Disorder Phenomena in Nd-doped $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ Manganites
(Fenomena Ketidak-tertiban dalam Sebatian Mangan $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ Berdop Nd

H. Abdullah* & S.A. Halim

ABSTRACT

Polycrystalline samples of $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ with x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833, and 1.0 have been prepared using the solid state reaction. The samples were calcined at 900ºC for 12 hours, pelletized and sintered at 1300ºC for 24 hours. The structures were investigated via X-ray diffraction (XRD) method. XRD patterns showed orthorhombic distorted perovskite structures. The scanning electron microscopy (SEM) micrographs showed the disorder of the structure in all substitutions. This influenced the value of the magnetoresistance (MR). The MR effects are measured using the four point probe technique with a magnetic field of $B \leq 1T$ at temperatures of 90, 100, 150, 200, 250, 270 and 300 K. Overall, the MR increased as the temperature decreased. All doping concentrations gave a small variation range (~10% to ~56%). The highest MR value of 56.5 % is observed at 100 K for a sample with x = 1.0. The influence of disorder on the magnetoresistance in $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ manganites at low temperatures was also discussed in this paper.

Keywords: Disordered structure; low-field magnetoresistance; orthorhombic

ABSTRAK

Sample polihablur $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ dengan x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833 dan 1.0) telah disediakan melalui tindak balas keadaan pepejal. Sampel telah dipanaskan pada 900ºC selama 12 jam, dipeletkan dan dipanaskan pada 1300ºC selama 24 jam. Strukturnya dikaji melalui kaedah pembelauan sinar-X (XRD). Corak-corak XRD menunjukkan struktur herotan ortorombus. Mikrograf-mikrograf bagi mikroskop imbasan elektron (SEM) menunjukkan struktur yang tak teratur yang terlibat dalam setiap penggantian. Ini juga mempengaruhi nilai magnetorintangan (MR). Kesan-kesan magnetorintangan (MR) diukur menggunakan teknik empat titik penduga, pada medan magnet $B \leq 1T$ pada 90, 100, 150, 200, 250, 270 dan 300 K. MR meningkat bila suhu yang dikenakan menurun. Semua kepekatan dopan memberi jurang perubahan yang kecil (~10% hingga ~56%). Nilai MR yang tertinggi adalah 56.5% diperhatikan pada 100 K untuk sampel x = 1.0. Pengaruh ketidak-tertiban terhadap magnetorintangan dalam sistem sebatian mangan $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ pada suhu rendah juga dibincangkan.

Kata kunci: Ketidak-tertiban struktur; medan-rendah magnetorintangan; ortorombus

INTRODUCTION

Interest in mixed valence transition metal oxides has been revived since the discovery of high temperature superconductivity in perovskite copper oxides. Transition metal (TM) based mixed oxides exhibit a very rich spectrum of remarkable electric, magnetic, and optical properties that are tunable by the composition over a broad limit. Among these materials $Ln_{1-x}A_xMnO_3$, where Ln is a rare earth metal (Ln = La, Pr, Nd, Sm) and A is a divalent metal (A = Ca, Ba, Sr), are fascinating due to their extraordinary behaviour (Xial 2003). Colossal magnetoresistance (CMR) materials, which exhibit a large decrease in electrical resistivity under the application of a magnetic field, have attracted wide interest due to their potential technological application and the need for a better theoretical understanding. In this structure, the Mn^{3+} atom, which is surrounded by six oxygen atoms, is a Jahn-Teller (JT) atom. The d-shell electronic energy levels (t_{2g} (triplet) and e_g (doublet)), as a consequence, split under a distortion of the octahedrally coordinated Mn-O bonds. The JT splitting reduces the electronic energy. Three strongly coupled and localised (t_{2g}) electrons occupy the bottom-most levels and form the core spin, S = 3/2. The fourth electron, which occupies the first level, e_g, is coupled to the core spin through the intra-atomic Hund's coupling constant, J > 0, which is estimated on the scale of ~1 eV.

The CMR effect was observed most prominently at a typical composition of $x \approx 0.33$. It is believed that the magnetotransport properties and the spin structure are correlated via the double exchange (DE) interaction, which is influenced by the motion of the e_g electrons from the Mn^{3+} to the Mn^{4+} ions (Zener 1951).

