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# INFLUENCE OF $La^{3+}$ WITH $Pr^{3+}$ TO STRUCTURE, MICROSTRUCTURE, AND MAGNETOTRANSPORT PROPERTIES IN BARIUM MANGANITE PEROVSKITE

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## ABSTRACT

Polycrystalline perovskite manganite of $(La,Pr)_{0.67}Ba_{0.33}MnO_3$ bulk ceramic samples were synthesized by conventional solid-state route. The structure, microstructure, electrical and magnetic properties were studied. Substitution of $La^{3+}$ with $Pr^{3+}$ promote coarsening of microstructure formation and influencing the connectivity of grains which resulting an increase in resistance. This substitution promotes magnetic dilution and consequently leading to the suppression of magnetic behaviour. The metal-insulator transition temperature, $T_P$ drops drastically from 264K (LBMO) to 127K (PBMO). PBMO displayed higher %MR in 10kG applied external magnetic field at room temperature which is -8.8% as compared to LBMO (-5.2%) because of magnetic dilution and reduced the magnetic saturation. Meanwhile, reduction in bond angle and bond length of $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ due to the distortion in $MnO_6$ might enhance DE and JT mechanism. In this work, the %MR at room temperature enhanced by replacing $La^{3+}$ with $Pr^{3+}$ but weaken the LFMR effect.

## INTRODUCTION

Colossal magnetoresistance (CMR) in the perovskite manganites $A_{1-x}B_xMnO_3$ (A is a rare earth ions, and B is a divalent cation) have attracted many interest due to the high negative magnetoresistance (MR) value [1]. The electrical and magnetic properties are commonly explained using the double exchange (DE) theory which considers the magnetic coupling in $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ and Jahn-Teller (JT) distortion of $MnO_6$ octahedral and both categorized as intrinsic effect. Beside intrinsic effect, extrinsic effect named as low field magnetoresistance (LFMR) effect which show a dramatic drop in the resistance when low magnetic field was applied. This is believed to be due to the spin-polarized tunneling or spin-dependent scattering across the grain boundaries between neighbouring grains or interlayer [2,3]. Both effects could lead to a complex metallic-insulator electrical behaviour which governed by phase transition temperature, $T_P$. Since both intrinsic and extrinsic CMR effect are present at the same time in polycrystalline compound [3], changing in $\langle r_A \rangle$ of $A_{0.67}Ba_{0.33}MnO_3$ in A-site with smaller rare earths seems interesting in modifying $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ neighbouring interaction and bond angle which directly influences DE and JT. In this work, we compare the results of substitution $La^{3+}$ with $Pr^{3+}$ in A site of perovskite manganite on structure, microstructure, magnetic and electrical properties as well as MR.

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## MATERIALS AND METHOD

Polycrystalline $La_{0.67}Ba_{0.33}MnO_3$ (LBMO) and $Pr_{0.67}Ba_{0.33}MnO_3$ (PBMO) samples were prepared through conventional solid-state reaction. High purity (99.9%) starting powder of $La_2O_3$, $Pr_6O_{11}$, $BaCO_3$ and $MnCO_3$ were initially dried at 100 °C. Stoichimetric amount of dried samples then mixed with agate ball and wet milled in acetone (HmbG Chemicals). The milled powders then dried and ground before calcination at 800°C in air for 12 hours. Samples were then reground and sieved (<25 μm) before pressed into pellets and sintered at 1300 °C in air for 12 hours. The structure was characterized using X-ray Diffraction (XRD, Phillips PW 3040/60 Xpert Pro) technique with radiation of $CuK_\alpha$ in range of 20°-80° and the surface morphology was investigated using Scanning Electron Microscope (SEM, LEO1455 VPSEM). At room temperature, MR and magnetic properties of samples were measured using Hall Measurement System (Model 7604) and Vibrating Sample Magnetometer (VSM, Lakeshore 7400 series) respectively. Resistance at various temperatures (20K-300K, warming-up mode) was taken by Keithley Delta Mode system.

## RESULTS AND DISCUSSION

Figure 1 show the XRD patterns of LBMO and PBMO at room temperature. It reveals that LBMO and PBMO are in single phase. LBMO was found in orthorhombic (*Imma*) and PBMO in tetragonal (*I4/m*) perovskite structure which matched the ICDD standards (ICDD: 01-089-0569 and 01-080-1139 respectively). The inset in Figure 1 shows main peak (112) of PBMO system shifted to higher Bragg's angle compared to (121) of LBMO indicating that there are reduction in d-spacing since d is inversely proportional to sinθ ($\lambda = 2d\sin\theta$). This might be due to the influences of different ionic radius of $La^{3+}$ (1.172 Å) and $Pr^{3+}$ (1.13 Å). The data of ionic radius in this paper are obtained from Ref. [8].

