 Å*) and *10° ≤ 2θ ≤ 100°* with a step size of *0.02°* and a counting time of *18 s* per step. The magnetization measurements were performed using a Foner magnetometer equipped with a super-conducting coil in different magnetic field. The DC electrical resistivity was measured with Keithley electrometer equipment, model 617, as a function of the temperature (*80-400 K*).

3. RESULTS AND DISCUSSIONS

a) Structural Properties

In order to make sure that all the samples are single phase and all chemical elements (Ca, Pr, Mn, and O) are present in $Ca_{2-x}Pr_xMnO_4$ compounds, XRD and EDAX analysis have been realized. Using Fullprof program, the diffraction peaks corresponding to *x = 0.000* can be indexed in the tetragonal system with *I41/acd* space group. The substitution of Ca with Pr generates spectral modifications (Fig. **1**) and the diffraction peaks can be indexed in the orthorhombic system with *Aba2* space group. Fig. (**2**) shows an example of EDAX spectrum analyzed at room temperature of the $Ca_{1.9}Pr_{0.1}MnO_4$ compound (*x = 0.100*). This analysis reveals that, for all the compositions, all elements (*Ca, Pr, Mn and O*) remain present in the course of the sintering.

b) Magnetic Properties

Using constant applied magnetic field of *0.045 T*, the temperature (T) dependence of the magnetization (M), for

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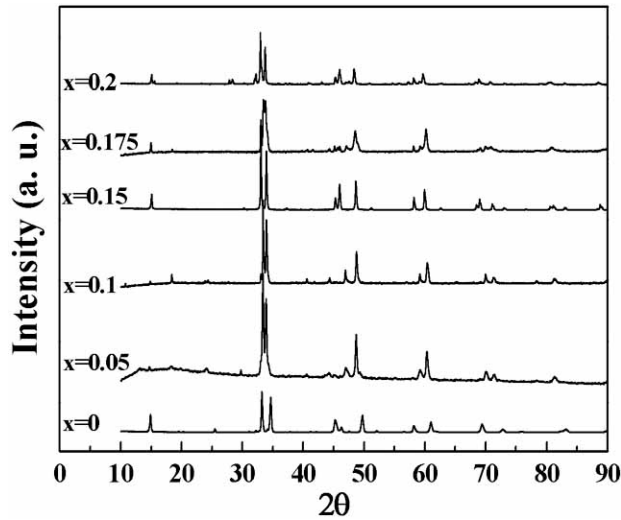
Fig. (1). X-ray diffraction patterns at room temperature of $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.0$ to 0.2).
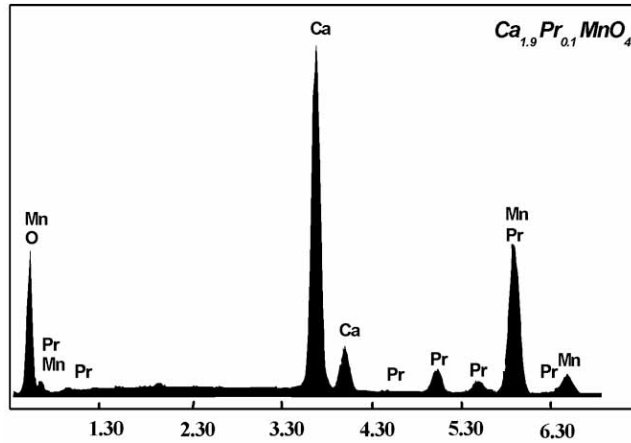

Fig. (2). Example of EDAX analysis spectral at room temperature of $Ca_{1.9}Pr_{0.1}MnO_4$ sample ($x = 0.100$).

$Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000$ to 0.200) is visualized in Fig. (**3**). From $x = 0.000$ to 0.150, the magnetization level increases and reaches the maximum at $x = 0.150$ and then exhibit an abrupt decrease for $x = 0.175$ and 0.200. On the other hand, all the samples present a magnetic transition from a paramagnetic to a ferromagnetic state, by decreasing the temperature. This transition occurs at the Curie temperature (T$_C$) determined from the peak of (-dM/dT) *vs* T curves (Fig. **4**). For all the *x-values*, T$_C$ is around 105 K and independent of the applied field (Fig. **5**). For $x<0.150$, the PM-FM transitions is induced by the partial substitution of the Ca^{2+} sites by a trivalent alkaline earth ion Pr^{3+} in $Ca_{2-x}^{2+}Pr_x^{3+}Mn_x^{3+}Mn_{1-x}^{4+}O_4^{2-}$ compounds. This magnetic behavior can be explained by the increase of the Mn^{3+}/Mn^{4+} ratio. So that, the rise of *x-value* means a partial substitution of the tetravalent ions Mn^{4+} by the trivalent ions Mn^{3+}. The mixed valence state induces a double exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions [16], which increases until $x = 0.150$ (Figs. **3**, **6**). Fig. (**6**) shows the magnetic results of Pr-doping. For all the temperatures less than *110 K*, the