Recent studies have shown that the double exchange alone cannot explain the observed behaviour 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 play a crucial role in the behaviour of these systems as stated by Abdelmoula et al. (2000). Thus, by doping the

rare earth ions at the Pr site, we have studied how the physical properties, such as structure, microstructure, and magnetoresistance are influenced by both the variance in the A-site disorder and the rare earth ion–Mn ion coupling at low temperatures.

EXPERIMENTAL DETAILS

Neodymium substituted praseodymium barium manganite samples, $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$, with concentrations of x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833, and 1.0 were prepared via conventional solid-state reaction methods. A well-mixed stoichiometric mixture of Pr_6O_{11}, Nd_2O_3, $BaCO_3$, and $MnCO_3$ for $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ with 99.9% purity was mixed and grinded for 2 hours. The dried powder was heated at 900°C in air for 12 hours to produce a highly reactive powder. After calcinations, the black powdery mixture was reground, palletised, and sintered in air at 1300°C for 24 hours. Characterisations of the samples were done with a Philips X-ray diffractometer for structural parameters. The MR effects were measured by using the four point probe technique. The magnetoresistance was measured with a magnetic field of B ≤ 1T at temperatures of 90, 100, 150, 200, 250, 270 and 300 K.

RESULTS AND DISCUSSION

The XRD patterns of polycrystalline samples of $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ (PNBMO) with concentrations of x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833 and 1.0 are presented in Figure 1. The patterns show the single-phase with orthorhombic distorted perovskite structures. The most prominent peaks are demonstrated in the <121> and <200> directions. Samples with x = 0.5, 0.67 and 0.833 exhibit low intensity impurity phases with the PBMO phase. Table 1 shows that the lattice parameters (a, b, and c) change with an increase of Nd concentration. This leads to the distortion of the manganites perovskite structure. The distortion increases the Mn-O distance and the Mn-O-Mn angle, which leads to a decrease in the double exchange (DE) interactions between the Mn ions. 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 orthorhombic and thus removes orbital degeneracy.

The microstructures of $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ with x = 0.000, 0.167, 0.333, 0.500, 0.677, 0.833, and 1.000 are shown in Figures 2(a) - (f). The pure sample, with x = 0.0, has uniform grain size, with a grain size range from 0.1 μm to 1 μm and an average size of 1 μm. The grains were well compacted for the sample with x = 0.167. The grain size increases from 0.5 μm to 1.2 μm for x = 0.167 to x = 0.833, respectively. The grains of all samples were observed to be round in shape, except for the sample with x = 0.5, where it formed square shapes. As the doping concentration increased from x = 0.167 to 0.833, the grain size increased gradually. The grain boundary is not very

TABLE 1. Lattice Parameter and Unit cell volume of Nd doped in $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ system

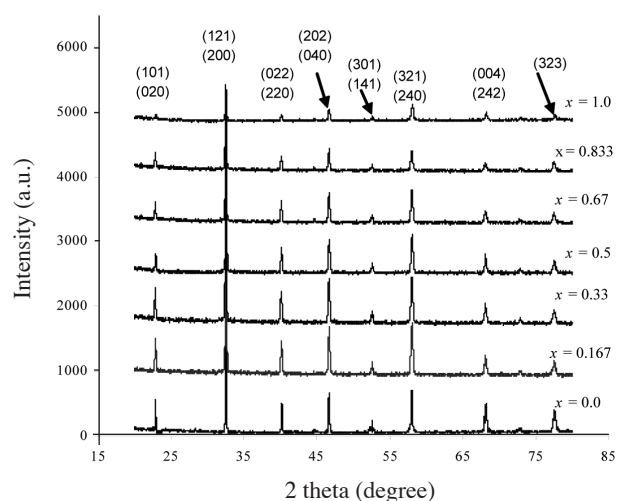| x	a (Å)	$b/\sqrt{2}$ (Å)	c (Å)	Volume (Å)^3
0.000	5.484	5.499	5.474	233.503
0.167	5.494	5.509	5.487	234.898
0.333	5.494	5.526	5.481	235.355
0.500	5.495	5.506	5.484	234.665
0.670	5.491	5.513	5.483	234.765
0.833	5.486	5.484	5.469	232.750
1.000	5.484	5.450	5.463	230.949

FIGURE 1. The X-ray diffractogram for PNBMO samples (x = 0.0, 0.167, 0.33, 0.5, 0.67, 0.833 and 1.0)

visible to see since the grains are too fine. The thickness of the grain boundary can be explained by the increment of the MR value.