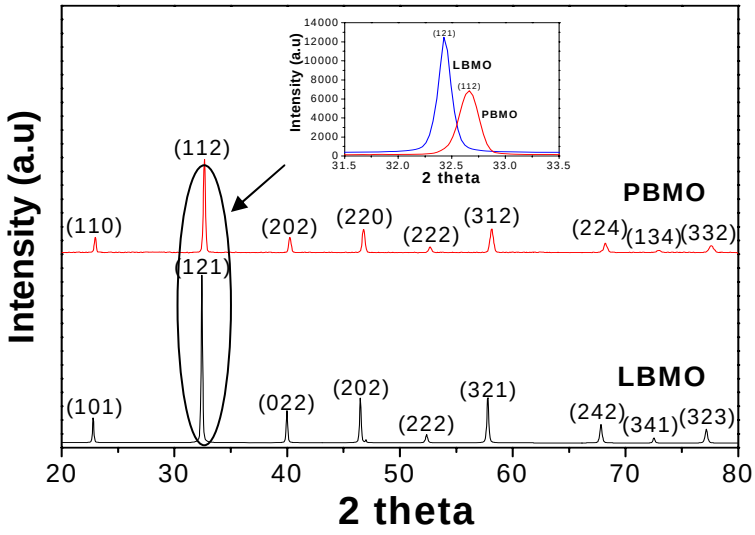


Figure 1: XRD spectrums of LBMO and PBMO at room temperature.

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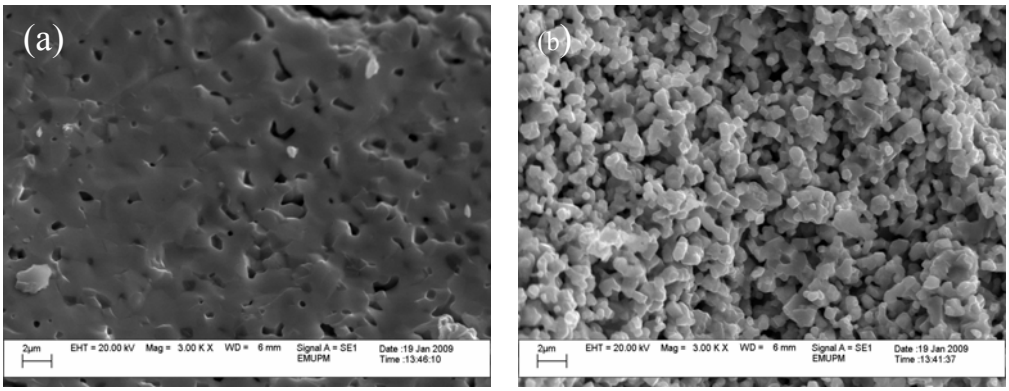


Figure 2: SEM micrograph of a) LBMO and b) PBMO.

Figure 2(a) show that all grains of LBMO sample are in melted-like form and well connected with the present of some pores. There is no clear grain boundary that can be observed where grain size is hard to be identified. However, the grain size ranging from 0.5 to 2 μm with bigger pores are observed in PBMO system (Figure 2(b)). Melted-like form was found in LBMO since La having smaller enthalpy of fusion (6.2 kJ/mole) as compared to Pr (6.89 kJ/mole), indicated that amount of thermal energy required to change from solid to liquid is lesser. During sintering process, stronger diffusion among ions in LBMO probably occurred and form melted-like grains while PBMO was found in the coarsening form.

Figure 3 show a hysteresis loop of LBMO and PBMO at room temperature. It shows that LBMO probably ferromagnetic because of the hysteresis loop (soft magnetic hysteresis loop with no remanence and coercivity) and PBMO is paramagnetic since it was a straight line pass through origin. Substitution of $La^{3+}$ with $Pr^{3+}$ leads to magnetic dilution, in fact $La^{3+}$ ion is non-magnetic and $Pr^{3+}$ is magnetic with magnetic moment of $3.58\mu_B$ [8]. Therefore, the net magnetic moment of LBMO system was reduced when $La^{3+}$ was replaced by $Pr^{3+}$ and consequently leads to the suppression of ferromagnetic to paramagnetic transition temperature. In fact, the reduction in magnetization also influences the DE mechanism resulting from ferromagnetic alignment of Mn ions. Also, the spins in ferromagnetic material have the potential to align easily in an applied magnetic field and achieve magnetic saturation easily as compared to paramagnetic material. This behaviour indirectly tells us that magnetic dilution can reduce the magnetic saturation. At 10kG, the magnetization value for LBMO and PBMO are 52.9 emu/g and 2.4 emu/g respectively.

