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# STRUCTURAL AND ELECTRICAL PROPERTIES OF $Pr_{1-x}AE_xMnO_3$ (AE = Sr, Ba)

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## ABSTRACT

Bulk samples of $Pr_{1-x}AE_xMnO_3$ (AE = Sr, Ba) were prepared through conventional solid state method. XRD analysis shows that $Pr_{0.67}Sr_{0.33}MnO_3$ (PSMO) and $Pr_{0.67}Ba_{0.33}MnO_3$ (PBMO) exhibited single phase orthorhombic structure with space group of Pnma and Imma, respectively. The lattice parameters (*a*,*b*,*c*), Mn-O-Mn bond angle and volume of the structure increased when smaller Sr atom was replaced with bigger Ba atom. SEM micrograph shows different grain size with 1.6μm for PBMO and 9.1μm for PSMO. The metal-insulator transition temperature, Tp was found different where PBMO show double Tp value (150K, 182K), where PSMO give single Tp value of 286K. The difference is believed to be due to the different phases of the surface and core of the grain. Typical polycrystalline type of MR behavior (intrinsic accompany with extrinsic MR effect) is observed. However, the intrinsic effect is more dominant in both cases. In this study, substitution of various atomic radius in Pr site greatly influences the structural and electrical properties in $Pr_{0.67}(Ba, Sr)_{0.33}MnO_3$ system.

*Keywords: metal-insulator transition temperature; manganese oxide*

## INTRODUCTION

In recent years, many researchers have paid their attention on the electrical, magnetic and catalytic properties exhibit by polycrystalline doped manganite. These manganites have perovskite structure with general formula as $Ln_{1-x}AE_xMnO_3$ where Ln is a rare earth element and AE is an alkaline earth element [1]. The electrical and magnetic properties were highly depends on the bond angle and distance of Mn-O-Mn and this usually sensitive to the average ionic radius from the A-site cation. Besides, ratio of $Mn^{3+}/Mn^{4+}$ also played an important role in determining the magnetic state [2]. From previous report [3], the mismatch of ionic radius will caused tilting of MnO6 octahedral thus influence the perovskite structure and magnetic state. The other structural distortion which is contributed by Jahn-Teller effect also has to take in consideration. In present paper, the study of structural and electrical properties of $Pr_{0.67}AE_{0.33}MnO_3$ (AE = Sr, Ba) have been studied.

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## EXPERIMENTAL DETAILS

All CMR samples were synthesis by conventional solid state reaction merhod. Samples have been prepared by weighing in respective stoichiometric portion according to the formula $Pr_{0.67}AE_{0.33}MnO_3$ (AE= Sr, Ba). The mixtures were milled and heat to 900°C for 12 hours. The samples undergo grinding and sieving using 25μm sieve. Finally, all samples were sintered at 1300$^o$C for 24 hours. All samples were characterized by XRD diffraction technique Philips PW300/60 ranged from 20$^o$-80$^o$ with 0.016$^o$ step size in room temperature. Micrograph was obtained using scanning electron microscope LEO1455. The electrical resistance at variable fields and variable temperatures were measured using 4 point probe technique by LakeShore Hall Effect EM4-HVA machine. During the measurement, the temperature range was set from 80K to 300K while the magnetic field was set at 0T, 0.1T, 0.2T, 0.5T and 1.0T. Rietveld refinement technique was used to analysis the bond angle and distance of Mn-O-Mn, lattice parameter, crystal volume, and space group of the sample

## RESULTS AND DISCUSSION

Figure 1 shows the micrograph for $Pr_{0.67}Sr_{0.33}MnO_3$ (PSMO) and $Pr_{0.67}Ba_{0.33}MnO_3$ (PBMO) samples. Compact microstructure is observed for both samples. All grains are well arranged and clear grain boundary can be seen with some small pores. The average grain size for PBMO and PSMO are 1.6 μm and 9.1 μm respectively. Refer to PSMO sample, pore is located within the grain. This evidence the consequences of agglomeration or strong diffusion of two or more grain to form a bigger grain. Hence, both sample had different effective grain boundaries where smaller grain size (PBMO) give higher grain boundary effect since it having bigger surface over volume ratio and vice versa for bigger grain size.