Figure 3 shows the graph of the sample grain size diameter versus the concentration of Nd. The increment of x from 0.167 to 0.833 demonstrates that the grain size change is not significant. The disorder of the grain size was due to the radii size of the particle itself. The radii size plays a primary role since the Pr^{3+} ions are similar in size to the Nd^{3+} atoms. As the Nd ion concentration is increased, more Nd^{3+} ions will take the place of Pr^{3+} ions. In the $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ system, substitution of Nd^{3+} ions for the Pr^{3+} site in $LaBaMnO_3$ leads to grain growth inhibition, disorder in the grain size, Lanthanum segregation, and second phase formation. The disorder of structure and connectivity between the particles are clearly seen as the samples are doped for several concentrations.

The corresponding MR ratio is shown in Figure 4. The MR ratio is calculated according to MR (%) = [($\rho(B)$ − $\rho(0)$) / $\rho(0)$] × 100%; where $\rho(0)$ is the zero field resistivity and $\rho(B)$ is the resistivity with a magnetic field of B = 1T. The MR was measured at 90, 100, 150, 200, 250, 270 and 300 K for various concentrations. Overall,
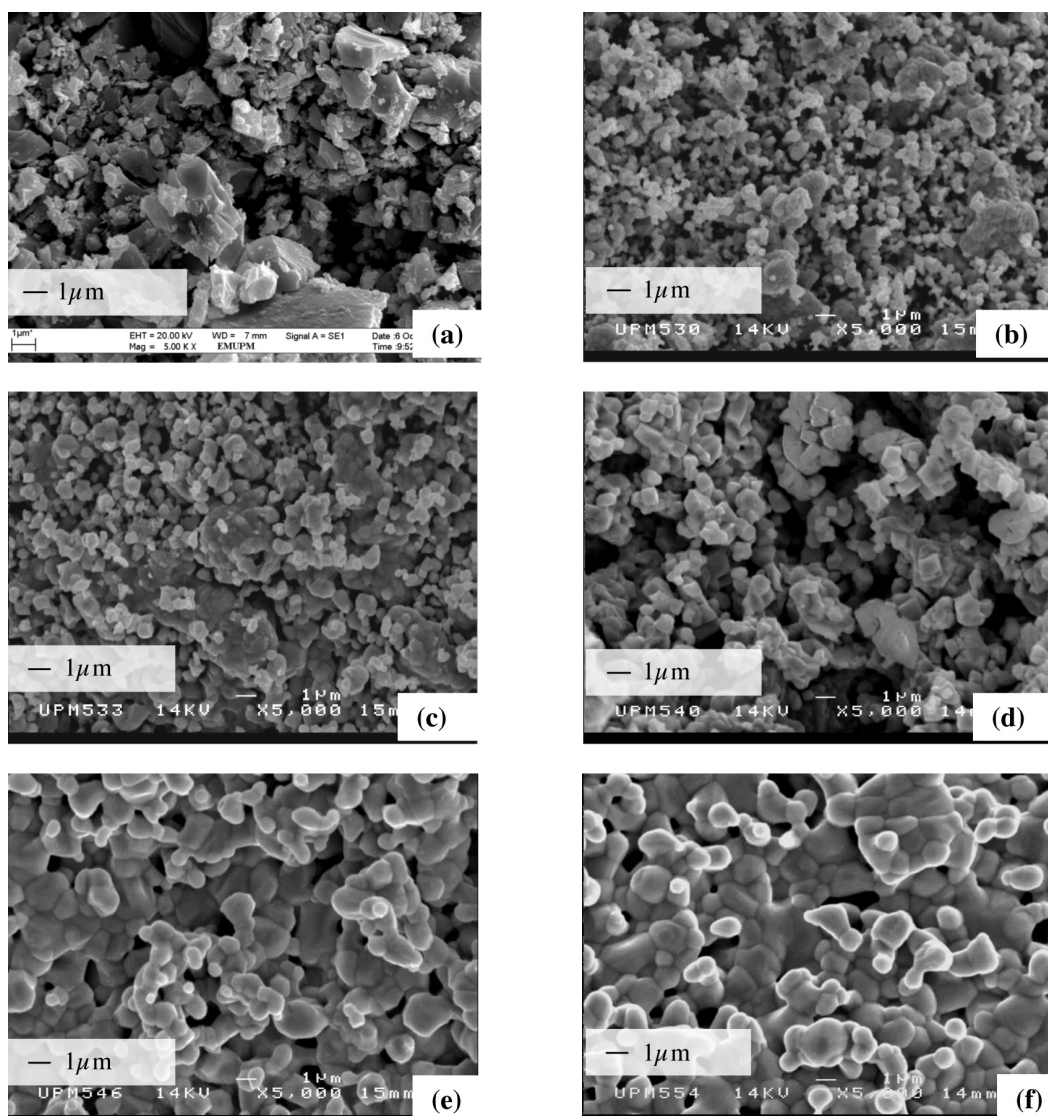
FIGURE 2. SEM images of the fractured surface of $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ samples with (a) x=0.0 (b) x=0.167 (c) x=0.33 and (d) x=0.5 (e) x= 0.67 (f) x=0.833