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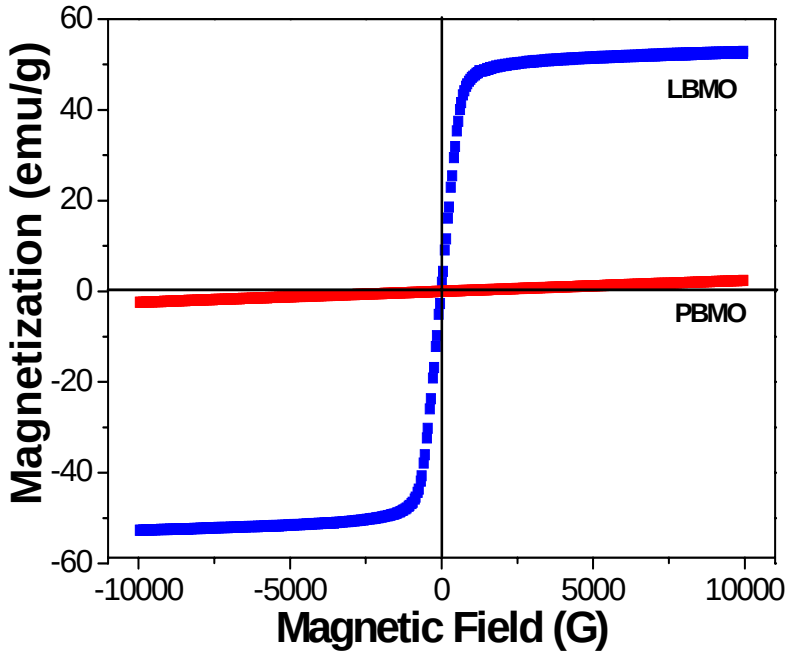


Figure 3. Magnetization as a function of applied external magnetic field at room temperature.

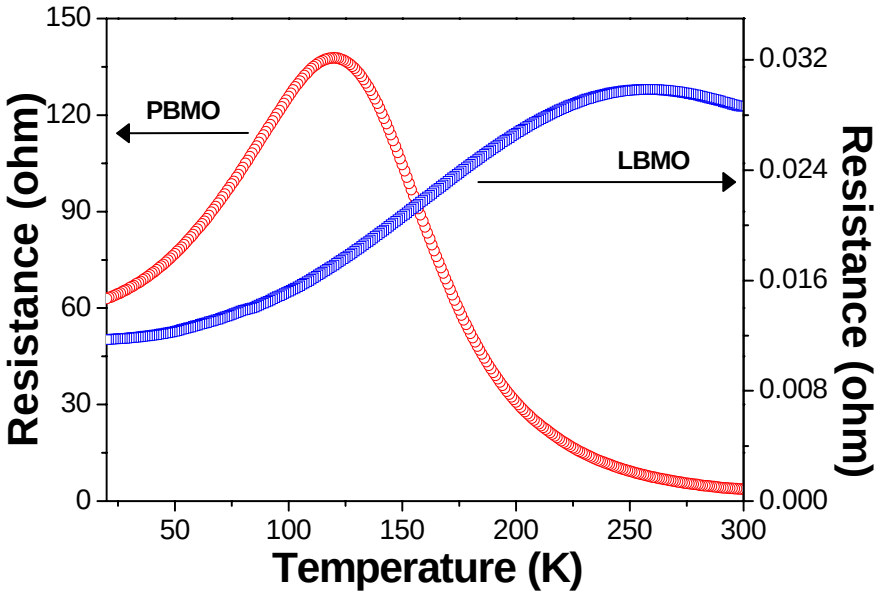


Figure 4**.** Resistance as a function of temperature.

Figure 4 shows the resistance as a function of temperature of LBMO and PBMO

samples in the warming-up mode condition. It is found that the $T_P$ for LBMO and PBMO are 264K and 127K respectively. $T_P$ for PBMO was found in lower temperature and having greater resistance compared to that of LBMO.
The grains connectivity directly influence the resistance of whole system and it is found that LBMO having lower resistance due to the melted like grain as compared to PBMO which is quite porous and smaller grain size. These phenomena indirectly influence the increase in electron scattering or tunnelling across grain boundary, resulting in more barriers for an electron to pass through and hence resistance increased [6]. As $La^{3+}$ replaced by $Pr^{3+}$, $T_P$ drops drastically. The drastic drop of $T_P$ in PBMO might due to magnetic dilution which weakened the DE effect.

