Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2010, 2(2): 94-100
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Magnetic and magneto transport properties of $Pr_{0.7}Sr_{0.3}MnO_3$ synthesized by an improved chemical coprecipitation method

Umesh Chand[*] and G. D. Varma

Department of Physics, Indian Institute of Technology Roorkee, Uttarakhand, India

---

Abstract

In the present work, $Pr_{0.7}Sr_{0.3}MnO_3$ particles were prepared by improved chemical coprecipitation method. Structural properties of as prepared sample were investigated using x-ray diffraction and field emission scanning electron microscopy. The analysis of the structure and surface morphologies shows that the sample is in single-phase with the space group of R □3C and grain sizes are distributed between 1.5 to 2.0μm. The composition of $Pr_{0.7}Sr_{0.3}MnO_3$ sample was confirmed by energy-dispersive spectroscopy. FTIR spectrum also demonstrate that PSMO particle have formed at $800^{O}C$. The magnetization measurements were done using SQUID magnetometer, which shows a reduction in magnetization with temperature. The paramagnetic-ferromagnetic (PM-FM) transition temperature (T_C) was appeared at 203K. Resistivity as a function of temperature was measured by a standard four-probe method by using Keithley instruments without or with magnetic fields (0-1T).It has been found that the low-field MR is enhanced owing to tunneling between the large and small $Pr_{0.7}Sr_{0.3}MnO_3$ grains.

Keywords: Magnetoresistance, electrical transport, grain boundary, perovskite material.

INTRODUCTION

Colossal magnetoresistive (CMR) materials, which have a general formula of $R_{1-x}A_xMnO_3$ where R is a rare earth ion like La, Pr etc and A is an alkaline earth ion like Sr, Ca etc., show a huge change in resistance on application of a magnetic field (~ 99% in a field of about 6-7 T) [1-5]. The x = 0.3 composition of $Pr_{0.7}Sr_{0.3}MnO_3$ perovskites was chosen for study, because it has the largest MR near room temperature and has the most practical applications [6–8]. It is already widely recognized that the double-exchange (DE) interaction between pairs of Mn3+ and Mn4+ ions through an oxygen atom is responsible for the ferromagnetic and metallic properties in these manganese oxides, because the electrical and magnetic properties strongly depend on the particle size. Several routes have been used to prepare LSMO, including the sol–gel process [9], solid-state method [10], molten salt route [11], and glycine-assisted combustion synthesis [12]. However, most of these methods cannot be economically applied on a large scale because they require expensive and often toxic reagents, high reaction temperatures, and long reaction times. This not only results in waste of energy but also does harm to our environment. As it is well known, the chemical coprecipitation method is usually used to synthesize magnetic oxides due to its simplicity and good-control of grain size. In this paper, single-phase $Pr_{0.7}Sr_{0.3}MnO_3$ particles are successfully prepared at high temperature by means of a improved chemical coprecipitation method [12]. In the processing, ammonium oxalate monohydrate was used as a precipitator instead of alkali in order to control the nucleation and growth of PSMO particles.

RESULTS AND DISCUSSION

The XRD pattern of $Pr_{0.7}Sr_{0.3}MnO_3$ synthesized by the co-precipitation method is shown in Fig.1. The XRD results indicate that the sample correspond to pure PSMO orthorhombic perovskites phase with no detectable secondary phase. We have calculated the lattice parameters from XRD data and found that the unit cell parameters a=5.474 **Å**, b=5.476 **Å**, c=7.740 **Å** & cell volume V=232.01 **Å**^{3}. The FESEM images of the sample are shown in Fig. 2. FESEM images reveal that the grain boundaries are not clear and there is poor homogeneity and much porosity in the sample. The average grain sizes calculated from FESEM micrographs is ~1.5 μm. The smaller grains have the large number of grain boundaries so the grain boundary effect will dominate in sample. The EDAX data indicates that the Pr, Sr, Mn, & O atoms in the sample are as per composition.

