

EFFECT OF PRASEODYMIUM SUBSTITUTED ON THE STRUCTURAL AND ELECTRICAL TRANSPORT PROPERTIES OF $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ PEROVSKITE

A. Huda, S.A.Halim, S.Elias, A.A.Sidek, Z.Hishamuddin, K.P.Lim, K.K.Kabashi

*Superconductor and Thin Films Laboratory, Department of Physics,
Faculty of Science & Environmental, University Putra Malaysia,
43400 Serdang, Selangor, Malaysia*

ABSTRACT

The influence of praseodymium substituting at La-site in $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ has been investigated, in magnetotransport and structural properties. The doping Pr at La site on La-Ba-Mn-O ceramics was using solid state reaction. Polycrystalline $(\text{La}_{1-x}\text{Pr}_x)_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ ($x = 0, 0.167, 0.33, 0.5, 0.67, 0.833, 1$) is doped with Pr site based manganites, calcined at 900°C for 12 hours, pelletized and sintered at 1300°C for 24 hours have been synthesized and investigated. The electrical property, T_p was determined by using standard four-point probe resistivity measurement in a temperature range of 30 K to 300 K. With increasing the Pr doping, T_p for the films shifted to lower temperatures, which are 254, 248, 228, 220, 196, 180, 158 K for the bulks with $x = 0, 0.167, 0.33, 0.5, 0.67, 0.833, 1$, respectively. As the Praseodymium concentration increases, the metal-insulator transition temperature (T_p) decreases while the activation energy in the insulating region ($T > T_p$) and resistivity increases. The structural property of bulk samples have been investigated via X-Ray Diffractometer (XRD). XRD patterns show that these systems are in single-phase. The lattice parameters of undoped sample, $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ can be observed at, $a \approx 15.120 \text{ \AA}$, $b \approx 7.776 \text{ \AA}$ and $c \approx 4.335 \text{ \AA}$. All the samples are in orthorhombic distortion perovskite structure with $a > b > c$. The unit cell volume decreases as Pr concentration increases.

INTRODUCTION

Interest in mixed valence transition metal oxides has been revived since the discovery of high temperature superconductivity in perovskite copper oxides. The perovskite manganese oxides of general formula $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$, where Ln is the rare earth ($\text{Ln} = \text{La, Pr, Nd, Sm}$) and A is the divalent metal ($\text{A} = \text{Ca, Ba, Sr}$) has been studied (Abdullah *et.al.* 2003). Colossal magnetoresistance (CMR) material, which exhibits a large decrease in electrical resistivity under application of a magnetic field, has attracted wide interest due to its potential technological application and the need for better theoretical understanding (M.R. Ibarra *et.al.* 1998). In this structure Mn^{3+} , surrounded by six oxygen atoms, is a Jahn-Teller (JT) atom. The d-shell electronic energy levels t_{2g} (triplet) and e_g (doublet), in consequence, split under a distortion of the octahedrally coordinated Mn-O bonds. The JT splitting reduces the electronic energy. Three strongly coupled and localized (t_{2g}) electrons, occupy the bottom-most levels and form the core spin $S = 3/2$. The fourth electron, occupying the first e_g level, is coupled to the core spin through the

intra-atomic Hund's coupling constant $J > 0$, estimated on the scale of ~ 1 eV. The CMR effect was observed most prominent at typical composition $x \approx 0.33$. It is believed that the magnetotransport properties and the spin structure were correlated via the double exchange (DE) interaction, influenced by the motion of the e_g electrons from the Mn^{3+} to Mn^{4+} ions (Zener *et. al.* 1951). Recent studies have shown that double exchange alone cannot explain the observed behavior in these systems, the average size of the A and B site cations, the mismatch effect and the vacancy in the A and B sites plays a crucial role (Abdelmoula *et. al.* 2000). In the doped rare earth manganites, the Mn^{3+}/Mn^{4+} ratio plays a key role in the attributed physical properties of the compounds, especially transport properties.

