STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES IN Pr_{1-x}A_xMnO_3 (A = Ag, Na, Ag) PEROVSKITE

S. Zouari¹, A. Cheikh-Rouhou¹*, P. Strobel², M. Pernet², J. Pierre³

¹Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B. P. 802, 3018 Sfax, Tunisia
²Laboratoire de Cristallographie, CNRS, B. P. 166X, 38042 Grenoble, France
³Laboratoire Louis NEEL, CNRS, B. P. 166X, 38042 Grenoble, France
* Corresponding author. E-mail : Abdel.Cheikhrouhou@fss.rnu.tn
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Abstract
We studied structural, magnetic and electrical properties of perovskite type manganese oxides Pr_{0.9}Ag_{0.1}MnO_3 and Pr_{0.8}Na_{0.2}MnO_3. Samples have been elaborated by two different methods. Powder X-ray diffraction patterns have been indexed in an orthorhombic structure with Pbnm space group. Magnetic measurements show that magnetization and transition temperature depend on the substituted element.

Keywords : Perovskite; Manganite; Magnetization; Curie temperature.

1. Introduction
The perovskite manganese oxides R_{1-x}A_xMnO_3 where R is a trivalent rare-earth element and A is a divalent alkaline-earth element have been known many years ago [1-2]. These materials have attracted considerable attention recently owing to their colossal magnetoresistance (CMR) effects [3-6]. However, only few studies have been carried on alkali metal substitution elements such as Na or K [7-8]. Substitution of the rare-earth element by divalent or monovalent element or vacancy leads to a mixed valence manganese Mn^{3+} - Mn^{4+} responsible of the magnetic and electrical properties [9-10].

In this work, we studied structural, magnetic and electrical properties of Pr_{0.9}Ag_{0.1}MnO_3 and Pr_{0.8}Na_{0.2}MnO_3 perovskite compounds.

2. Experimental methods
Perovskite oxides Pr_{0.9}Ag_{0.1}MnO_3 and Pr_{0.8}Na_{0.2}MnO_3 have been prepared using the conventional solid state reaction by mixing: praseodymium oxide (Pr_6O_{11}), manganese oxide (MnO_2) and sodium carbonate (Na_2CO_3), or silver nitrate (AgNO_3) of 99.9 % purity. The starting materials are intimately mixed in an agate mortar and heated in air at 1150°C for 72 hours.

Our samples have been also prepared by the same conventional solid state reaction by mixing lacunar compounds Pr_{1-x}A_xMnO_3 with x = 0.1 and 0.2 and sodium carbonate or silver nitrate in excess according to the following reactions:

\[ \text{Pr}_{0.9}^{3+}\text{MnO}_3 + 0.1\text{AgNO}_3 \rightarrow \text{Pr}_{0.9}\text{Ag}_{0.1}\text{MnO}_3 + \delta \text{O}_2 + \delta' \text{N}_2 \]

or

\[ \text{Pr}_{0.8}^{3+}\text{MnO}_3 + 0.1\text{Na}_2\text{CO}_3 \rightarrow \text{Pr}_{0.8}\text{Na}_{0.2}\text{MnO}_3 + \delta \text{CO}_2 \]

and heated at 800°C for 2 days.

The lacunar compounds have been elaborated by the same conventional solid state reaction in stoichiometric proportion and heated at 1400°C.

X-ray powder diffraction data are collected at room temperature with a Siemens D5000 powder diffractometer system using CuK\(_\alpha\) radiation. Unit cell dimensions are obtained by least square calculations. Magnetization measurements versus temperature have been performed using a vibrating sample magnetometer in the temperature range 10-350K, with an applied field of 0.2T, whereas the electrical measurements have been performed by the standard four probe technique in the earth magnetic field.

