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Synthesis and magnetic properties of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$

N. Balchev[1], **B. Kunev**[2], **J. Pirov**[3], **A. Souleva**[4], **K. Nenkov**[5,6]

[1]Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

[2]Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

[3]Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

[4]University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

[5]Institut fur Festkorper- und Werkstofforschung, 01171 Dresden, Germany

[6]International Laboratory of High Magnetic Fields and Low Temperatures, 53-421 Wroclaw, Poland

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Abstract. Polycrystalline samples with nominal compositions of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ were synthesized and their magnetical properties were investigated. It was shown that $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ has an AFM state accompanied by a weak FM. The $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ material has a PM-FM transition beginning at $T_c \approx 325$ K and a FM-AFM one – at about 160 K. The low magnetization values, field and temperature dependence of the magnetization suggest a phase separation of an anomalous FM state and AFM state far below the FM-AFM transition.

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1 Introduction

The discovery of the High-T_c superconductivity [1] was followed by an increased interest towards the materials with colossal magnetoresistance (CMR) [2-4]. The interplay of structural, magnetic and transport properties in the two classes of materials is due to their common structure–the oxygen-deficient perovskite $ABO_{3-\delta}$. If B=Cu, various cuprate materials could be found, including the Bednorz and Muller superconductor. The general formula of the manganites with CMR can be obtained if B=Mn. The A-site substitution in $ABO_{3-\delta}$ mainly influences the carrier density and lattice distortion. The B (Mn)-site substitution introduces interesting interactions between Mn ions and the substituted cations. Various cations were used to investigate the Mn-site substitution. In the case of nonmagnetic elements, it was suggested that their valence and size governed the change of the magnetic phases [5-9]. Cu(II) and Mn(III) are called strong Jahn-Teller ions with an antiferromagnetic (AFM) and ferromagnetic (FM) ordering respectively [3]. The investigation of the Cu-doped manganites could elucidate the result of the interaction of strong Jahn-Teller ions. The authors of [10-12] examined $La_{2/3}Ca_{1/3}MnO_3$ samples doped with up to 5% Cu and found a sharp drop in resistivity and large decrease of the insulator-metal (IM) transition temperature. Several authors investigated the Ru substitution in the manganites but high doping levels were not achieved [8,9]. The lightly doped with Ru samples have an extended metallic FM phase and an increased T_c [8]. The purpose of the present work is to synthesize highly doped with Cu or Ru samples with nominal compositions of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ and to investigate their magnetic properties.

2 Results and Discussion

The investigated samples with nominal compositions of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ were prepared by a solid state reaction from starting materials MnO_2, $SrCO_3$, Pr_6O_{11}, CuO and Ru with a purity of 99.9%. They were mixed, homogenized and heated at 980°C for 20 h. After that they were homogenized, pressed into pellets and sintered at 1100-1150°C for 60-70 hours in air with intermediate regrinding, then slowly cooled down to 800°C and quenched to room temperature. X-ray diffraction (XRD) at room temperature was used to examine the samples using a TUR-M62 diffractometer and CoK_α radiation. An EDX on SEM analysis was performed on the pellets using a SEM-505 Philips microscope combined with an EDAX 9100 device. The susceptibility and magnetization of the samples were measured using a Lake Shore 7000 Series AC susceptometer-DC magnetometer at a frequency of 133 Hz and $H_{AC} = 1$ Oe.

Figure 1a shows the XRD pattern of a $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ sample. It may be seen in the figure that the sample is XRD single phased and the peaks can be indexed according to an orthorhombic structure, space group Pnma. The calculated lattice parameters are $a = 5.536$ $\AA$, $b = 7.664$ $\AA$ and $c = 5.412$ $\AA$. For comparison, the $Pr_{0.5}Ca_{0.09}Sr_{0.41}MnO_3$ compound has lattice parameters $a = 5.431$ $\AA$, $b = 7.625$ $\AA$ and $c = 5.472$ $\AA$ [13]. According to the EDX analysis, the chemical composition of the $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ sample is $Pr_{0.51}Sr_{0.46}Mn_{0.47}Cu_{0.56}O_3$. This result is obtained by comparing the theoretical values of the elements in the stoichiometric compound with the experimental ones. Figure 2 shows the $\chi'(T)$ dependences (FC at $H = 0$ and $H = 0.05$ T) of the $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ sample. It may be seen the presence of a broad transition ending at about 295 K and an increase of χ' at low temperatures.