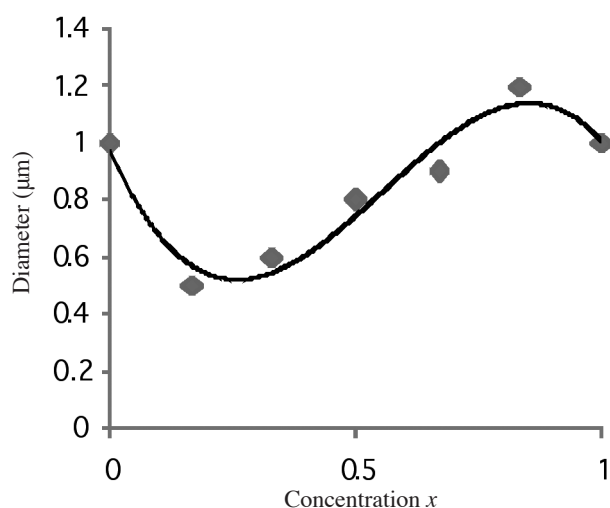FIGURE 3. Sample grain size of the $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ system

the MR decreased with increasing doping concentration and increased with decreasing temperature. This is due to enhanced inter-grain tunnelling magnetoresistance at low temperatures, which arises as a result of the varying Mn environment at the interfaces. The MR of granular systems consists of Low-Field Magnetoresistance (LFMR) and High-Field Magnetoresistance (HFMR), which are closely related to the surface effects of the grains. The region of Low-Field Magnetoresistance (LFMR) is considered to exist from 0T to 0.1T, while the region of High-Field