The Effect of Sr-substitution on the Electrical and Structural Properties in Colossal Magnetoresistive La$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.05, 0.12, 0.18, 0.30$ and $0.40$

Nor Azah Nik-Jaafar$^1$*, R. Abd-Shukor$^2$

$^1$Pusat PERMATApintar Negara®, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
$^2$School of Applied Physics, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

*norazah_nj@ukm.edu.my

Abstract. The effect of Sr-substitution at the La-site in colossal magnetoresistive La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.05, 0.12, 0.18, 0.30$ and $0.40$) on the electrical transport and structural property has been studied. Investigations were conducted through X-ray diffraction (XRD) analysis, temperature-dependent electrical resistance measurements and scanning electron microscope (SEM). Between $x = 0.05$ to $0.30$, XRD analysis showed that at room temperature, the composition has orthorhombic structure. At $x = 0.40$ composition, the structure is rhombohedral. Electrical resistance measurements (30-290 K) showed that the material was insulating between $x = 0.05$ to $0.12$, whereas increased substitution from $x = 0.18$ to $0.40$ transformed the electrical property from insulating to metallic. The transformation in the transport property along with the conspicuous change in structure with increase Sr-substitution $x$ provide a strong indication of a large electron-lattice coupling in this material.

1. Introduction

The novel properties of Ln$_{1-x}$A$_x$MnO$_3$ (Ln = La, Nd, Pr; A = Sr, Ca, Ba, Pb) remain a subject of research interest after more than two decades since the colossal magnetoresistance effect (CMR) was discovered in this material. At the time upon its discovery, CMR effect attracted wide attention due to its potential technological applications, therefore spurred intense research activity on this manganese oxide of perovskite structure.

Equally interesting is the rich structure-properties phase diagram of La$_{1-x}$A$_x$MnO$_3$ as a function of composition ($0.0 \leq x \leq 1.0$) and temperature. At both $x = 0.0$ and $1.0$, La$_{1-x}$A$_x$MnO$_3$ is an antiferromagnetic (AFM) insulator at low temperatures. The insulating nature of the parent compound ($x = 0.0$) as well as the anisotropic magnetic interaction is particularly due to the Jahn-Teller distortion around Mn$^{3+}$ ions. When the compound is progressively hole-doped (substitution of divalent cation at the La-site), the proportion of Mn$^{4+}$ ions increases, which in turn decreases the orthorhombic distortion, leading to more cubic structures. The composition becomes rhombohedral or pseudocubic at certain value of $x$. In La$_{1-x}$Sr$_x$MnO$_3$, substitution of Sr transforms the compound from AFM insulator to ferromagnetic (FM) insulator at $x \approx 0.1$, and to ferromagnetic metal at $x \approx 0.16$ [1,2]. At $0.2 < x < 0.5$ a transition from a high temperature paramagnetic insulator (PMI) to a low temperature ferromagnetic metallic (FMM) phase occurs. It is in this composition range CMR effect the strongest [3]. The magnitude of decrease in resistivity upon the application of magnetic field is the highest in the region...
of Curie temperature $T_C$, which is accompanied by an insulator-metal transition at $T_{IM}$ [4,5]. This simultaneous observation of itinerant electron and ferromagnetism is explained by Zener’s double exchange mechanism [6]. Millis et al. argued that in addition of double exchange physics, there must be a strong electron-phonon interaction which arise from the Jahn-Teller splitting of the outer Mn d level [7]. This suggests the crucial role of the lattice and electron-lattice coupling. Therefore, in understanding the novel transport properties of perovskite manganites, it is imperative to consider the overall lattice symmetry as well as the local lattice distortions.

In this work, the effect of Sr-substitution on the structural and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at doping compositions $x = 0.05, 0.12, 0.18, 0.30$ and $0.40$ have been investigated.