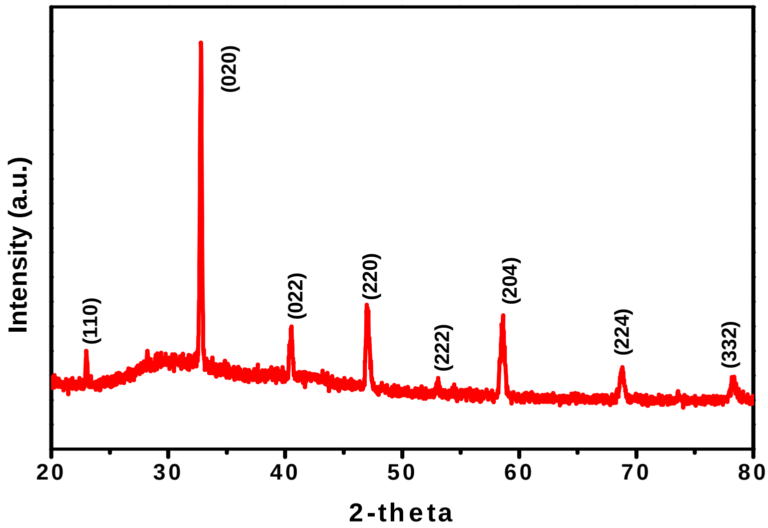

Fig. 1: The XRD pattern of PSMO sample

The chemistry for the formation of PSMO perovskite materials by the chemical coprecipitation method can be inferred from the FTIR spectrum. Fig. 3 shows a clean FTIR spectrum with a moderately sharps spectral peak at 600cm^{-1}. Since the metal– oxygen bonds are subsequently organized into a MnO6 octahedral structure, as evidenced by the appearance of a well-defined spectral band at about 600cm^{-1}. This represents a crystalline powder containing solely the PSMO perovskite-structure materials [13]. The peak at 1634cm^{-1} is due to the deformation mode of absorbed molecular water and the peak around 3448cm^{-1} is due to O–H stretching of the same [14].