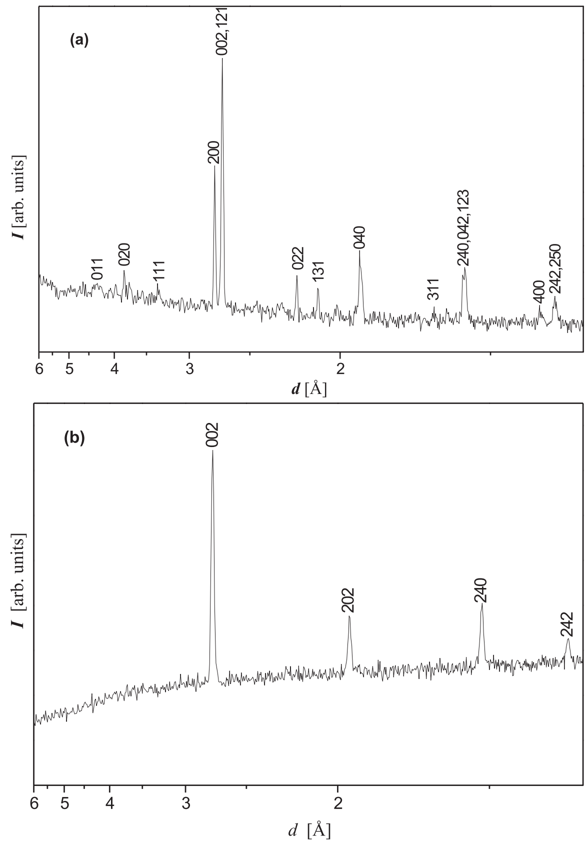

Figure 1. Room temperature XRD patterns of: (a) $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$; and (b) $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$.

A similar behaviour have $CoSr_2YCu_2O_z$ [14] and the multilayered manganites [15,16]. The high transition-end temperature is probably related to the Goldschmidt tolerance factor of the Cu-doped system. At low temperatures the FC curve is weakly affected by the magnetic field. Figure 3 shows the temperature dependences of the ZFC and FC magnetizations at $H = 100$ Oe. The two curves deviate as in [17] but the irreversibility is weak and no low temperature maximum is observed. The dependences of the magnetization $M\ vs\ H$ at 5 and 295 K are shown in Figure 4. The curve at 5 K is linear above about 5 T and shows a hysteresis at lower fields. This behaviour is different from that of the long-range ordered Ca_3CuMnO_6 [18] and the spin-glass $(Tb,La)_{2/3}Ca_{1/3}MnO_3$ [17]. The former shows a linearity of $M(H)$ at low fields and no hysteresis at all the fields used and the latter does not display any linearity and saturation. The presence of a hysteresis and linearity in the $M(H)$ curve at 5 K is indicative

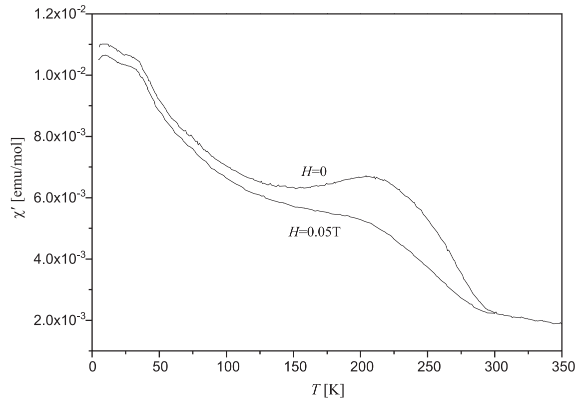

Figure 2. $\chi'(T)$ dependence (FC at $H = 0$ and 0.05 T) of the $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ sample. $H_{AC} = 1$ Oe.

for an AFM state accompanied by a weak FM (Jirak *et al.* [13] pointed out that the persistence of FM at low temperatures is not unusual in the Sr-rich manganites). Figure 5 shows the $\chi^{-1}(T)$ dependence, where $\chi = (\chi'^2 + \chi''^2)^{1/2}$. The obtained Curie-Weiss temperature Θ using the relation $\chi = C/(T - \Theta)$ is negative. The negative value of Θ shows a dominance of AFM interactions. From the slope of the straight line in Figure 6 the experimental value of the Curie-Weiss constant is estimated: $C_{exp} = 1.84$ emu K/mol. This value is close to the theoretical one of 1.92, which corresponds to the presence of Pr^{3+}, Cu^{2+} and Mn^{4+} ions in the system.

