# STRUCTURAL AND MAGNETIC STUDY
# OF PEROVSKITE MANGANITES OXIDES $Pr_{1-x}\square_xMnO_3$

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**Abstract**

Structural and magnetic properties in a self doped $Pr_{1-x}\square_xMnO_3$ system are investigated. X-ray diffraction patterns show that samples with composition range 0.0-0.3 crystallize in orthorhombic perovskite structure with Pbnm space group. Our samples exhibit an antiferromagnetic behavior at low temperature. The temperature ordering as a function of the vacancy content remains constant, however the magnetization magnitude at low temperature (T = 10 K) increases with increasing deficiency content.

## 1. Introduction

The discovery of giant magnetoresistance (GMR) properties in manganese oxides $Ln_{1-x}A_xMnO_3$, where Ln is a trivalent rare earth element and A is a divalent one, has attracted great attention with regard to scientific study and technological applications [1-4]. Oxides with general formula $RMnO_3$ where R is a rare earth from $La^{3+}$ to $Dy^{3+}$, belong to the group of orthorhombically distorted perovskites. Structural and magnetic properties of one of these compounds, namely $PrMnO_3$, have been studied previously by several authors. Quesel–Ambrunaz [5] determined its crystallographic structure and found by neutron diffraction analysis, an antiferromagnetic ordering of the Ay-layer type below 91K. Divalent element substitution effects on $PrMnO_3$ manganite had been extensively studied [6-8]. However there are no several studies on lacunar praseodymium samples.

We are interested in studying the praseodymium deficiency $Pr_{1-x}\square_xMnO_3$ perovskite manganite samples, we therefore carried out X-ray diffraction and magnetic analysis on bulk ceramic samples $Pr_{1-x}\square_xMnO_3$. The praseodymium deficiency results in internal doping of the system without need for divalent or monovalent ions substitution. Deficiency produces a mixed $Mn^{3+}/Mn^{4+}$ valence similar to that in substituted compounds.

## 2. Experimental procedures

Powder $Pr_{1-x}\square_xMnO_3$ (x=0.0-0.3) samples were synthesized by the classical solid state reaction, starting from stoichiometric mixtures of $Pr_6O_{11}$ and $Mn_2O_3$ of 99.9% purity in adequate proportions according to the reaction:

$(1-x) Pr_6O_{11} + 3 Mn_2O_3 \rightarrow 6 Pr_{1-x}\square_xMnO_3 + \delta CO_2$.
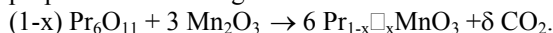
The starting materials were intimately mixed in an agate mortar and heated in air at 900°C for 72 hours. Firing at 1000 °C for 4 periods of 10-15h was done, interrupted by intensive grinding. To ensure complete reaction, a high temperature ceramic route was systematically used. The resulting powders were pressed into pellets (of about 1 mm thickness) and sintered at 1400°C in air for 48 hours with several grinding and repelling periods. Finally these pellets were rapidly quenched in water at room temperature. Phase purity and homogeneity were characterized by powder X-ray diffraction at room temperature (Diffractometer using $CuK\alpha1$ radiation and Si powder as internal standard). Unit cell dimensions were obtained by least-squares calculations. Magnetization measurements versus temperature were recorded with a vibrating sample magnetometer in the temperature range 10 - 340 K, using an applied field of 500 Oe.

## 3. Results and discussion
### 3.1. X-ray diffraction analysis

Vacancies at the praseodymium sites imply partial conversion of $Mn^{3+}$ to $Mn^{4+}$. Such compounds represent a self-doping system.

X-ray analysis of all powder samples were characteristic of single phases, however for $0.25 < x < 0.3$ traces of a second $Mn_3O_4$ phase could be identified.

At room temperature, structural investigations showed that all the obtained samples have a distorted perovskite structure. We listed in Table 1, crystallographic data for all samples. X-ray diffraction patterns of samples could be indexed in an orthorhombic perovskite phase strongly distorted.

We plotted in Fig. 1 the unit cell evolution as a function of the vacancy content. This curve showed a decrease of the unit cell volume as x increases. This decrease can be explained by the oxidation of a part of $Mn^{3+}$ cations to $Mn^{4+}$ ones as a function of the vacancy substitution. In fact, the $Mn^{4+}$ ionic radius (0.68Å) is smaller than that of $Mn^{3+}$ (0.785 Å) [9].