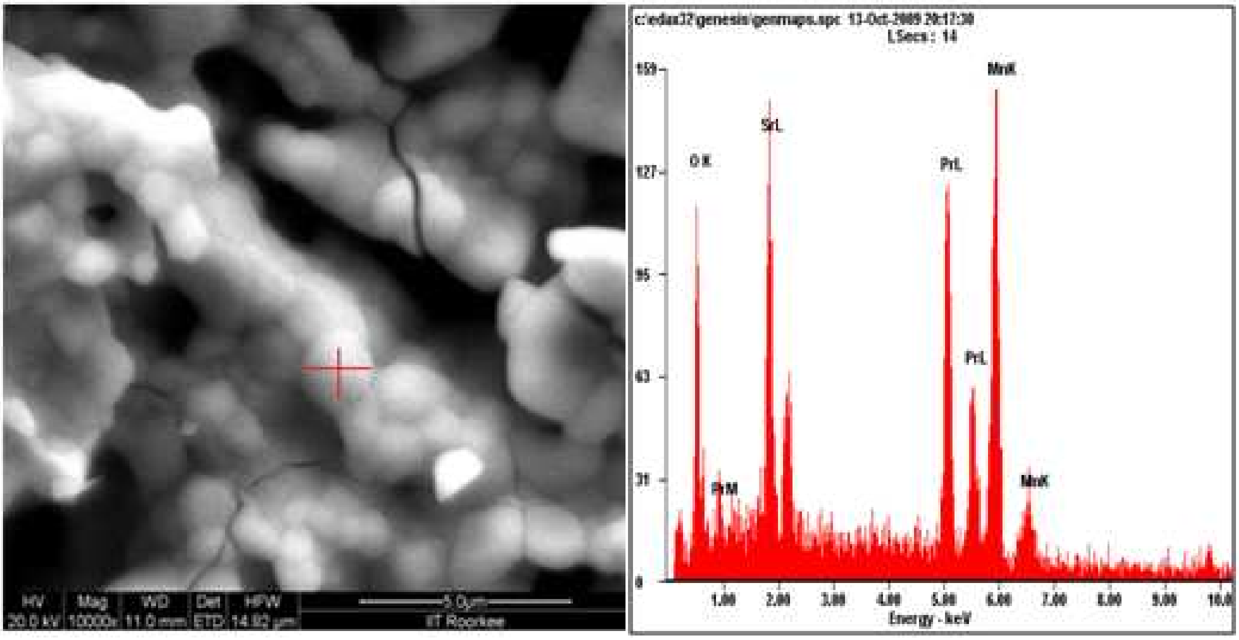

Fig. 2: FESEM micrographs and EDAX spectra of PSMO sample

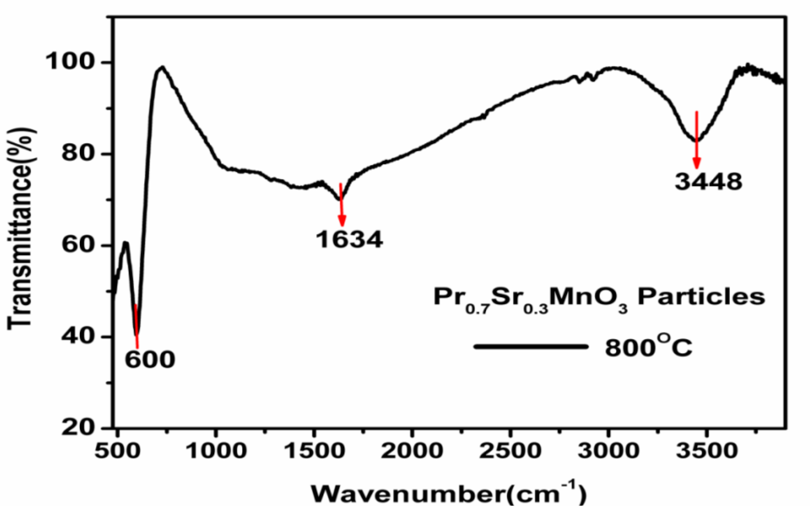

Fig.3: FTIR spectrum of PSMO particles prepared at 800 ^{O}C

The magnetization versus temperature curve for the sample in field cooled (FC) & zero field cooled (ZFC) mode measured at 500 Oe field, is shown in Fig 4. The curve shows the paramagnetic to ferromagnetic (PM-FM) transition at a particular temperature (T_c). The transition temperatures determined from the peak in $\frac{dM}{dT} - T$ curve is 203 K from the inset of Fig.4. The value of magnetization (M) at 5 K for the sample is 22.90 emu/g.

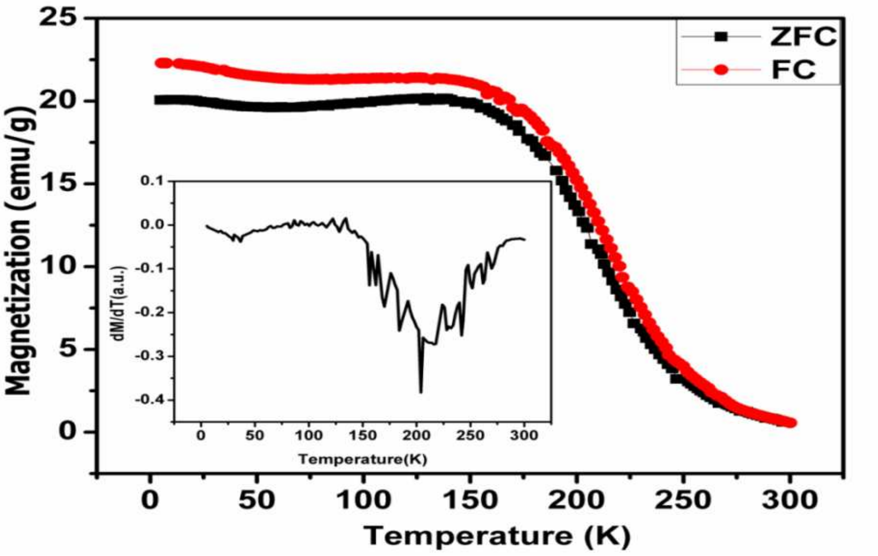

Fig. 4: M-T curve under ZFC & FC conditions of PSMO sample

It is observed from M-T curves that at low temperatures, M_{FC} value of the sample is higher than those of M_{ZFC} while the M_{ZFC} & M_{FC} curves coincide above T_c. This may be attributed to the fact that at lower temperatures, the movement of magnetic domains along the magnetic field direction is restricted due to pinning of domain walls resulting in an incomplete magnetization.