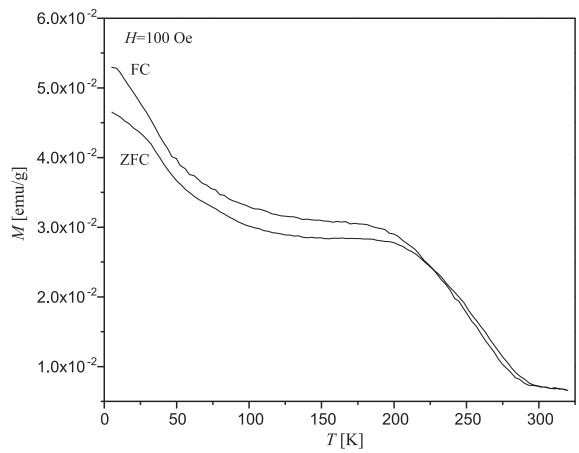

Figure 3. ZFC and FC magnetization curves at $H = 100$ Oe.

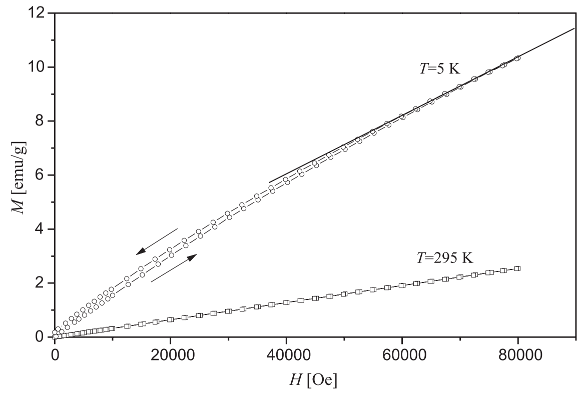

Figure 4. $M(H)$ dependence of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ at 5 K and 295 K.

In order to enhance the FM in the system, Ru was used instead of Cu. The XRD analysis showed that the obtained $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ sample is single phase and the peaks can be indexed according to a tetragonal structure. The lattice parameters are $a = c = 5.508$ Å and $b = 7.273$ Å (Figure 1b). The EDX analysis denoted a chemical composition of $Pr_{0.49}Sr_{0.47}Mn_{0.48}Ru_{0.54}O_3$. The investigated microcrystals have an average size below 1 μm and different orientations. Figure 6 shows the $\chi'(T)$ dependence of this material. It may be seen that the curve has a broad PM-FM transition from about 325 K to about 160 K and a second FM-AFM one from 160 K with a step around 60 K. The PM-FM transition begins at $T_c \approx 325$ K. To our knowledge, the obtained value of T_c is the highest reported in the Pr-containing manganites. The maximum of $T_c = 360$ K is achieved for rhombohedral $La_{0.5}Sr_{0.5}MnO_3$ [13]. Figure 7

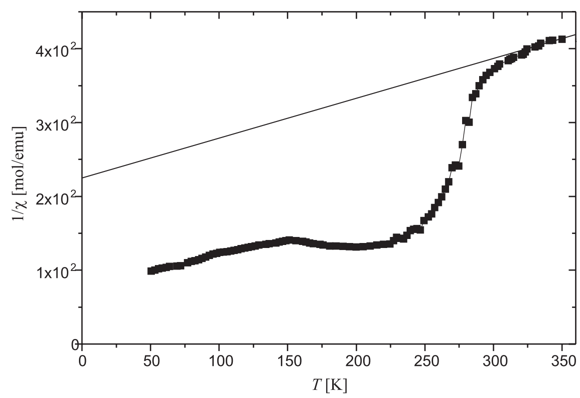

Figure 5. $\chi^{-1}(T)$ dependence of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ at $H = 0$.