EXPERIMENTAL

Polycrystalline praseodymium substituted lanthanum barium manganite samples, $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ with concentration $x = 0, 0.167, 0.33, 0.5, 0.67, 0.833, 1$ were prepared via conventional solid-state reaction method. A well-mixed stoichiometric mixture of $La_2O_3, Pr_6O_{11}, BaCO_3, MnCO_3$ for $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ of 99.9% purities were mixed and grinded for 2 hours. The dried powder was heated at $900^\circ C$ in air for 12 hours to produce a highly reactive powder. After calcinations, the black powdery mixture was reground, palletized, and sintered in air at $1300^\circ C$ for 24 hours. Characterization of the samples were done by Philip x-ray diffractometer with a rotating anode at room temperature with Cu K- α radiation, DC four probe method with closed cycle helium refrigerator in the temperature range of 30 to 300 K.

RESULTS AND DISCUSSION

Structural

The x-ray diffraction patterns of polycrystalline samples of $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ (LPBMO) samples of concentration of $x = 0, 1/6, 1/3, 1/2, 2/3, 5/6$ are presented in Fig. 1. The pattern shows single phase. Samples with 0.5 and 0.67 exhibit low intensity impurity phases with LBMO phase, suggesting these samples do not have clean single phase. From all the samples, the most prominent peak is given by the (200) peak. The unknown peak was appear at concentration of $x = 0.5$ and 0.67 for Pr-doped.

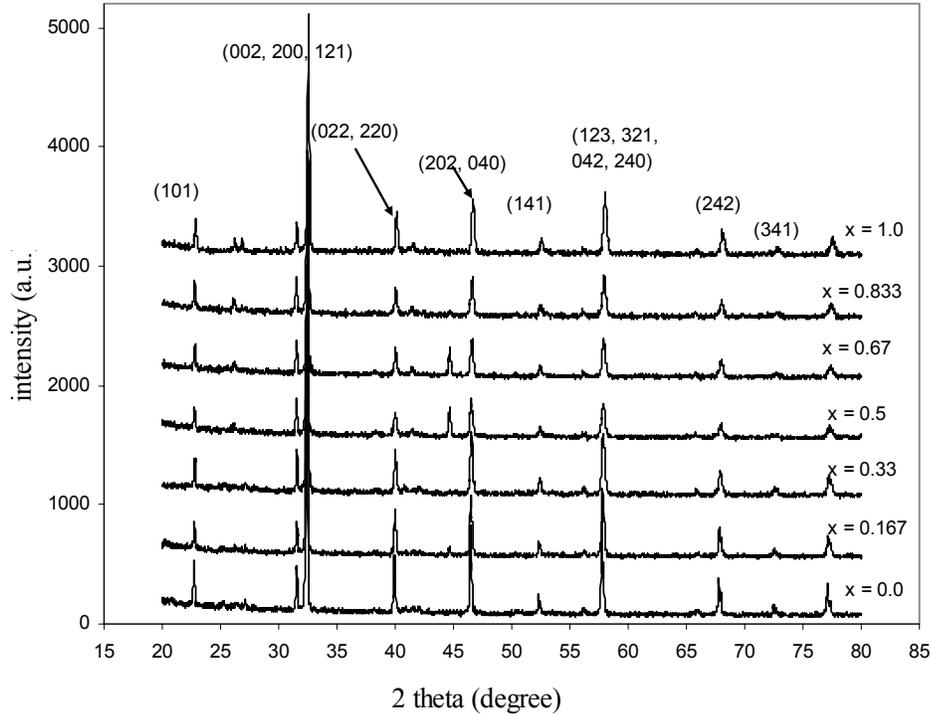


Figure 1: The xrd diffractogram for sample LPBMO $x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833$ and 1 .

The table 1 shows the lattice parameters for LPBMO samples. The result of lattice parameters of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ is $a \approx 5.553 \text{ \AA}$, $b \approx 7.812 \text{ \AA}$ and $c \approx 5.528 \text{ \AA}$. All the samples are in orthorhombic distortion perovskite structure with $a \neq b \neq c$. As the unit cell volume decrease, the concentration of Pr increases. According to Li et al. (1998), the orbital degeneracy leads to a Jahn-teller instability, which causes the oxygen octahedral to distort and lower its site symmetry to tetragonal or orthorhombic and thus removing orbital degeneracy. This distortion increases the Mn-O distance and the Mn-O-Mn angle, which leads to decrease of the DE interactions between Mn ions.