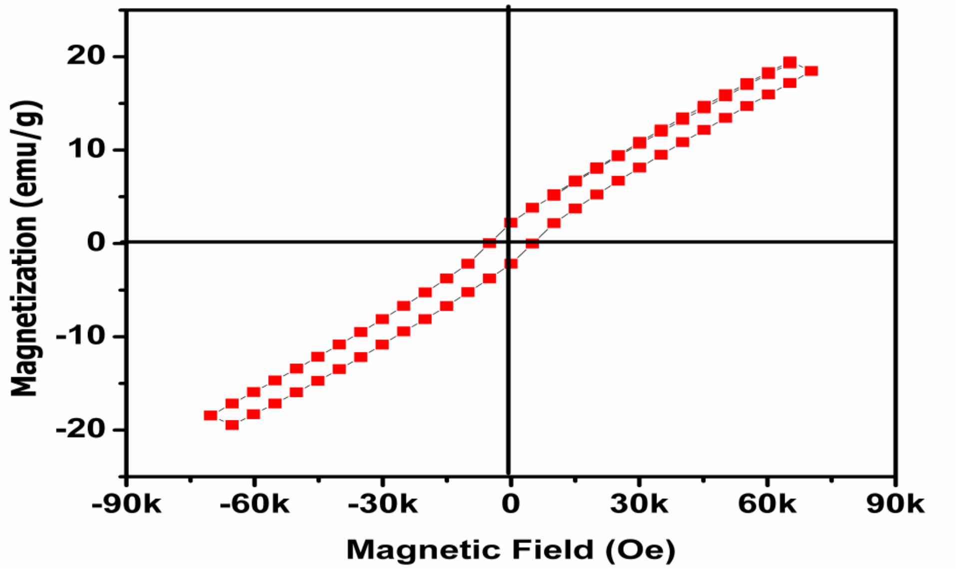

Fig. 5: M-H curves at 300 K of PSMO sample

We have observed cusp at low temperature (~ 50K) may have arisen due to the frustration caused by the competition between FM (double-exchange) and AFM (super-exchange) interactions. Such behavior might be the reentrant-type spin glass behavior (RSG) occurring at temperatures lower than T_c [15]. Furthermore, the magnetization of the sample is increasing with magnetic field and not getting saturated even up 70 kOe as shown in Fig.5. Therefore, one may conclude that PSMO sample have paramagnetic nature at room temperature.

The temperature dependence of resistivity for the sample without and with an applied field (H = 0.5T & 1T) in temperature range (80-325K) is shown in Fig 6. It is observed that the resistivity has a reduction under the applied field. The values of resistivity measured at room temperature (300 K) are 28.90 Ω-cm and the value of insulator to metal transition temperatures is 243 K.