3. Results and discussion
3.1 X-ray diffraction analysis

At room temperature, structural investigations show that lacunar Pr_{1-x}A_xMnO_3 and substituted Pr_{1-x}A_xMnO_3 (A = Ag, Na) x = 0.1 and 0.2 samples are single phase; however for the lacunar compound corresponding to x = 0.2, we observe the presence of diffraction peaks with very small intensities which can be attributed to traces of MnO_4^-

We show in figure 1, X-ray diffraction patterns of Pr_{0.9}Na_{0.2}MnO_3 elaborated by both methods.

Samples elaborated by both methods crystallized in a perovskite structure less distorted than the PrMnO_3 one.
3.2 Magnetic characterizations

Magnetization evolution versus applied field shows an increase of the saturated magnetization when temperature decreases. Our samples exhibit a ferromagnetic behavior at low temperatures (Figures 2a and 2b). The PrMnO₃ compound is antiferromagnetic. It is clear, that the substitution of praseodymium by a monovalent alkali metal Ag or Na, leading to a mixed valence Mn ions, gives rise to ferromagnetism. In fact the Mn⁺⁺⁻⁻ Mn⁺⁺ exchange in PrMnO₃ is antiferromagnetic, however, the Mn⁺⁺⁻⁻ Mn⁺⁺ exchange in the substituted samples is ferromagnetic. This exchanged is responsible of the ferromagnetic behavior at low temperatures.

Figure 2 shows that both Pr₀.₉Ag₀.₁MnO₃ samples do not saturated totally even for high applied fields indicating probably a spin canted state at low temperature, however, both Pr₀.₈Na₀.₂MnO₃ samples saturate more rapidly at low temperature. This result can be explained by the Mn⁺⁺amount more important in these samples which leads to an increase of the ferromagnetic double exchange in the Mn⁺⁺⁻⁻Mn⁺⁺ ions.

Assuming fixed valences for Pr(3⁺), A⁺ and stoichiometric O(2⁻), the calculated spin-only saturated magnetization for full alignment of the Mn spins as a function of x given by

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Space group</th>
<th>Cell parameters (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrMnO₃</td>
<td>Pbnm</td>
<td>5.4434 5.8004 7.5768</td>
<td>1.392</td>
<td>239.234</td>
</tr>
<tr>
<td>Pr₀.₉₋₀.₁MnO₃</td>
<td>Pbnm</td>
<td>5.4312 5.705 7.5921</td>
<td>1.398</td>
<td>235.224</td>
</tr>
<tr>
<td>Pr₀.₈₋₀.₂MnO₃</td>
<td>Pbnm</td>
<td>5.4321 5.7089 7.591</td>
<td>1.397</td>
<td>235.421</td>
</tr>
<tr>
<td>Pr₀.₈Na₀.₂MnO₃ (S)</td>
<td>Pbnm</td>
<td>5.4534 5.4644 7.7105</td>
<td>1.413</td>
<td>229.769</td>
</tr>
<tr>
<td>Pr₀.₈Na₀.₂MnO₃ (A)</td>
<td>Pbnm</td>
<td>5.4467 5.4393 7.6923</td>
<td>1.412</td>
<td>227.895</td>
</tr>
<tr>
<td>Pr₀.₉Ag₀.₁MnO₃ (S)</td>
<td>Pbnm</td>
<td>5.4502 5.6309 7.6423</td>
<td>1.402</td>
<td>234.538</td>
</tr>
<tr>
<td>Pr₀.₉Ag₀.₁MnO₃ (A)</td>
<td>Pbnm</td>
<td>5.4791 5.5156 7.7326</td>
<td>1.411</td>
<td>233.683</td>
</tr>
</tbody>
</table>

Table 1: Crystallographic data of Pr₁-xAxMnO₃ (A = Ag, Na and Ag) samples

S : samples prepared from precursors, A : samples prepared from lacunar compounds.