2. Experimental Details

Samples of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.05, 0.12, 0.18, 0.30$ and $0.40$) were prepared by conventional solid state reaction method. Starting materials of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$ and $\text{MnO}_2$ with purity of $\geq 99.9\%$ were used. The mixed powders were ground thoroughly and were calcined at $900^\circ C$ for a period of 24 hours with intermediate grinding. The calcined materials were pressed into pellets of 13 mm in diameter and ~1.5 mm in thickness. This was followed by sintering in air at $1300^\circ C$ for 12 hours and left to furnace-cooled.

The temperature-dependent electrical resistance measurements were carried out using the d.c. four-point probe method with silver paint contacts. Samples’ crystallization were characterized by X-ray powder diffraction (XRD) technique using Bruker AXS D8 Advance Diffractometer with Cu-K$\alpha$ radiation. The microstructure of the samples was examined using a Philips XL 30 Scanning Electron Microscope (SEM).

3. Results and Discussion

Figure 1 shows the XRD diffraction pattern of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.05, 0.12, 0.18, 0.30$ and $0.40$. In the composition range between $x = 0.05$ to $x = 0.30$ the material crystallizes in orthorhombic structure. Increased doping at $x = 0.40$ change the crystallization to rhombohedral structure with space group $R-3c$. Table 1 shows the lattice constants of the samples.

| Sample $x$ | Lattice parameters [Å] | Structure (Space group) | Volume [Å$^3$] |
|------------|-------------------------|-------------------------|----------------|
| 0.05       | 5.5368 5.5539 7.7506    | Orthorhombic ($Pbnm$)   | 238.34         |
| 0.12       | 5.5093 5.5430 7.7944    | Orthorhombic ($Pcmn$)   | 238.03         |
| 0.18       | 5.5373 5.5023 7.7853    | Orthorhombic ($Pbnm$)   | 237.20         |
| 0.30       | 5.4512 7.7386 5.4981    | Orthorhombic ($Pnma$)   | 231.94         |
| 0.40       | 5.4926 5.4926 13.361    | Rhombohedral ($R-3c$)   | 403.08         |
Figure 1. XRD patterns of La$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.05$, 0.12, 0.18, 0.30 and 0.40.
Figure 2. Normalized resistance versus temperature of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) for \(x = 0.05\) and 0.12.

Figure 2 shows the results of temperature-dependent resistance measurement (30–300 K) for \(x = 0.05\) and 0.12 samples. As temperature decreased, the \(x = 0.05\) sample at first showed an insulating behavior until it reached a peak in resistance at 151 K. Below 151 K the resistance was decreasing with temperature characteristics of a metallic state although the resistivity remains at ~10 folds higher than that at room temperature. Sample \(x = 0.12\) is an insulator over the whole measurement range.

Figure 3. Normalized resistance versus temperature of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) for \(x = 0.18\), 0.30 and 0.40.
Figure 3 shows the results of temperature-dependent resistance measurement (30–300 K) for \( x = 0.18, 0.30 \) and 0.40. At these compositions, the materials showed metallic resistivity, while the resistance variation with temperature suggests of a peak in resistivity at ~270 K for \( x = 0.30 \). It can be concluded that within composition range between \( x = 0.18 \) to 0.40, the material had low temperature metallic conductivity.

Figure 4(a) and 4(b) show the SEM micrograph at 3000× magnification for \( x = 0.05 \) and 0.30 respectively. The average grain size for \( x = 0.15 \) is ~5 μm, and the average grain size for \( x = 0.30 \) was 1-2 μm. Based on the SEM micrographs of all the compositions, it was shown in general that sample’s grain size decreased with the increment in \( x \).

**Figure 4.** Scanning electron micrograph of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) for (a) \( x = 0.05 \), and (b) \( x = 0.30 \).

At the amount of hole doping which corresponds to \( x = 0.18, 0.30 \) and 0.40, the resistivity of the compound was metallic below 300 K. By inferring the temperature-composition phase diagram of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) [1], it can be safely assumed that the insular-metal transition preceded the metallic phase at somewhere above 300 K, which is outside our measurement range. Hence, at \( x = 0.18 \) the low temperature transport property in La\(_{1-x}\)Sr\(_x\)MnO\(_3\) was transformed from insulating to metallic. Previous works reported that the transformation from high temperature paramagnetic insulator into low temperature ferromagnetic metal was manifested at composition \( x > 0.15 \). The insulating resistivity was shown by the \( x = 0.05 \) and 0.12 compositions in this study were as expected as the insulating nature of the composition below \( x = 0.15 \) has been well established [4].