Table 1: The lattice parameter for $(\text{La}_{1-x}\text{Pr}_x)_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ samples

Al concentration	a (\AA)	b/ $\sqrt{2}$ (\AA)	c (\AA)	Volume (\AA^3)
0.000	5.553	5.524	5.528	239.839
0.167	5.522	5.526	5.523	238.372
0.330	5.561	5.523	5.518	239.685
0.500	5.522	5.516	5.500	236.954
0.670	5.520	5.516	5.516	237.527
0.833	5.512	5.516	5.518	237.269
1.000	5.510	5.515	5.516	237.066

Electrical Transport Property

The resistivities, ρ , of the $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ at zero field shown in Figure 2. The resistivity plot of undoped and doped samples shows Metal-Insulator Transition (MIT) at T_p . The manganates doped with larger cations such as Sr, Ba and Pb, have larger bandwidth. As a result the paramagnetic phase can be paramagnetic metal (PMM) or paramagnetic insulator (PMI) transition (PMI) with a small gap. This leads to a weak dependence of ρ on T . There is an interesting dependence of E_a on the Mn-O distance wherein it increases with the Mn-O distance. All samples show semiconducting transport behaviour above T_p and metallic behavior below T_p . With increasing the Pr doping, T_p for the films shifted to lower temperatures, which are 254, 248, 228, 220, 196, 180, 158 K for the bulks with $x = 0, 0.167, 0.33, 0.5, 0.67, 0.833, 1$, respectively. The metal to insulator temperature T_p shifted to lower temperature as Pr doping increases, which indicates the loss of ferromagnetic order. On one hand, impurity dopant shifts the value of T_p to a lower temperature.

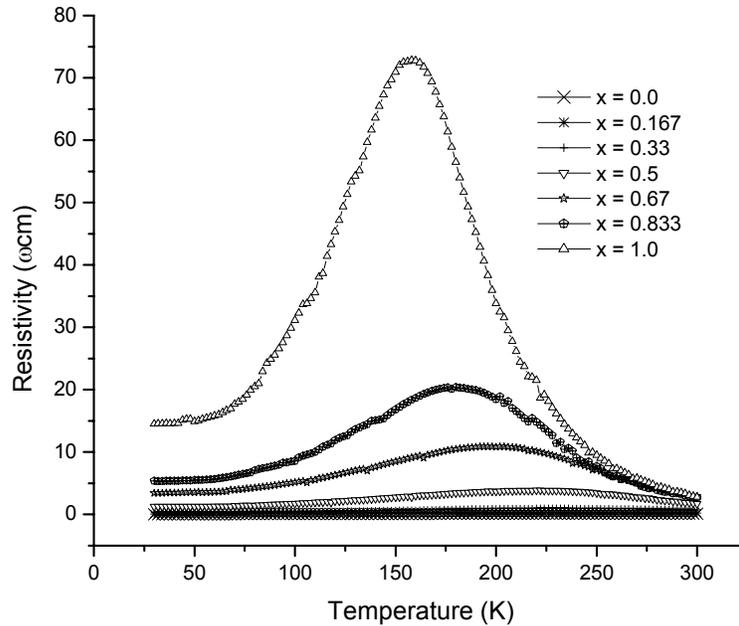


Figure 2: The temperature variation resistance of $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ samples

Figure 3 show the systematic dependence of the peak resistivity temperature (T_p) as a function of Pr concentration. The T_p of LPBMO decreases linearly in the range. All samples show the metal-like variation of resistivity for $T < T_p$. When the temperature, $T > T_p$, the resistivity curves show semiconducting behavior of all the samples above their T_p . Hopping of the itinerant electron, e_g^1 between Mn^{3+} to Mn^{4+} sites is affected by the relative alignment of core spins, t_{2g}^3 , being maximal when the t_{2g}^3 spins are in

parallel and minimal when they are in antiparallel. The structure distortion leads to the decrease of the electron hopping between Mn sites. As a result, DE has been suppressed and T_p are lowered as the hopping concentration increases.