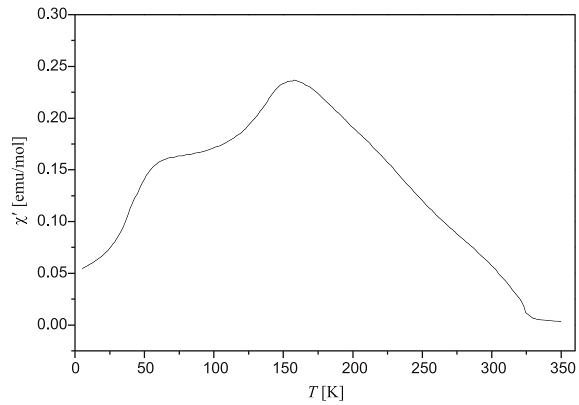

Figure 6. Dependence of χ' on T for the $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ sample at $H = 0$.

shows the temperature dependence of the magnetization at $H = 5$ T. It may be seen that the curve is similar to that obtained by Kim *et al.* [8]. In Figure 8 we show the field dependence of the magnetization of the Ru-doped sample at 5 and 295 K. The curve at 5 K has an increase, bending and wide hysteresis at low fields but also a linearity and lack of saturation at higher fields. These features show the presence of a FM state far below the FM-AFM transition. A similar phenomenon is observed in polycrystalline $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ [19] and is called phase separation. The evaluated magnetic moment at 5 K is 1.1 μ_B. This value is far below the theoretical one (about 3 μ_B) and shows that the observed

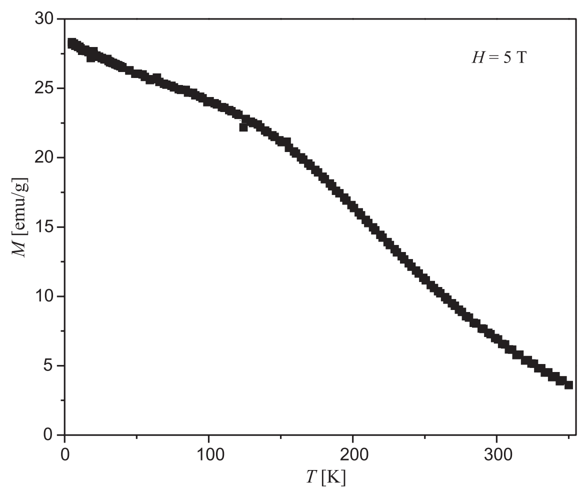

Figure 7. $M(T)$ dependence of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ at $H = 5$ T.

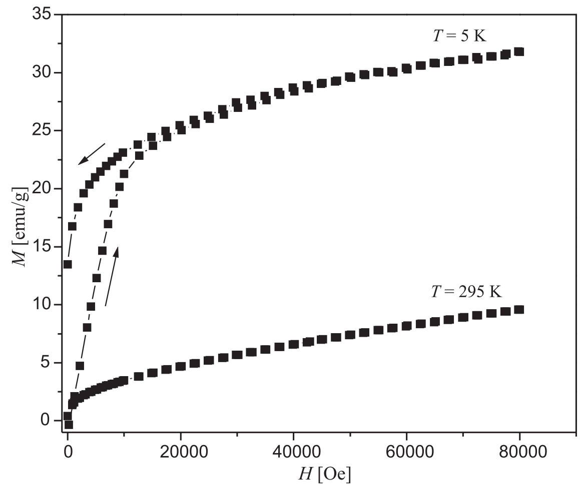

Figure 8. $M(H)$ dependence at 5 and 295 K of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$.

FM state is not a conventional one. The low magnetic moment, broadness of the M(T) dependence and the two maxima in the $\chi'(T)$ dependence suggest a phase separation between an anomalous FM state and AFM state, as in the case of $Sm_{0.2}Ca_{0.8}Mn_{1-y}Ru_yO_3$ [20]. This anomaly is due to the fact that with the increase of the Ru content T_c increases but the homogeneity of the Ru distribution in the matrix decreases for y values above 0.12-0.15. Therefore the highly doping with Ru increases the T_c but does not induce a metallic FM in the system.

3 Conclusion

Polycrystalline single phased samples with nominal compositions of $Pr_{0.5}Sr_{0.5}Mn_{0.5}Cu_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ were synthesized by a solid state reaction in air and their magnetic properties were investigated. The presence of linearity and hysteresis in the M(H) dependency show that the highly doped with Cu manganite has an AFM state accompanied by a weak FM. The magnetic moment of the Mn ions was estimated to be close to that of Mn^{4+}. The $Pr_{0.5}Sr_{0.5}Mn_{0.5}Ru_{0.5}O_3$ material has a PM-FM transition beginning at $T_c \approx 325$ K and a FM-AFM one – at about 160 K. The low magnetization values, field and temperature dependence of the magnetization suggest a phase separation of an anomalous FM state and AFM state far below the FM-AFM transition.

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