Between \( x = 0.05 \) to \( x = 0.30 \) composition, the structure of the sample at room temperature was orthorhombic. At \( x = 0.40 \), the composition had rhombohedral structure. Previous study on La\(_{1-x}\)Sr\(_x\)MnO\(_3\) in the form of melt-grown crystals [1], structural transition from rhombohedral (R\( \bar{3} \)c) to orthorhombic (Pbnm) has been reported to occur for \( x = 0.15, 0.175 \) and 0.2 compositions at temperatures near 300 K. This structural transition accounted for the resistivity anomalies was shown by these compositions at those temperatures, whereby for the \( x = 0.175 \) composition this anomaly was exhibited at ~200 K, that was below the room temperature. Thus, this implies of the possibility that for the \( x = 0.18 \) composition in our study, the rhombohedral to orthorhombic transition may have taken place at above the room temperature. The same argument also applies to the \( x = 0.3 \) composition. The \( x = 0.3 \) to 0.4 composition has been shown in that study to crystallize in the rhombohedral structure over the whole temperature range below 500 K.

4. Conclusion

In conclusion, the electrical and structural properties of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) for \( x = 0.05, 0.12, 0.18, 0.30 \) and 0.40 in the temperature range below 300 K has been investigated. The electrical resistivity was insulating for \( x = 0.05 \) and 0.12, and metallic for \( x = 0.18, 0.30 \) and 0.40. The room temperature structural formation
of all the compositions was orthorhombic, except for \( x = 0.40 \) which was rhombohedral. Sr-substitution at the La-site in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) was tantamount to hole doping, which increased Mn\(^{4+}\) proportion, therefore decreased the Jahn-Teller distortion. This effects the transformation from the insulating to metallic resistivity as observed at \( x = 0.18 \). The structural transformation from orthorhombic to rhombohedral at \( x = 0.40 \) was attributed to the decrease in the Jahn-Teller distortion around Mn\(^{3+}\) as La was progressively substituted with Sr [4]. The transformation of the transport property along with the conspicuous change in structure with increase Sr-substitution provided substantial evidence of a strong electron-lattice coupling in this manganese oxide of perovskite structure.

Acknowledgement
This work has been supported by the Ministry of Higher Education, Malaysia under research grant ERGS/1/2012/STG02/CUCMS/03/2. Nor Azah Nik-Jaafar would like to express her gratitude to Cyberjaya University College of Medical Sciences (CUCMS) for facilitating this research work throughout the whole duration of this project.

References
[1] Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 Insulator-metal transition and giant magnetoresistance in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) *Phys. Rev.* B 51 14103-14109
[2] Moritomo Y, Asamitsu A and Tokura Y 1997 Enhanced electron-lattice coupling in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) near the metal-insulator phase boundary *Phy. Rev.* B 56 12190-12195
[3] Bishop A R and Röder H 1997 Theory of colossal magnetoresistance *Current Opinion in Solid State and Materials Science* 2 244-251
[4] Rao C N R and Raychaudhuri A K 1998 Colossal magnetoresistance, charge ordering and other novel properties of manganites and related materials *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides* ed Rao C N R and Raveau B (Singapore: World Scientific Publishing Co. Pte. Ltd.) pp 1-42
[5] Kusters R M, Singelton J, Keen D A, McGreevy R and Hayes W 1989 Magnetoresistance measurements on the magnetic semiconductor \( \text{Nd}_{0.3}\text{Pb}_{0.7}\text{MnO}_3 \) *Physica* B 155 362-365
[6] 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
[7] Millis A J, Littlewood P B and Shraiman B I 1995 Double exchange alone does not explain the resistivity of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) *Phy. Rev. Lett.* 74 5144-5147