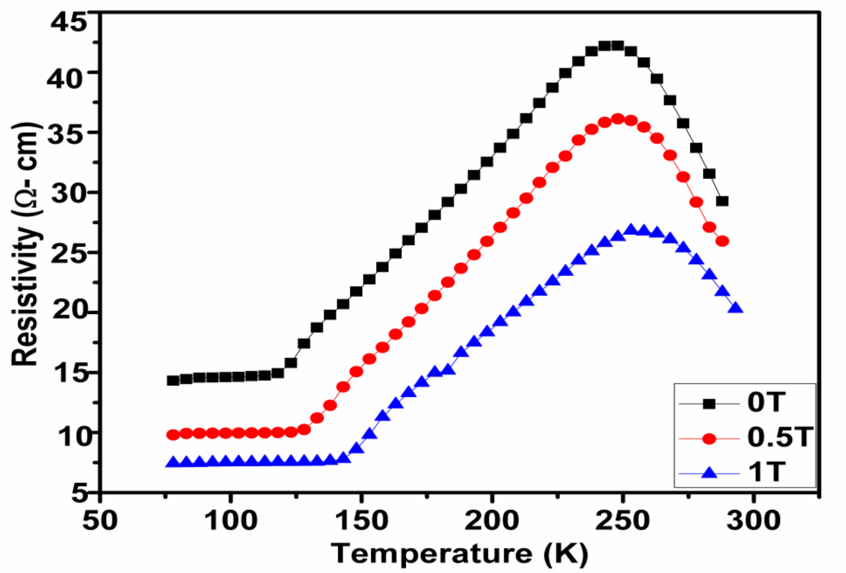

Fig. 6: Temperature dependence of resistivity at zero and an applied field H = 0.5T & 1T of PSMO sample

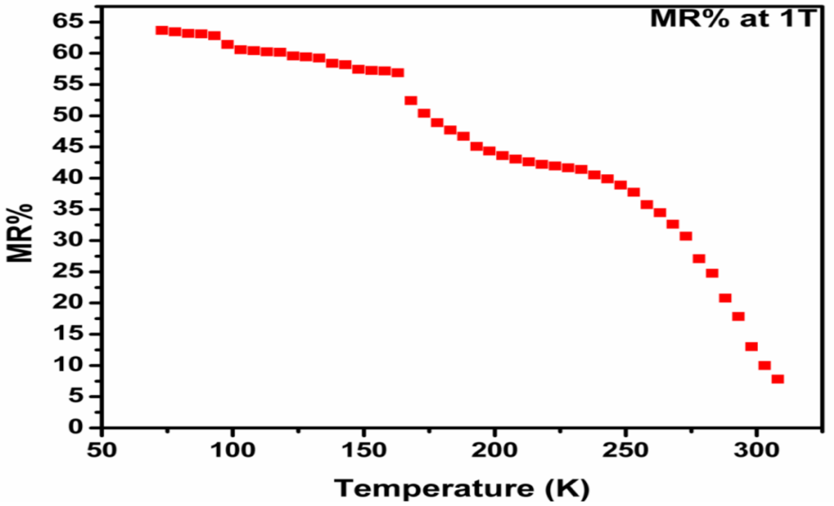

Fig. 7: Temperature dependence magnetoresistance (MR) in a field of 1T of PSMO sample

The MR increases as the temperature decreases as shown in Fig.7, due to enhanced spin-polarized tunneling by increasing the grain boundary contribution and more disordered surface at low temperature [16, 17].

MATERIALS AND METHODS

First, $Pr(NO_3)_3.6H_2O$, $Sr(NO_3)_2$ and $Mn(NO_3)_2.2H_2O$, with Pr:Sr:Mn atomic ratio of 0.7:0.3:1.0 were dissolved in de-ionized water by gentle heating. Then the aqueous mixture was slowly poured into $(NH_3)_2C_2O_4.H_2O$ solution and stirred magnetically for several minutes. The gelatinous precipitate was filter and washed for several times using de-ionized water until the pH value of the solution became neutral. Finally, the gelatinous precipitate was dried at 150 ^{0}C in air. To prepare mono-disperse PSMO particles, the powder was dispersed by ultrasonic bath in ethanol, centrifuged and washed with ethanol and calcined at 800 ^{0}C. The dried powder pressed into pellets and was heat treated in air at 1200 ^{0}C for 15h.

The structural characterization was examined by using X-ray diffraction (Bruker AXS D-8 advance, CuK_α radiation) technique at room temperature and surface morphology was investigated by using a field emission scanning electron microscope (FEI, Quanta 200 F). Fourier transform infrared (FTIR) spectroscopy was undertaken with a Nicolet Magna-IR 550 FTIR spectrometer. The elemental analysis was carried out using energy dispersive X-ray analyzer (EDAX' TSL, AMETEK) coupled with FE-SEM. Resistivity as a function of temperature was measured by a standard four-probe method by using Keithley instruments without or with magnetic fields (0-1T). The magnetization measurements were done by using SQUID magnetometer.