Figure 2 shows the XRD pattern for PSMO and PBMO samples. Both samples exhibit orthorhombic crystal structure but with different space group. From the Rietveld refinement analysis, PSMO and PBMO having space group of Pnma (ICSD: 98-002-9573) and Imma (ICSD: 98-002-6298) respectively. The peak was slightly shifted to the left when $Sr^{2+}$ replaced with $Ba^{2+}$. These probably due to bigger ionic radius of $Ba^{2+}$ (1.49Å) compare to $Sr^{2+}$ (1.32Å) in the structure and this will increase their d-spacing thus decrease 2-theta value. Mn-O-Mn bond angle, lattice parameter (*a*, *b* and *c*) and volume increased when $Sr^{2+}$ replaced with $Ba^{2+}$. However, Mn-O distances remain unchanged. Hence, the structure experience some stress along all direction of the structure and this resulted the tilting of $MnO_6$ octahedral as shown in Figure 3. This cause the increases in volume without changing of it bond distance.

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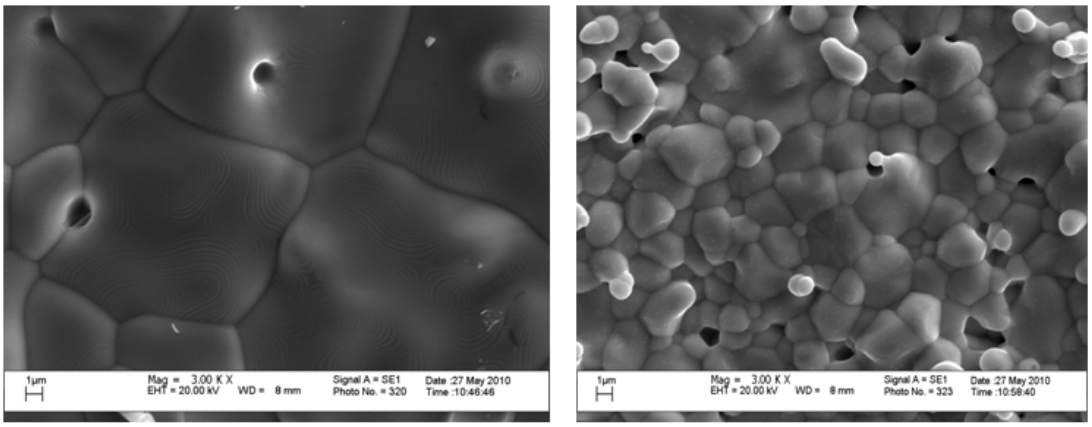


Figure 1: (a) $Pr_{0.67}Sr_{0.33}MnO_3$ and (b) $Pr_{0.67}Ba_{0.33}MnO_3$ SEM micrograph under 3,000X magnifications