Magnetoresistance (LFMR) is considered to exist from 0.1T to 1T. Figures 3(c), (d), (e) and (f) indicate the existence of a LFMR. At a low field (about 0.1T), a MR gradient of 150% MR/tesla was observed for $x = 0.833$ at 90 K. This value is useful for low field applications. For high field (0.1 – 1T), the gradient is about 39.1% MR/tesla. This value is also acceptable as a requirement for a sensing element. A normal negative CMR effect with a non-saturation condition has been observed
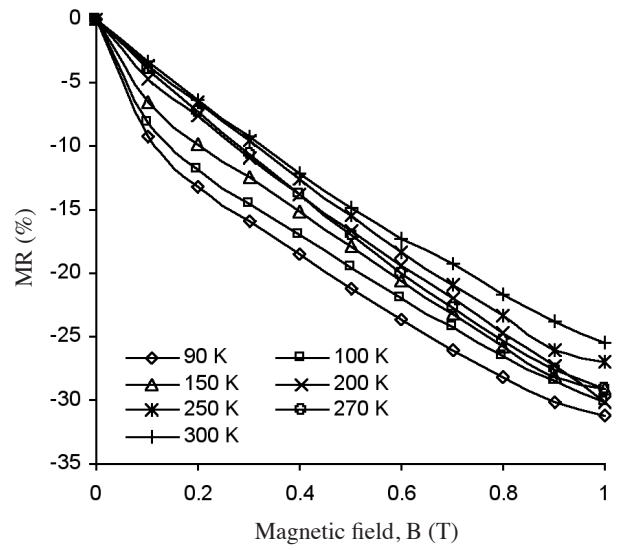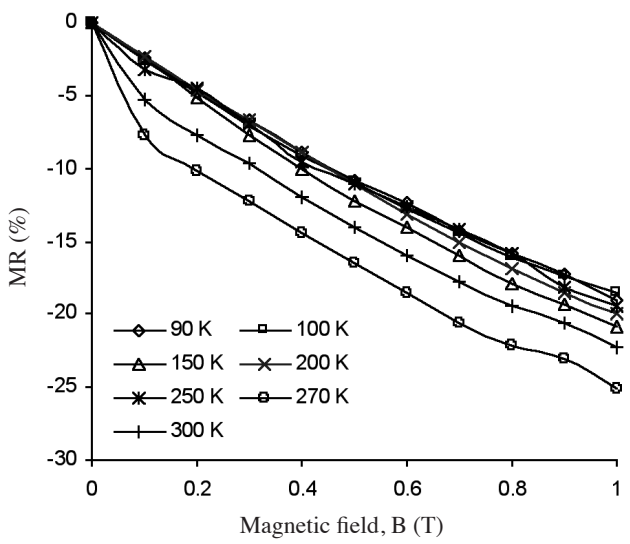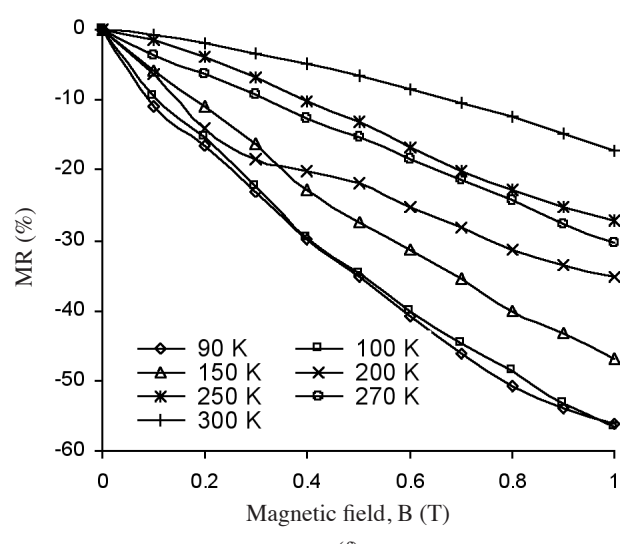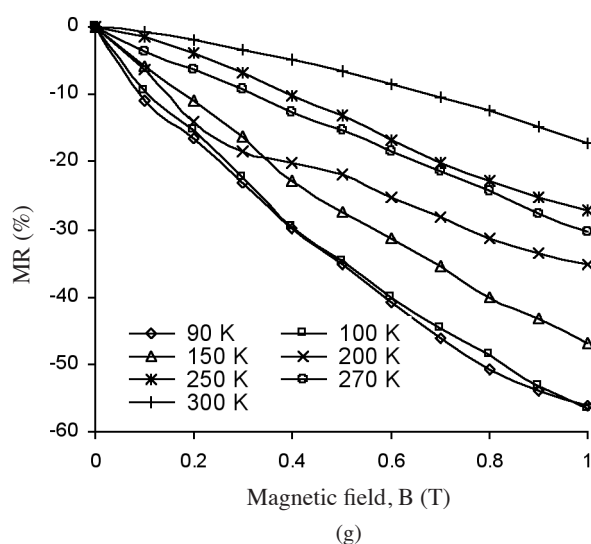
(a)

(b)

(c)

(d)

(e)

(f)

cont.

