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## LETTER TO THE EDITOR

**Effect of oxygen content on the magnetic and transport properties of  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\gamma}$** 

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**Abstract.** It is shown that oxidized  $\text{La}_{0.5}\text{Sr}_{0.5}(\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{4+})\text{O}_3$  and reduced  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{Mn}^{3+}\text{O}_{2.75}$  samples show similar magnetic and magnetoresistive properties. Both compounds, characterized by  $T_C \approx 320$  K, exhibit a ferromagnetic–antiferromagnetic transition around 200 K, where a large magnetoresistance develops. However, the reduced sample has a much larger resistivity than the oxidized one. These data suggest that some of the intriguing properties of the manganites can also be realized without mixed manganese valences.

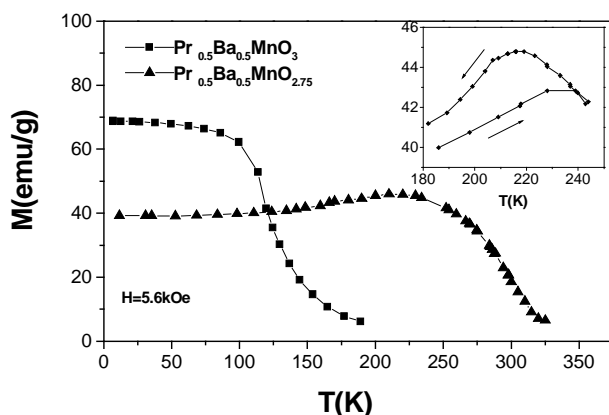
The properties of  $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ ) have been the subject of a number of previous studies [1–4]. It has been established that these manganites show a first-order phase transition around  $T \sim 180$  K, associated with a ferromagnetic–antiferromagnetic transition. The Curie point decreases slightly from 320 K ( $\text{Ln} = \text{La}$ ) down to 250 K ( $\text{Ln} = \text{Nd}$ ) with decreasing lanthanide ionic radii. For  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  the antiferromagnetic–ferromagnetic transition develops simultaneously with charge ordering [4].

The magnetic properties of  $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  are much less studied. It is known that  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  is a ferromagnet with  $T_C$  close to 340 K [5]. According to [6]  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  has a Curie point of 120 K. However, the spontaneous magnetic moment is lower than expected for a collinear ferromagnet. These compounds do not show the antiferromagnetic–ferromagnetic and charge order–disorder transition. In this paper we report on the magnetization and magnetotransport properties for both oxidized and reduced  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\gamma}$  polycrystalline samples and compare them with the properties of oxidized polycrystalline  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ .

The oxidized samples were obtained from a mixture of  $\text{Ln}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{BaCO}_3$  or  $\text{SrCO}_3$  taken in stoichiometric ratios. The synthesis was performed in air at  $T = 1540$  °C. After synthesis the samples were held for 24 h at 900 °C, followed by cooling to room temperature at a rate of  $100$  °C  $\text{h}^{-1}$ . The reduction was made in flowing argon at  $T = 1100$  °C. In order to reach the effective reduction the samples were put under carbon crucible.

The oxygen loss during reduction was determined from the difference between the starting and the final weight of the sample, assuming that the sample was stoichiometric before this procedure was begun.

X-ray powder diffraction patterns have confirmed a single phase with a pseudocubic structure ( $a = 3.895$  Å; lattice volume  $V = 59.079$  Å<sup>3</sup>) for  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  and a tetragonal structure ( $a = 3.881$  Å;  $c = 3.847$  Å;  $V = 57.954$  Å<sup>3</sup>) for  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . According to



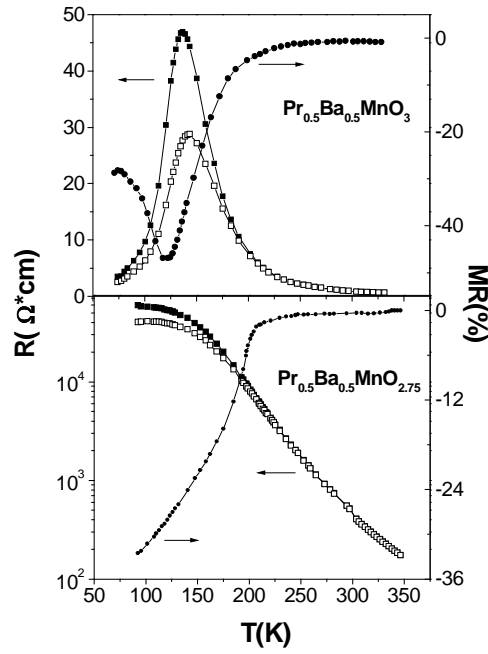
**Figure 1.** Magnetization as a function of temperature for  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\gamma}$ . The inset shows temperature hysteresis of the magnetization for  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$ .

x-ray diffraction data the reduced sample has a tetragonal crystal lattice with  $a = 3.905 \text{ \AA}$ ,  $c = 3.881 \text{ \AA}$  and  $V = 59.174 \text{ \AA}^3$ .