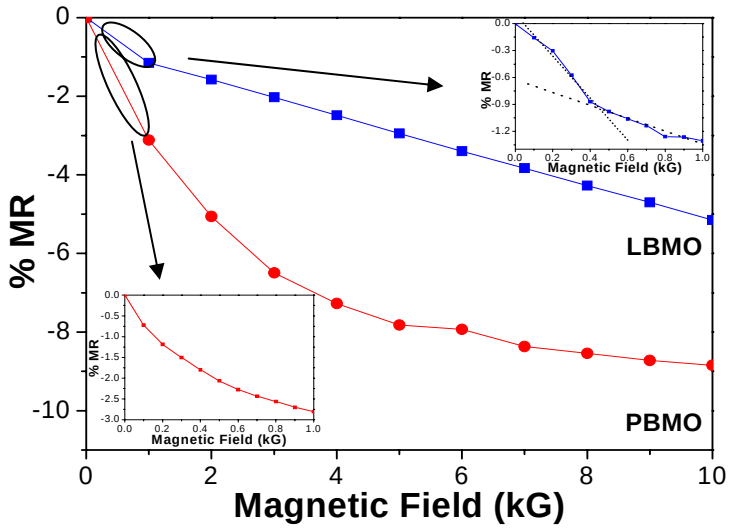


Figure 5**.** %MR curves as a function of external applied magnetic field at room temperature.

The % MR value is calculated using $\%MR= (R_{(H)}-R_{(o)}/R_{(o)})\times 100$, where $R_{(o)}$ and $R_{(H)}$ is the resistance at zero magnetic field and in an applied external magnetic field respectively. Figure 5 shows the %MR value of LBMO and PBMO, LBMO sample shows LFMR behaviour and PBMO show an ordinary %MR which can be clearly seen in the inset of the figure. Since LFMR in polycrystalline materials are governed by the spin-dependent scattering and spin-polarized tunnelling across grain boundary. As low external magnetic field (<1kG) was applied, the spins at the grain boundaries layer were aligned and enhanced the conduction according to DE theory. The resistance further drop as stronger magnetic field was applied because the spin in the core begins to align. However, LFMR effect does not happen in PBMO. One of the reasons is due to grains connection which influenced the flowing of electrons across grain boundaries so called extrinsic effect. PBMO which is more porous, directly reduce the number of hopping electrons while weakened in magnetization value were believed to be the main reason of losing LFMR effect [4]. Beside extrinsic effect, intrinsic effect also influences the %MR value. PBMO exhibit higher %MR because of the larger anisotropy which

originate from spin states in $Pr^{3+}$ ions (non-magnetic $La^{3+}$ ion is replaced by $Pr^{3+}$ which contains unpaired *f*-electrons) [5]. These phenomena can reduce the magnetic saturation and enhance MR as explained previously. In the other hand, decreasing ionic radius of trivalent ions ($La^{3+}$ replaced with $Pr^{3+}$) can reduce the bond angle as well as bond length of $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ due to the distortion of $MnO_6$ octahedral and favoured the intrinsic effect [7], these further explain the phenomena of %MR in PBMO greater than LBMO.

## CONCLUSION

Substitution $La^{3+}$ with $Pr^{3+}$ lead to smaller grain size formation, a great porosity in PBMO and a melted like LBMO grains. Meanwhile, substitution of $La^{3+}$ with $Pr^{3+}$ resulting magnetic dilution and consequently leads to the suppression of ferromagnetic to paramagnetic transition temperature. The phase transition temperature, $T_p$ of LBMO is 264K and greatly reduced to 127K in PBMO. Although PBMO could contribute higher %MR (-8.84%) compared to LBMO (-5.15%) in 10kG applied external magnetic field at room temperature, replacement of $La^{3+}$ with $Pr^{3+}$ weaken the LFMR effect.

## ACKNOWLEDGMENT

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## REFERENCES

[1] Y. Tokura, Y. Tomioka (1999). *Journal of Magnetism and Magnetic Materials* **200**, 1-23.

[2] H.Y. Hwang, S.W. Cheong, N.P. Ong, B. Batlogg (1996). *Phys. Rev. Lett*. **77**, 2041.

[3] P. K. Siwach, H. K. Singh, O. N. Srivastava (2008). *Journal of Physics: Condensed Matter* **20**, 273201.

[4] L. W. Lei, Z. Y. Fu, J. Y. Zhang, H. Wang (2006). *Solid State Communications* **140**, 261-266.

[5] P. S. Anil Kumar, P. A. Joy and S. K. Date (1998). *Solid State Communications*, **108**, No 2, 67-70.

[6] P. Kameli, H. Salamati, A. Aezami (2008). *Journal of Alloys and Coumpounds* **450**, 7-11.

[7] Yun-Hui Huang, Chun-Hua Yan, Zhe-Ming Wang, Chun-Sheng Liao, Guang-Xian Xu (2001). *Solid State Communications* **118**, 541-546.

[8] Aspinall, Helen C. (2001). *Chemistry of the f-block Elements* (Advanced chemistry texts; v. 5) p. 10