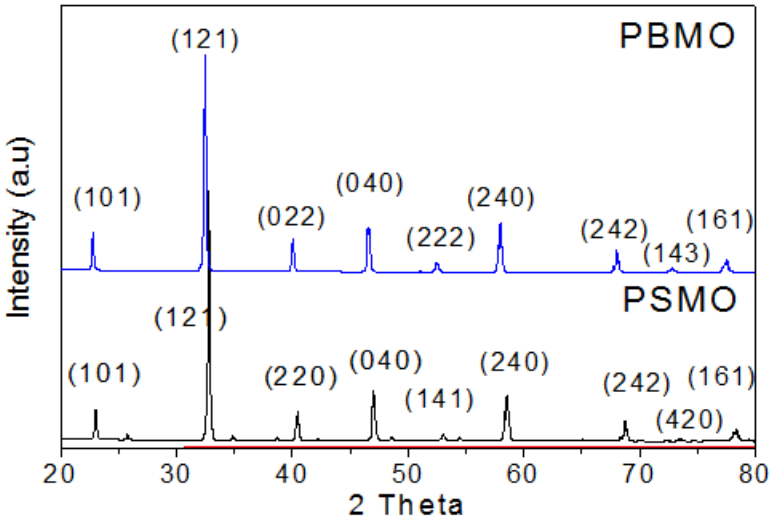



Figure 2: XRD pattern for PSMO and PBMO

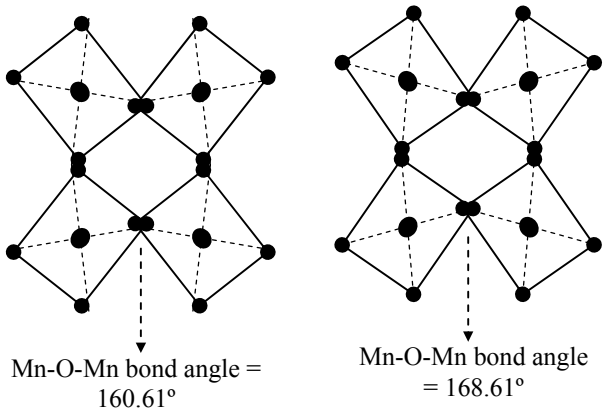



Figure 3: Top view of the $MnO_6$ octahedral

Table 1: Rietveld Refinement data of PSMO and PBMO

| Sample | $Pr_{0.67}Sr_{0.33}MnO_3$ | $Pr_{0.67}Ba_{0.33}MnO_3$ |
|---|---|---|
| Crystal structure | Orthorhombic | Orthorhombic |
| Space group | Pnma (62) | Imma (74) |
| *a*(Å) | 5.454 (2) | 5.525 (2) |
| *b*(Å) | 7.708 (2) | 7.774 (2) |
| *c*(Å) | 5.484 (2) | 5.502 (2) |
| V(Å$^3$) | 230.519 | 236.311 |
| Mn-O1-Mn (°) | 160.610 | 168.613 |
| Mn-O2-Mn ($^o$) | 158.040 | 163.886 |
| Mn-O1 (Å) | 1.960 | 1.959 |
| Mn-O2 (Å) | 1.963 | 1.963 |
| $R_{exp}$(%) | 3.611 | 4.252 |
| $R_p$(%) | 4.969 | 6.652 |
| GOF | 3.490 | 3.940 |

The resistance versus temperature plot for PSMO and PBMO sample is shown in Figure 4. Tp values were shown in Table 2. When magnetic field is applied, the value of transition temperature will slightly shifted to higher value. When higher field was applied, more electrons was aligned thus stronger DE effect shifted Tp to higher temperature. The resistance value for PSMO is lower compare to PBMO. This is probably due to the effective grain boundary exist in PBMO and the smaller bond angle between Mn-O-Mn of PSMO which can enhances DE effect. Overall Tp values for PSMO are higher. This was mainly due to the increase of average ionic radius of the cation when $Ba^{2+}$ is substituted which will increase the bond angle thus affecting Tp [4]. The existence of 2 Tp can be explained by Zhang's model. This model assumed that the grain in perovskite manganite can be divided into two phase system, the core phase and the surface phase. Both of these phases have their own resistance. When temperature increases, the grain surface becomes more disorder while the grains were still in the ferromagnetic state [5]. Lower Tp was contributed by grain surface and this was due to the magnetically disordered states in the surface. Magnetically disordered can caused by several factors [6]. The big ionic size difference between $Pr^{3+}$ (1.18Å) and $Ba^{2+}$ produce extra strain in the structure. The lattice strain transferred from the grain to the grain surface resulted the structure to be extra distorted thus affected Mn-O-Mn bond angle and distance and weakens the transfer of electron. Double exchange effect is stronger in the grain compare to grain surface which is in more chaotic condition. However, $Tp_2$ of PBMO with higher value was disappeared when the magnetic field is increasing. In PSMO, the grain and grain surface effect does not separate because the ionic size difference is not too large [7,8].