magnetization reaches the maximum around $x = 0.15$. For $x>0.150$, the superexchange (SE) interactions become dominant and increase with x increasing. As a further consequence, the magnetization undergoes an abrupt decreasing. The PM-FM phase transition is relatively sharp for $x = 0.100$ to 0.150. However, in compounds with $x>0.150$, the magnetic behavior is different. A second phase transition appears below Curie temperature and becomes clearly visible by increasing Pr-doping level.-dM/dT *vs* T curves (Fig. **4**) show two peaks for higher values of x ($x>0.150$). The first one, at $T = T_C$, is attributed to PM-FM phase transition. The second one, detected at T_{sg} (spin-glass temperature) around *90 K*, can be attributed to the competition between the ferromagnetic (FM) and the antiferromagnetic (AFM) interaction, leading to the appearance of an antiferromagnetic spin-glass state [29, 30]. This state becomes dominating for $x = 0.175$ and $x = 0.200$, which explains the decrease of the magnetization.
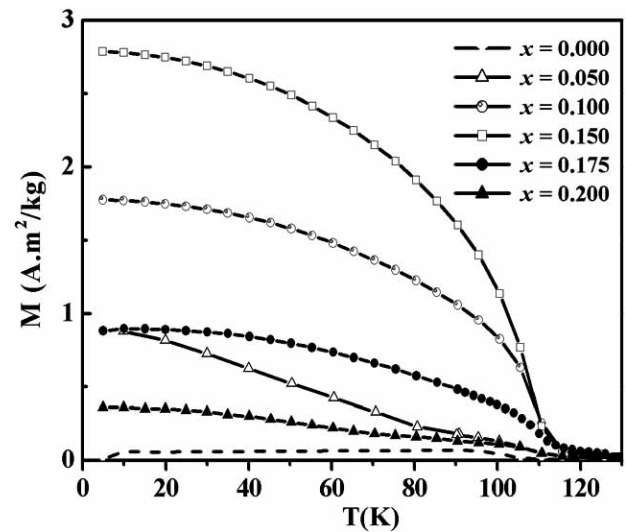

Fig. (3). Magnetization *vs* temperature for $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000$ to 0.200), at an applied magnetic field of 0.045 T.