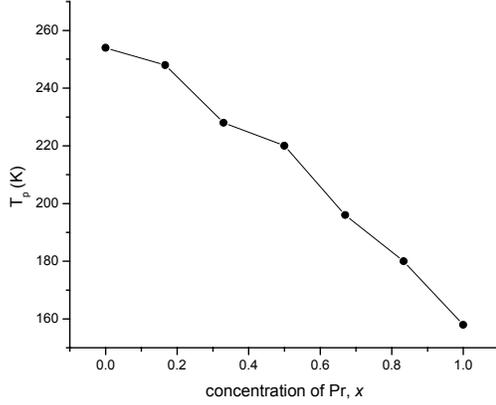


Figure 3: T_p of $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ system as function of Pr concentration

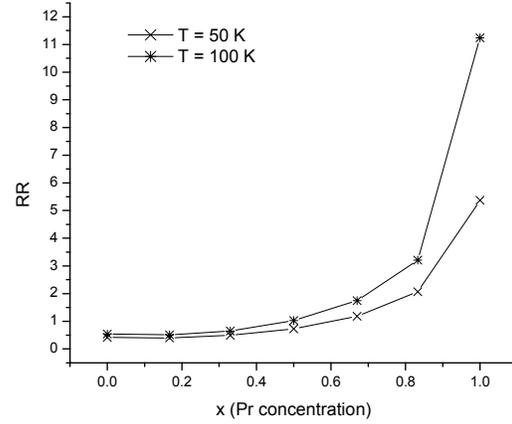


Figure 4: Dependence of resistivity ratio ($RR = \rho_{(TP)}/\rho_{(RT)}$) on the Pr doping concentration.

Figure 4 shows the resistivity ratio as the function of Pr concentration. The resistivity ratio (RR) is defined as $\rho_{(TP)}/\rho_{(RT)}$. Here $\rho_{(TP)}$ and $\rho_{(RT)}$ are the resistivity values at peak temperature and room temperature respectively. The doping at La site induces decrease in T_p , which leads to higher resistivity ratio.

Polaron hopping

The resistivity data for above T_c can be fitted using the nearest-neighbour small-olaronhopping model in the Emin–Holstein theorem (Q. Huang *et. al.* 2001), which gives

$$\rho = BT \exp\left(\frac{E_{hop}}{kT}\right) \quad (1)$$

with

$$B = g_d k_B / ne^2 a^2 v_0 \quad (2)$$

where E_{hop} is the activation energy, B the resistivity coefficient, g_d the lattice geometry factor, k_B the Boltzmann constant, n the polaron concentration, e the electronic charge, a the hopping distance and v_0 the longitudinal optical phonon frequency. To get B and E_{hop} , the experimental data were plotted as $\ln(\rho/T)$ against $1/T$ and fitted using a linear regression method. The fitted lines are presented in figure 5.

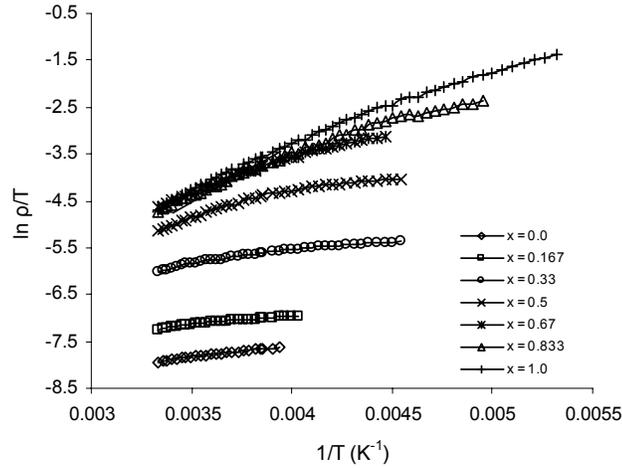


Figure 5: E_a of $(La_{1-x}Pr_x)_{0.5}Ba_{0.5}MnO_3$ systems as a function of Pr concentration