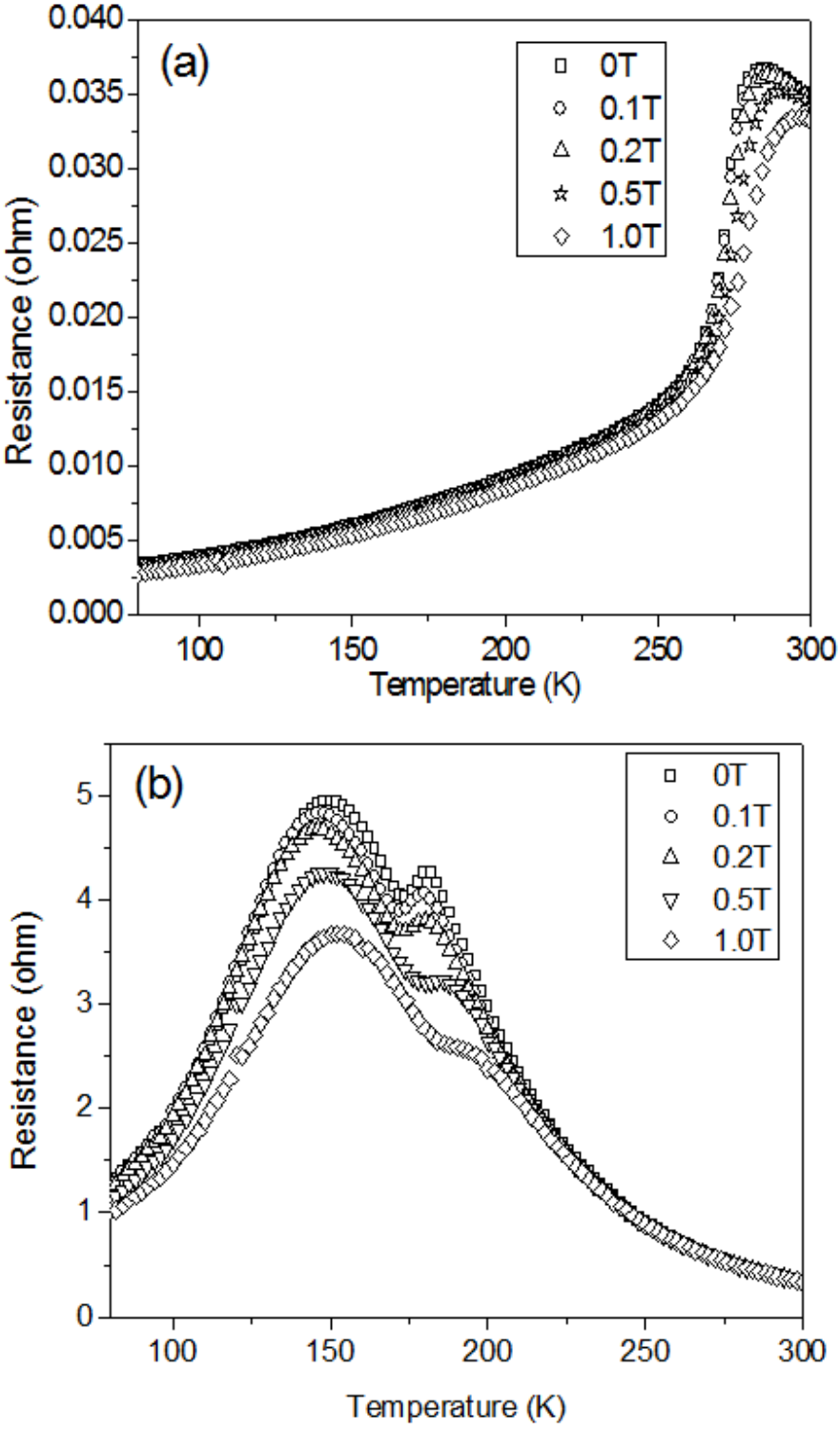
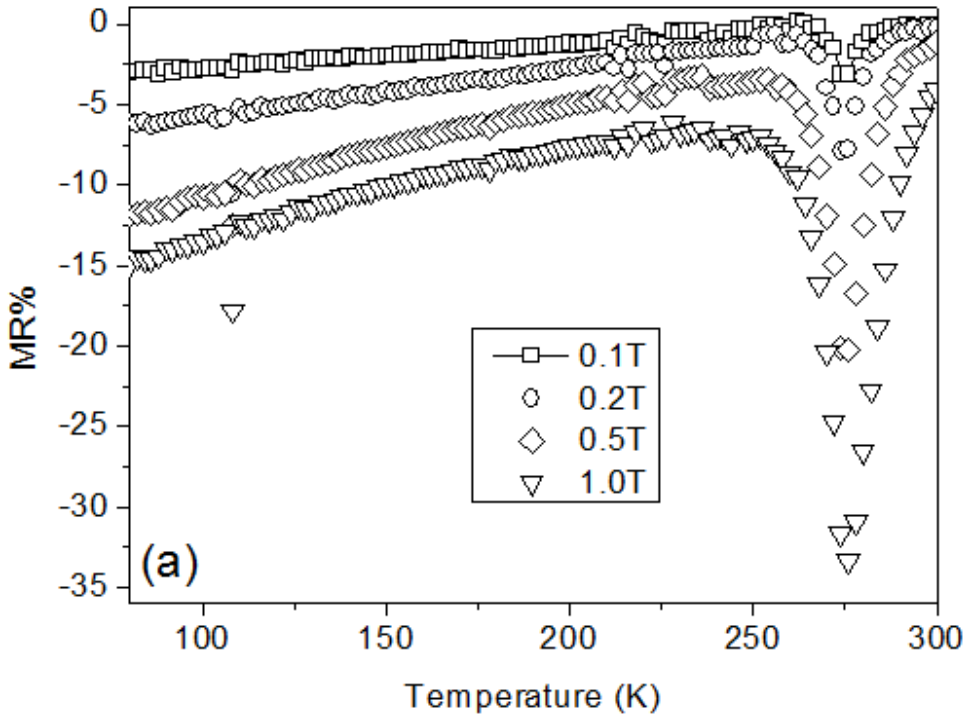