c) Electrical Properties

From resistivity curves $\rho(T)$ (Fig. **7**), we can conclude that all samples present a semiconductor behaviour at high temperatures ($T>100$ K). On the other hand, at fixed temperatures (Fig. **8**), each $\rho(x)$ curve goes over a minimum at $x = x_{min}$ depending on the temperature. At low temperatures ($T<155$ K), the minimum of the resistivity (ρ_{min}) corresponds to $x_{min} = 0.15$. This result is in good agreement with that found for the magnetic study, which reveals that the maximum of the magnetization corresponds to $x = 0.15$. When the temperature increases, x_{min} shifts towards higher *x-values*. From Fig. (**7**), it can clearly be seen that $x_{min} = 0.175$ for the temperature range *155-210 K*, and $x_{min} = 0.2$ for higher temperatures ($T>210$ K). For $x<x_{min}$, the decrease of the resistivity with x increasing (Fig. **8**) can be explained by the increase of the transfer of electron between neighbouring Mn^{3+} and Mn^{4+} ions through the path $Mn-O-Mn$ indicating an amplification of the double-exchange (DE)
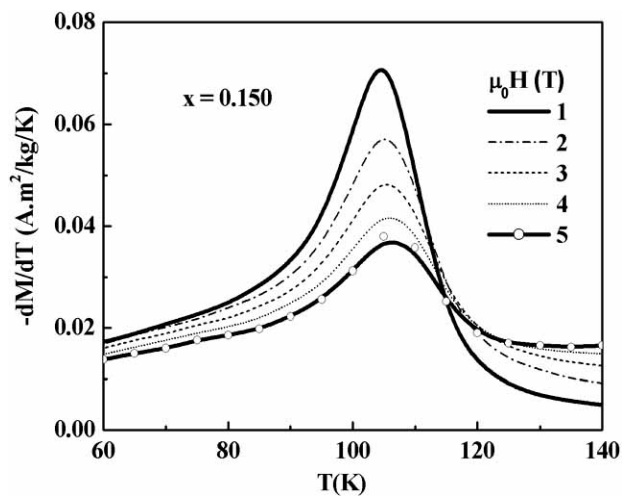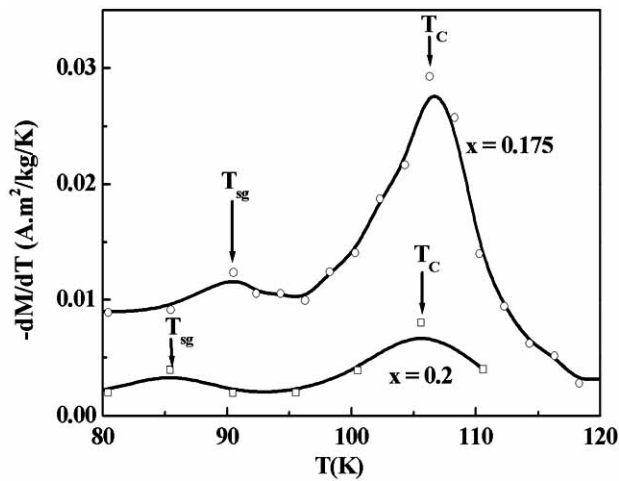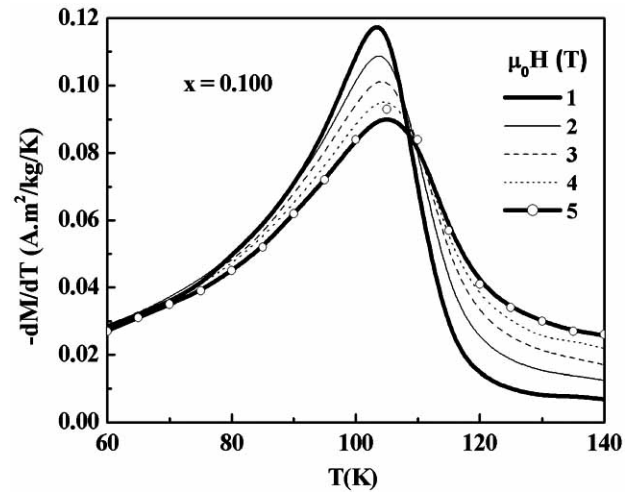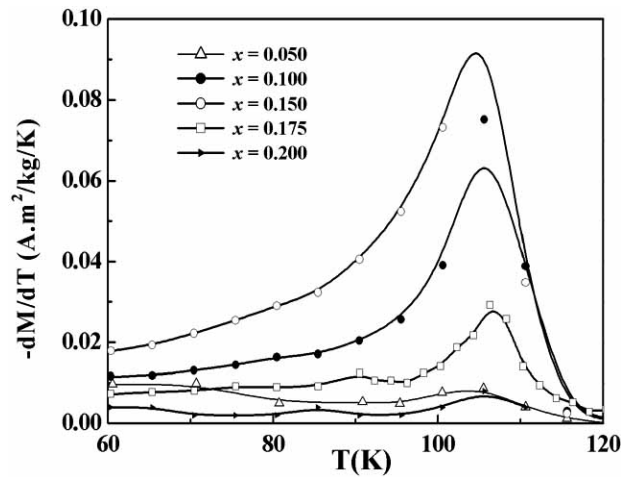
Fig. (4). Variation of (*-dM/dT*) as function of temperature *T* for *Ca₂₋ₓPrₓMnO₄* compounds (*x = 0.000, 0.100, 0.150, 0.175, 0.200*), at an applied magnetic field of *0.045 T*.

Fig. (5). Variation of (*-dM/dT*) as function of temperature *T* for *Ca₂₋ₓPrₓMnO₄* compounds (*x = 0.100* and *x = 0.150*), at different applied magnetic fields *μ₀H*.

mechanism. When *x* exceeds *x_min* (x>x_min), the local antiferromagnetic interactions, induced by the higher praseodymium concentration, become important and compete with the long-range ferromagnetism from the double exchange interactions between the Mn ions. So that, the increase of the Pr-doping level enhances the localization of the conduction electrons, witch explains the increase of resistivity. The increase in *x_min* and the decrease of the resistivity level with the temperature increasing, as it shown in isothermal curves (Fig. **8**), can be attributed to the increase of the vibration frequency which dominates the conductivity phenomenon at high temperatures.