CONCLUSION

In summary, we have successfully synthesized the $Pr_{0.7}Sr_{0.3}MnO_3$ polycrystalline sample by co-precipitation method and investigated their structural, magnetic & magneto-transport properties. The sample have pure PSMO phase with orthorhombic unit cells. FTIR spectrum also demonstrate that PSMO particle have formed at 800^{O}C. The values of resistivity measured at room temperature (300 K) are 28.90 Ω-cm and the value of insulator to metal transition temperatures is 243 K. The MR ratio at different temperatures was measured, and MR ratio 63% was observed in 1T field at 80 K. One may conclude that PSMO sample have paramagnetic nature at room temperature. We have observed that the sample show a large magnetoresistance (MR) not only near the ferromagnetic transition temperature but also at low temperature. The low temperature MR, which decreases with increasing temperature, is due to the grain boundary effect.

Acknowledgements
One of the authors, Mr Umesh Chand, is grateful to the Ministry of Human Resources and Development (MHRD), New Delhi, for financial support during this work.

REFERENCES

[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, K. Samwer, *Phys. Rev. Lett.*, **1993** 71, 2331.
[2] G. A. Prinz, K. Hathaway, *Phys. Today*, **1995,** 48, 24.
[3] R. Wood, *IEEE Trans. Mag*., **2000**, 36.
[4] A. Moser, K. Takano, D. T. Margulies, M. Albrecht, Y. Sonobe Ikeda, S. Sun, E. E. Fullerton, *J. Phys. D: Appl. Phys*., **2002,** 35, 157.
[5] P. K. Siwach, H. K. Singh, O. N. Srivastava, *J. Phys.: Condens. Matter*, **2008,** 20 2732015
[6] A. Urishibara, Y. Morimoto, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, *Phys. Rev. B*, **1995**, 51, 14103.
[7] M. Bibes, A. Barthele, *IEEE Trans. Electron. Devices*, **2007,** 54, 1003.
[8] C. Jooss, L. Wu, T. Beetz, R.F. Klie, M. Beleggia, M.A. Schofield, S. Schramm, J. Hoffmann, Y. Zhu, *Proc. Natl. Acad. Sci.* USA, **2007,** 104, 13597.
[9] Y.H. Huang, C.H. Yan, Z.M. Wang, C.S. Liao, G.X. Xu, J. Alloys Compd., **2003**, 349, 224.
[10] A. Gaur, G.D. Varma, *Solid State Commun*. **2006,** 139, 310.
[11] F. Luo, Y.H. Huang, C.H. Yan, S. Jiang, X.H. Li, Z.M. Wang, C.S. Liao, *J. Magn. Magn. Mater*. **2003**, 260, 173.

[12] D.R. Sahua, B.K. Roul, P. Pramanik, J.L. Huang, *Physica B*, **2005,** 369, 209.
[13] Z. F. Zi, Y. P. Sun ,X. B. Zhu, Z. R. Yang, J. M. Dai, H. Song, *J. Magn. Magn. Mater.* **2009,** 321, 2378.
[14] S. Roy, S. Bandyopadhyay, *J. Mater. Sci. Lett.*, **1996,** 15, 1872.
[15] G. Cao, J. Zhang, S. Wang, J. Yu, C. Jing, S. Cao, X. Shen, *J. Magn. Magn. Mater.*, **2007,** 310, 169.
[16] T. Zhu, B.G.Shen, J. R. Sun, H. W. Zhao, W. S. Zhan, *Appl. Phys. Lett.*, **2001**, 78, 3863.
[17] S. Lee, H. Y. Hwang, L. Boris, W. D. Shraiman, I. I. Ratcliff, S. W. Cheong, *Phys. Rev. Lett.*, **1999,** 82, 4508.