Figure 4: Resistance versus temperature with different applied field for (a) PSMO and (b) PBMO

Table 2: Tp with respect to the field applied

| Magnetic field applied | 0T | 0.1T | 0.2T | 0.5T | 1T |
|---|---|---|---|---|---|
| PSMO (Tp) | 286K | 286K | 286K | 290K | 296K |
| PBMO (Tp1) | 150K | 146K | 146K | 148K | 154K |
| PBMO (Tp2) | 182K | 180K | 180K | 184K | - |

In Figure 5, the magnetoresistance curve for PSMO and PBMO sample measured at variable temperature were shown. The samples exhibit highest MR% near the transition temperature at each applied field and the highest magnetoresistance value achieve by both sample was -33.33% and -36.62% at 1T for PSMO and PBMO respectively. Typical polycrystalline behaviour of MR effect, which is the coexisting of intrinsic and extrinsic MR, was observed where MR is increases when temperature drops below Tp. However, significant maximum MR peak is still observed near the Tp temperature. Hence, the intrinsic MR effect is still dominant where the grain boundary effect, which contributed to the extrinsic MR effect, is relatively weak as compared to the grain core effect.



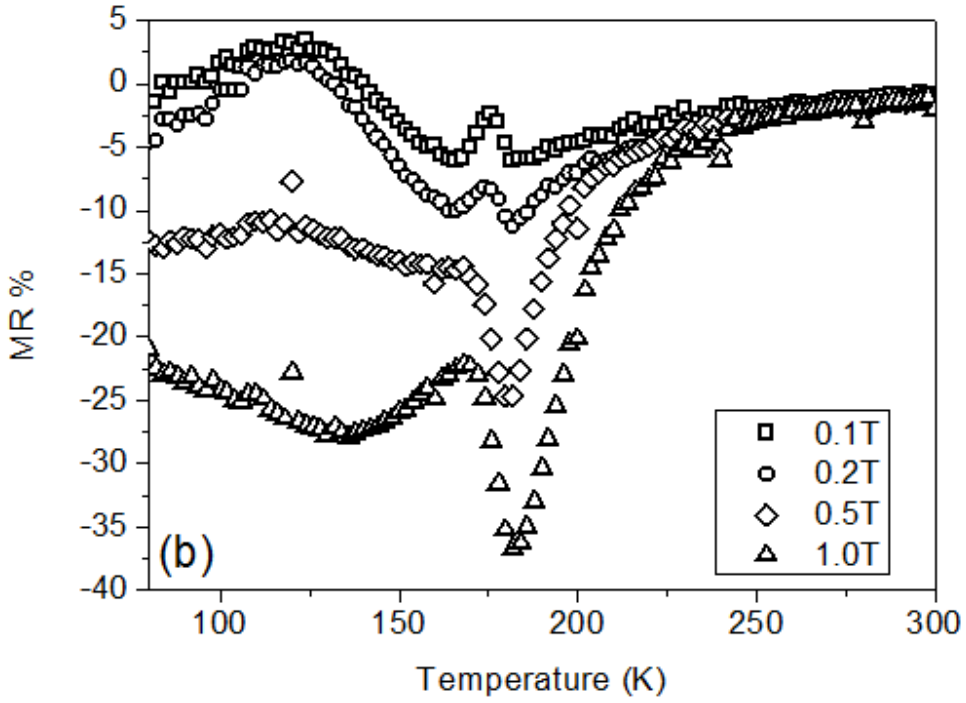



Figure 5: MR% versus temperature for (a) PSMO and (b) PBMO

## CONCLUSION

The magnetoresistance, structural and electrical properties of $Pr_{1-x}AE_xMnO_3$ where (AE = Sr, Ba) have studied. The lattice parameter (*a*, *b*, *c*), volume of the crystal structure and bond angle of Mn-O-Mn increased when $Ba^{2+}$ substitute $Sr^{2+}$. PSMO and PBMO showed orthorhombic crystal structure with space group Pnma(62) and Imma(74) respectively. PBMO have two Tp values, contributed from surface and core grain effect. However, $Tp_2$ disappeared at magnetic field at 1T. Tp for both samples shifted to higher temperature when applied magnetic field increased where the double exchange (DE) effect become stronger. Both sample show typical polycrystalline types of MR behaviour. However, the intrinsic MR effect is more dominated as compared to extrinsic MR effect. This study showed that the substitution of various atomic radius in Pr site were greatly influence the electrical and structural properties.

## ACKNOWLEDGEMENT

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