All samples present a ratio $c/a < \sqrt{2}$ characteristic of a cooperative Jahn-Teller deformation. The $PrMnO_3$ sample is more distorted than the deficiency samples (this sample have the highest b/a ratio). The strong orthorhombic distortion of the $PrMnO_3$ structure is due to the cooperative coupling of the $Mn^{3+}O_6$ Jahn-Teller distorted octahedral B sites. This long-range coupling is destroyed by the $Mn^{4+}$ content increase. In fact the Jahn-Teller distortion qualified by b/a ratio decreases when the vacancy content increases.
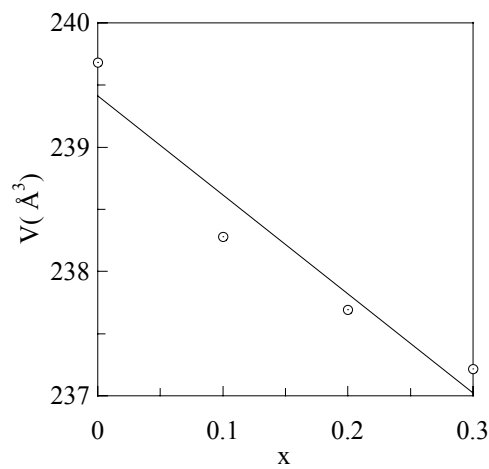


**Figure 1**: Unit cell volume evolution as a function of the vacancy content for $Pr_{1-x}\square_x MnO_3$ samples.

| (x) | Crystal structure | Lattice parameters (Å) | V (Å³) | c/a | b/a |
|-----|-----|-----|-----|-----|-----|
| 0.0 | O | a = 5.4451<br>b = 5.8051<br>c = 7.5826 | 239.68 | 1.3925 | 1.066 |
| 0.1 | O | a = 5.4419<br>b = 5.7687<br>c = 7.5903 | 238.28 | 1.3948 | 1.0600 |
| 0.2 | O | a = 5.4411<br>b = 5.7517<br>c = 7.5951 | 237.69 | 1.3959 | 1.0571 |
| 0.3 | O | a = 5.4305<br>b = 5.744<br>c = 7.605 | 237.22 | 1.3980 | 1.0559 |

**Table 1** : crystallographic data of $Pr_{1-x}\square_x MnO_3$ samples. The unit cell volume is given for four formula units, corresponding to the orthorhombic unit cell.

### 3.2. Magnetic properties

In Fig. 2 was plotted the magnetization evolution versus temperature in a magnetic applied field of 500 Oe for the $Pr_{1-x}\square_x MnO_3$ system.

The $PrMnO_3$ sample has an antiferromagnetic structure with $T_N = 110$ K and a magnetization at T=10 K equal to 0.066 $\mu_B$/mole. The M(T) curves show that our lacunar samples exhibit a paramagnetic to an ordered state with decreasing temperature. The increase of the magnetization with increasing praseodymium deficiency can be explained by the existence of a ferromagnetic component du to an antiferromagnetic spin canted state. Using the maximum slope of the curves M-T as a criterion to determine $T_N$, we remark that the Neel temperature $T_N$ remains constant as a function of the vacancy content. As the praseodymium vacancy leads to a mixed valence $Mn^{3+}/Mn^{4+}$, the ferromagnetic coupling between $Mn^{4+}$ and $Mn^{3+}$ cations on the B sites, called as "double exchange coupling" [10,11], is responsible for the increase in magnetization at low temperature in our samples.
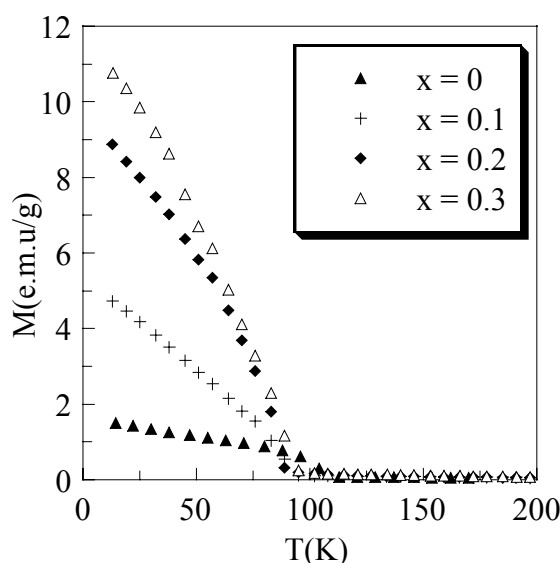


**Figure 2 :** Magnetization of $Pr_{1-x}\square_x MnO_3$ versus temperature at H = 500 Oe.

### 4. Conclusion

The present study was restricted to self-doping samples sintered at high temperature rapidly quenched in water. We characterized all samples by X-ray diffraction and we investigated the magnetic properties. Our study shows, a decrease of the unit cell volume and therefore an increase in the magnitude of the magnetization at low temperature. The decrease of unit cell volume and the magnetic behavior is considered to be correlated to the increase in the $Mn^{4+}$ content and consequently to the double exchange coupling.

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