It is suggested that a complex short-range magnetic order coupled with the lattice and related to the charge dynamics persists far above T_c . The polarons are magnetically dressed, as DE is still effective in the vicinity of the trapped carriers. The magnetic nature of the polaron lowers its binding energy. Thus the magnetically dressed polaron has a lower binding energy than a pure lattice polaron. Fe doping weakens the local DE ferromagnetism, so the magnetic nature of the lattice polaron decays, causing E_{hop} to increase. Figure 6 show the activation energy as a function of concentration for LPBMO was obtained from graph of figure 5. It is seen that “ E_{hop} ” increases with increase in Pr concentration from $x = 0.167$ to $x = 1.0$, indicating the widening of the band gap caused possibly by the presence of the Pr^{3+} and the possibility of the end of further oxygen intake, thus the radius and electronegativity factors again play the major role and promoting insulating behaviour.

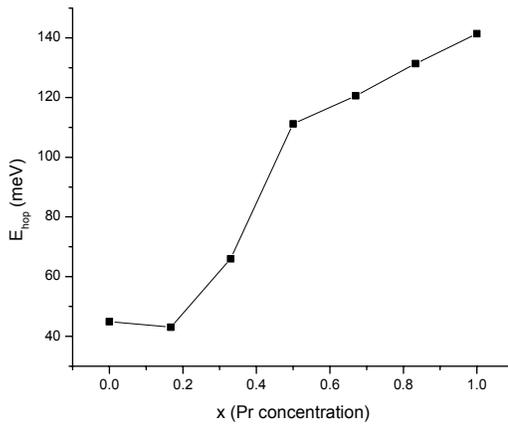


Figure 6: Dependence of activation energy (E_{hop}) on the Pr doping concentration.

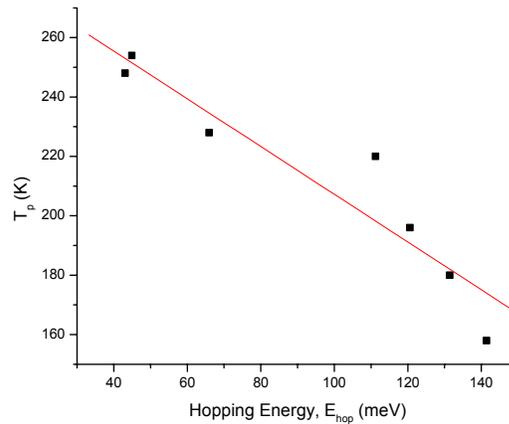


Figure 7: T_p vs. activation energy, E_a against Pr concentration of LBMO system

Figure 7 shows the correlation between T_p and the activation energy (E_a) for conduction in the PM phase, which is proportional to the polaron binding energy (E_a). The lattice distortions around the defects favor the localization of the polarons (E_a increases). This becomes apparent in the PM phase as an increase of E_a and a decrease of the temperature at which metallic behavior is observed (T_p). We can conclude that in samples without grain boundaries, the MIT temperature is related to the electron-lattice interaction, which is increased by the introduction of chemical defects.

CONCLUSION

In summary, the electrical and structural properties of sample LPBMO with Praseodymium (Pr) substitution at La site with Pr concentration $x = 0, 0.167, 0.33, 0.5, 0.67, 0.833$ and 1 were studied. All the samples exhibit Metal-Insulator Transition (MIT). With increasing the Pr doping, T_p for the films shifted to lower temperatures, which are 254, 248, 228, 220, 196, 180, 158 K for the bulks with $x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833$ and 1.0 respectively. As the Pr concentration increases, the metal-insulator transition temperature (T_p) decreases while the activation energy in the insulating region ($T > T_p$) and resistivity increases. The lowering of T_p is related to the weakening of double exchange ferromagnetic interactions. XRD data shows that these systems are single phase with orthorhombic distorted perovskite structures. As the unit cell volume decrease, the concentration of Pr increases. The most prominent peak is given by the (200) peak.

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