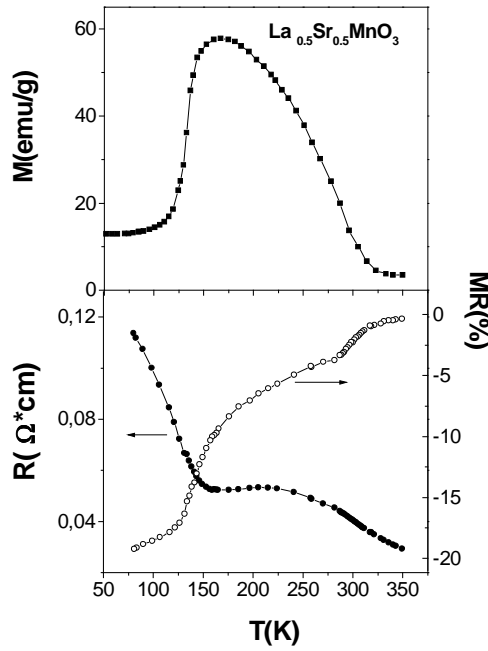
The magnetic moment was measured using a vibrational sample magnetometer. Figure 1 shows the temperature behaviour of the magnetic moment of the oxidized  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  sample. The magnetic moment  $3\mu_B$  as calculated from the magnetization value is slightly lower than expected in the case of parallel orientation of  $\mu(\text{Mn}^{3+}) \approx 4\mu_B$  and  $\mu(\text{Mn}^{4+}) \approx 3\mu_B$ . One can speculate that some domains of the sample are antiferromagnetic because the boundary of the concentrational ferromagnetic–antiferromagnetic transition in the  $\text{Ln}_{1-x}\text{Ba}_x\text{MnO}_3$  series is very close to  $x = 0.5$  [6]. Surprisingly, the Curie point  $T_C = 125 \text{ K}$  is much lower than that of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  ( $T_C = 340 \text{ K}$ ). Close to the Curie point a resistivity drop was observed (figure 2); however, the resistivity remains relatively high down to  $77 \text{ K}$ . The magnetoresistance, defined as  $\{[\rho(H = 9\text{kOe}) - \rho(H = 0)]/\rho(H = 0)\} * 100\%$  reaches its maximal magnitude, 50%, at  $T = 120 \text{ K}$ .

Figure 1 also shows the results obtained for a sample of  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$ . This compound has a spontaneous magnetization which is smaller than that of the oxidized sample; however, the Curie point reaches  $320 \text{ K}$ . Around  $200 \text{ K}$  we observe an anomalous behaviour of the magnetization as well as a large temperature hysteresis. These features indicate a first-order phase transition. The relatively low magnetic moment may be attributed to a canted magnetic state or to a mixture of two magnetic phases. In the last case some part of the sample would be ferromagnetic, whereas another part would be antiferromagnetic. It is difficult to distinguish these possibilities on the basis of magnetization data only. However, NMR experiments for quite a few manganites have been interpreted in terms of a mixture of magnetic states [7]. Neutron diffraction [8] and HREM results [9] also support this point of view. Thus, we assume that our  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\gamma}$  samples are also magnetically inhomogeneous. Around  $200 \text{ K}$  in some domains of the  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$  sample a transition from the ferromagnetic state into the antiferromagnetic state might occur.

It is interesting to note that our oxidized polycrystalline sample  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  exhibits similar magnetic and magnetoresistive properties. This sample is ferromagnetically ordered at  $320 \text{ K}$ , whereas at  $180 \text{ K}$  a ferromagnetic–antiferromagnetic transition occurs (figure 3). This sample also does not show any transition into the metallic state. A large magnetoresistance develops below the temperature of the ferromagnetic–antiferromagnetic transition, similar to the  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$  sample.



**Figure 2.** Resistivity and magnetoresistance as a function of temperature for  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$  (upper panel) and  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$  (lower panel).



**Figure 3.** Magnetization (upper panel), resistivity and magnetoresistance (lower panel) for  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  as a function of temperature.

We tried to convert  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$  into its oxidized form by heating in air. Surprisingly this compound is stable in air up to 1100 °C. The oxidized form, however, can be achieved by annealing at 1250 °C for 3 h. This compound exhibits properties similar to those of the oxidized sample presented in figure 1. The reasons for this behaviour are not clear at present, in particular if one takes into account that annealing at moderate temperatures ( $T < 1000$  °C) improves the sharpness of the antiferromagnetic–ferromagnetic transition without appreciable changes in the conductivity.

The magnetic and transport properties of the manganites are usually explained in the framework of a double exchange mechanism, where ferromagnetic ordering results from electron hopping between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions [10]. However, superexchange interactions between  $\text{Mn}^{3+}\text{--O--Mn}^{3+}$  are also ferromagnetic when static Jahn–Teller distortions are removed [11]. For example, stoichiometric  $\text{LaMnO}_3$  above 700 K shows a magnetic susceptibility which indicates ferromagnetic ordering at  $T_C = 160$  K [11].  $\text{La}_{0.7}\text{Ba}_{0.3}(\text{Mn}_{0.85}^{3+}\text{Nb}_{0.15}^{5+})\text{O}_3$  also exhibits ferromagnetic properties [12]. Some ferromagnetic compounds without  $\text{Mn}^{4+}$  ions have been created under high pressure conditions [13]. Unusual magnetic behaviour has been observed in the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_{3-\gamma}$  manganite [14]. It was established that as the oxygen content is decreased, this compound undergoes a sequence of transitions from an antiferromagnetic to a ferromagnetic state ( $\gamma \geq 0.04$ ), from the ferromagnetic to a spin-glass state ( $\gamma \geq 0.14$ ), and from the spin-glass to an inhomogeneous ferromagnetic state ( $\gamma \geq 0.25$ ). However, reduced manganites usually exhibit spin-glass or antiferromagnetic properties [15]. Such behaviour is associated with a change of sign of superexchange interaction  $\text{Mn}^{3+}\text{--O--Mn}^{3+}$  from positive to negative because in the case of five-fold coordination (around oxygen vacancies) this interaction becomes antiferromagnetic [16]. This consideration leads us to assume that the manganese coordination is close to six in the new  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$  compound. Certainly, in the future it is necessary to undertake a structural study to verify the eventual crystal structure peculiarities of  $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.75}$ .

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