4. CONCLUSIONS

Ca₂₋ₓPrₓMnO₄ compounds (*x = 0.000 to 0.2*00) were synthesized by a sol-gel method. X-ray diffraction peaks can be indexed in the tetragonal system for *I41/acd* space group for *x = 0.000* and in the orthorhombic system for *Aba2* space group, after doping with the praseodymium. The Curie temperature, *T_C*, is found to be around *105 K* for all samples. At low temperatures, the minimum of the resistivity corresponds to *x_min = 0.15*, which is in good agreement with
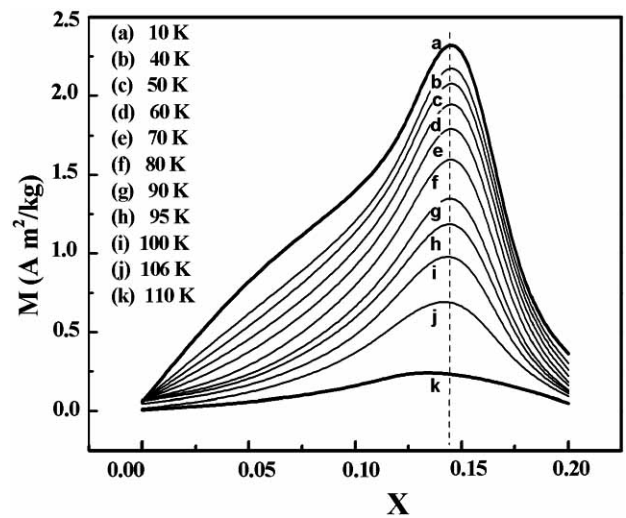

Fig. (6). Magnetization *vs x* for *Ca₂₋ₓPrₓMnO₄* compounds at low applied magnetic field (*0.045T*), at different temperatures.

that found for the magnetic study. For a temperatures range *155-210 K*, and for temperatures higher than *210 K*, $x_{min} = 0.175$ and 0.2, respectively. For low *x-values* $(x<x_{min})$, the increase of magnetization and the decrease of resistivity, can be explained by the importance of the double-exchange mechanism. For $x>x_{min}$, the antiferromagnetic interactions, become dominate and prevent the transfer of electrons between Mn^{3+} and Mn^{4+} ions, which reverses the variation senses of the magnetization and the resistivity.
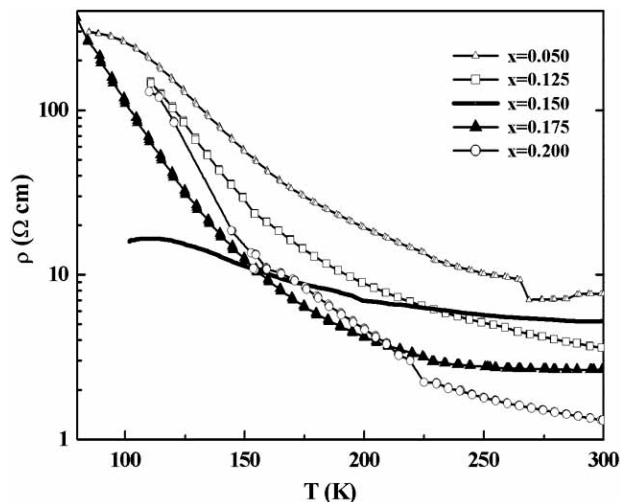

Fig. (7). Resistivity *vs* temperature without applied magnetic field for *Ca₂₋ₓPrₓMnO₄* compounds (*x = 0.050* to *0.200*).
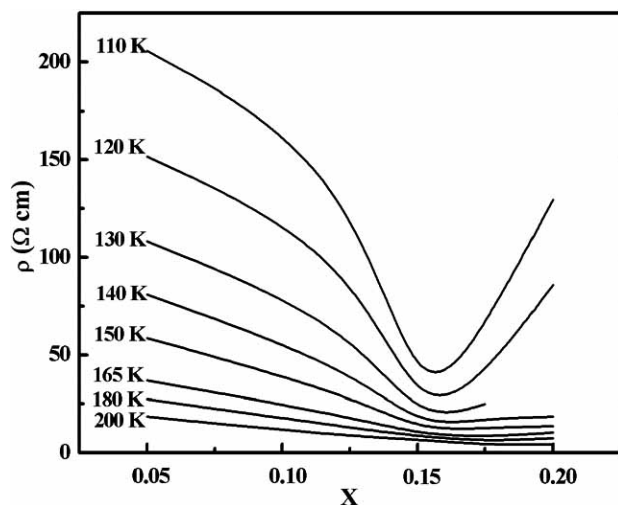

Fig. (8). Resistivity *vs* x for *Ca₂₋ₓPrₓMnO₄* compounds at different temperatures without applied magnetic field.

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