(g)
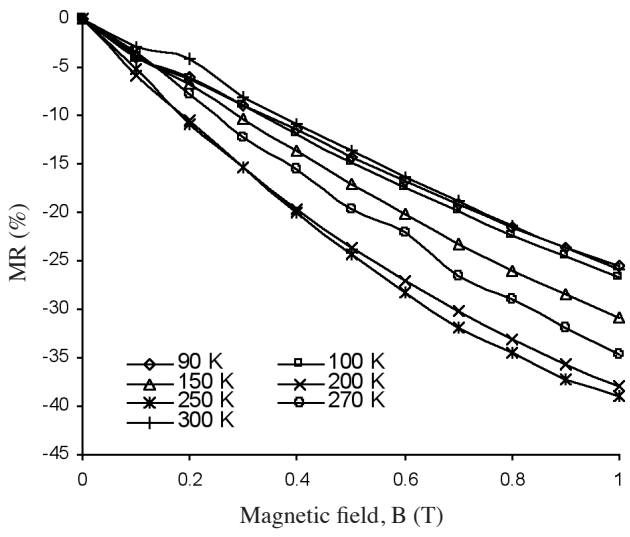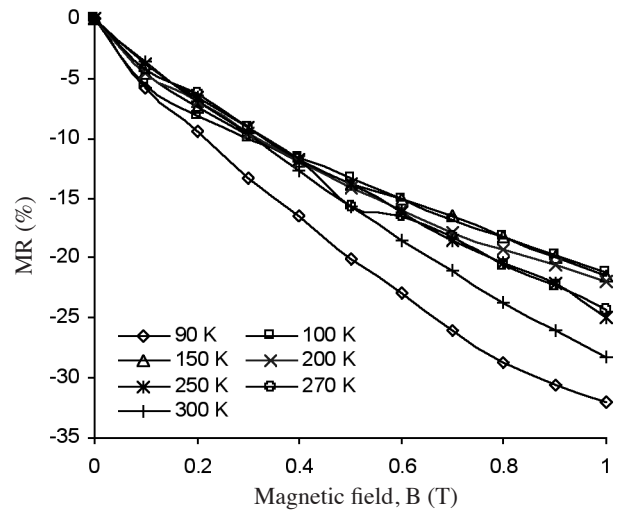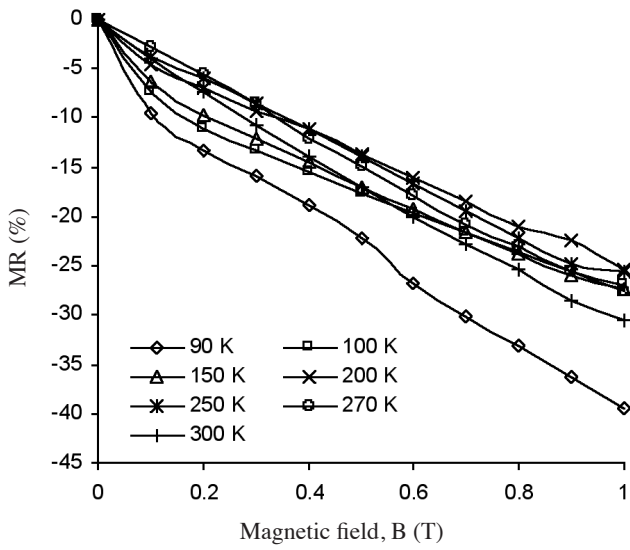
FIGURE 4. Temperature dependence of resistivity (under magnetic field of B = 1 T) as well as corresponding MR for PNBMO with (a) $x = 0.0$ (b) $x = 0.167$ (c) $x = 0.33$ and (d) $x = 0.5$ (e) $x = 0.67$ (f) $x = 0.833$ (g) $x = 1.0$

and demonstrates that a higher (more than 1 T) magnetic field is needed to fully reorient the spin. The middle doping concentration ($0.33 \leq x \leq 0.833$) demonstrates both LFMR and HFMR. However, at $x = 0.0$, 0.167, and 1.0, a linear relationship was observed. At low temperatures, MR decreases, which can be explained by the transportation of electrons within a single magnetic domain. The e_g electrons transfer between Mn^{3+} and Mn^{4+} ions is easy, and leads to decrease in MR. The pairs of Mn^{3+} and Mn^{4+} spins, which may not be parallel in the vicinity of domain wall boundaries, act as a hindrance for electron transport. The magnetic domains tend to align along the field direction in the presence of a sufficiently strong magnetic field. As a result, hopping of electrons becomes easy across the domain wall boundaries, and the resistivity decreases.