3.2 Magnetic characterizations

Magnetization evolution versus applied field shows an increase of the saturated magnetization when temperature decreases. Our samples exhibit a ferromagnetic behavior at low temperatures (Figures 2a and 2b). The PrMnO₃ compound is antiferromagnetic. It is clear, that the substitution of praseodymium by a monovalent alkali metal Ag or Na, leading to a mixed valence Mn ions, gives rise to ferromagnetism. In fact the Mn⁺⁺⁻⁻ Mn⁺⁺ exchange in PrMnO₃ is antiferromagnetic, however, the Mn⁺⁺⁻⁻ Mn⁺⁺ exchange in the substituted samples is ferromagnetic. This exchanged is responsible of the ferromagnetic behavior at low temperatures.

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Assuming fixed valences for Pr(3⁺), A⁺ and stoichiometric O(2⁻), the calculated spin-only saturated magnetization for full alignment of the Mn spins as a function of x given by

Mₘₙₙ (µₜ / Mn.atom) = 2×[3/2×2x + 4/2×(1−2x)]µₜ

(µₜ) is found to be equal to 3.8 µₜ/Mn.atom for x = 0.1 and 3.6 µₜ/Mn.atom for x = 0.2.
At low temperature and in an applied field of 8T, Pr$_{0.8}$Na$_{0.2}$MnO$_3$ elaborated using precursors seems to have full alignment of the Mn spins; however, for Pr$_{0.9}$Ag$_{0.1}$MnO$_3$ sample, the measured magnetization at low temperature and in an applied field of 8T is smaller than the calculated one. This result seems to confirm the spin canted state at low temperature in this compound. In figure 3, we have plotted the magnetization evolution as a function of temperature (M vs T) measured in an applied field of 0.2T. These curves show that the transition temperature, determined from the inflection point of the M vs T curves, does not depend on the elaborating method. In the paramagnetic phase, the temperature dependence of the magnetic susceptibility follows the Curie Weiss law. The Curie Weiss constants C and Curie temperatures $T_c$ are given in Table 2.

### Table 2: Magnetic data of Pr$_{1-x}$A$_x$MnO$_3$ (A = Na and Ag) samples.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_c$ (K)</th>
<th>C ($\mu_B$/T/Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$<em>{0.8}$Na$</em>{0.2}$MnO$_3$ (S)</td>
<td>135</td>
<td>7.892</td>
</tr>
<tr>
<td>Pr$<em>{0.8}$Na$</em>{0.2}$MnO$_3$ (A)</td>
<td>135</td>
<td>7.543</td>
</tr>
<tr>
<td>Pr$<em>{0.9}$Ag$</em>{0.1}$MnO$_3$ (S)</td>
<td>110</td>
<td>9.123</td>
</tr>
<tr>
<td>Pr$<em>{0.9}$Ag$</em>{0.1}$MnO$_3$ (A)</td>
<td>130</td>
<td>8.951</td>
</tr>
</tbody>
</table>

The Curie constants result from the addition of Mn and Pr contributions; experimental values are larger than the theoretical ones, as often observed due to polaronic effects. These effects are more and more pronounced as the temperature approaches $T_c$.

#### 3.3 Electrical resistivity

 Resistivity measurements have been performed on Pr$_{0.8}$Na$_{0.2}$MnO$_3$ samples prepared from precursors. We plot in figure 1 the temperature dependence of the resistivity registered in earth magnetic field. This curve shows an insulating behavior in the whole range.
4. Conclusion

Alkali (Na, Ag) substituted praseodymium manganese oxides have been elaborated by two methods.

Crystallographic study shows that all samples crystallize in the orthorhombic system with Pbnm space group.

Magnetic measurements show that magnetization and transition temperature depend on the Mn$^{4+}$ content and also on the nature of the substituted element. Our synthesized samples exhibit at low temperature a ferromagnetic behavior for Pr$_{0.8}$Na$_{0.2}$MnO$_3$ and a spin canted state for Pr$_{0.9}$Ag$_{0.1}$MnO$_3$.

Electrical properties for the sample Pr$_{0.8}$Na$_{0.2}$MnO$_3$ elaborated using precursors show an insulating behavior.

References