Figure 5 shows that the MR increased when the temperature decreased. All doping concentrations give a small variation range (~10% to ~56%). The highest MR value of 56.5 % was observed at 100K for the sample with $x = 1.0$. This proves that the MR change with temperature is due to the spin polarisation change and a slight spin flip occurs for the tunnelling of electrons between adjacent PNBMO grains. The MR fluctuation below 300K was believed to be related to the spin-glass transition, which has often been seen in crystalline manganites because of the canted spins in the grain surface region due to the disordered state or structure. This can be seen from the SEM micrographs. A similar spin-glass behaviour also has been reported by Goodenough (2002), in the system of $LaMn_{1-x}Sc_xO_3$.
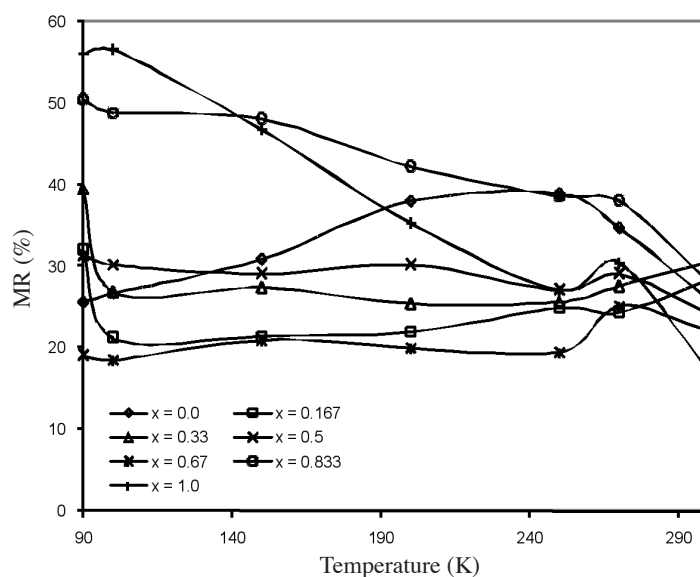

FIGURE 5. MR (%) of PNBMO systems as a function of temperature measured in a magnetic field of 1 T

CONCLUSION

A detailed magnetic field-dependent study on the structural and magnetoresistance properties of $(Pr_{1-x}Nd_x)_{0.67}Ba_{0.33}MnO_3$ (PNBMO) has been reported. Structural studies showed that these systems were single phase with orthorhombic distorted perovskite structures. Overall, the MR change with the temperature is due to spin polarisation changes. All doping concentrations showed a small variation range ($\sim$10% to $\sim$56%). The highest MR value of 56.5 % was observed at 100 K for the sample with x = 1.0. The MR fluctuation was believed to be related to the spin glass transition, which has often been seen in crystalline manganites because of the canted spins in the grain surface region due to the disordered state. The SEM micrographs showed the disorder of the structure involved in all substitution, which influenced the value of MR.

REFERENCES

Abdelmoula, N., Cheikh-Rouhou, A. & Reversat, L. 2001. Structural, magnetic and magnetoresistive properties of $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ manganites, *Journal of Physics: Condensed Matter* 13: 449-458.

Goodenough, J.B. Dass, R.I. & Zhou, J. 2002. Spin-glass to ferromagnet transition in $LaMn_{1-x}Sc_xO_3$. *Solid State Sciences* 4: 297-304.

Li, Y.M., N. d'Ambrumenil & Fulde, P. 1998. Thermodynamic properties of a band Jahn-Teller System, *Phys. Rev.* B57, R14016-R14019.

Xial, Z.C., Yuan, S.L., Feng, W., Zhang, L.J., Zhang, G.H., Tang, J., Liu, L., Liu, S., Peng, G., Niu, D.W., Chen, L., Zheng, Q.H., Fang, Z.H. & Tang, C.Q. 2003. Large room temperature magnetoresistance in YSZ doped $La_{0.67}Ba_{0.33}MnO_3$ composite, *Solid State Communications* 128: 291-294.

Zener, C. 1951. Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of Manganese with perovskite structure. *Phys. Rev.* 82: 403-405.

H. Abdullah*
Faculty of Engineering and Built Environment
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

S.A. Halim
Physics Department
Faculty of Sciences
Universiti Putra Malaysia
43400 UPM Serdang, Selangor D.E.
Malaysia

*Corresponding author; email: huda@vlsi.eng.ukm.my