



UNIVERSITI PUTRA MALAYSIA

***EFFECT OF NANOSIZED AL₂O₃ ADDED TO PR_{0.6}SR_{0.33}MNO₃
SYSTEM TOWARDS THE STRUCTURE, ELECTRICAL AND
MAGNETOTRANSPORT PROPERTIES***

NUR ALYANI NAZIRAH BINTI ROSLI

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Effect of nanosized Al_2O_3 added to $\text{Pr}_{0.6}\text{Sr}_{0.33}\text{MnO}_3$ system towards the structure, electrical and magnetotransport properties

By
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Thesis Submitted to the Department of Physics, Faculty of Science, University Putra Malaysia, in partial fulfillment of the Requirements for the Degree of Bachelor of Science in Physics with Education (Honours)
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ABSTRACT

Effect of nanosized Al_2O_3 added to $\text{Pr}_{0.6}\text{Sr}_{0.33}\text{MnO}_3$ system towards the structure, electrical and magnetotransport properties

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The importance of the perovskite manganites has been paid worldwide due to their colossal magnetoresistance effect and technological applications for magnetic field sensing devices. A higher magnetoresistance at low magnetic field (LFMR) with low temperature and electrical resistivity are needed by most of the magnetic devices. Previous research proved that the enhanced LFMR can be achieved by introducing secondary insulating phase. In this research, the $(1-x) \text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 - (x)\text{Al}_2\text{O}_3$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.10) composites have been prepared by using sol gel reaction method. The structure, electrical and magnetotransport properties are systematically investigated. The results of X-ray Diffraction (XRD) indicates that all the samples are single-phase without any detectable impurity or secondary phase of Al_2O_3 was observed. Other than that, the magnetic behavior of PSMO is ferromagnetic in room temperature, which the curie temperature of PSMO is predicted to be between 200K to 305K. Next, the enhancement of LFMR was detected and also the shifting of T_{MI} to the lower temperature when the Al_2O_3 was added due to the suppression of DE

effect and JT distortions were used after T_{MI} . Based on the results from XRD, ACS and also VSM, the secondary oxide was actually substituted into the parent compound.



ABSTRAK

Kesan terhadap struktur, elektrik dan magnetopengangkutan apabila nano-saiz Al_2O_3 ditambah ke $\text{Pr}_{0.6}\text{Sr}_{0.33}\text{MnO}_3$ sistem

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Kepentingan perovskite manganites telah mendapat perhatian yang besar disebabkan oleh kesan raksasa magnetorintangannya dan kegunaan teknologi untuk peranti pengesan medan magnet. Kebanyakan peranti magnet memerlukan magnetorintangan yang lebih tinggi dalam medan magnet yang rendah (LFMR) dengan suhu dan elektrik rintangan yang rendah.

Pencarian sebelum ini telah membuktikan bahawa LFMR dapat ditingkatkan dengan menambahkan fasa pennebat sekunder. Dalam kajian ini, $(1-x) \text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 - (x)\text{Al}_2\text{O}_3$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.10) telah disediakan melalui kaedah tindak balas sol-gel.

Sifat struktur, elektrik dan magnetopengangkutan oleh sampel ini telah dikaji dan disiasat.

Menurut belauan sinar-X, data menunjukkan bahawa sampel berada dalam keadaan tiada sebarang campuran atau fasa pennebat sekunder Al_2O_3 . Selain itu, sifat magnetik PSMO

adalah ferromagnetik semasa dalam suhu bilik dimana kajian lepas telah membuktikan

bahawa suhu curie PSMO adalah diantara 200K sehingga 305K. Kemudian, peningkatan

LFMR dan pergerakan T_{MI} ke suhu lebih rendah telah disiasat apabila Al_2O_3 ditambah,

disebabkan oleh tindakan kesan DE dan gangguan JT digunakan selepas T_{MI} . Berdasarkan keputusan yang diperolehi dari XRD, ACS dan VSM, penebat sekunder sebenarnya telah digantikan ke dalam sebatian asli.



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LIST OF ABBREVIATION AND KEYWORDS

Al_2O_3	Aluminium Oxide
PSMO	Praseodymium Strontium Manganese Oxide
LFMR	Low Field Magnetoresistance
CMR	Colossal Magnetoresistance
T_{MI}	Metal-insulator transition temperature
T_c	Curie Temperature
MR	Magnetoresistance
OMR	Ordinary Magnetoresistance
AMR	Anisotropic Magnetoresistance
GMR	Giant Magnetoresistance
TMR	Tunnelling Magnetoresistance
DE	Double Exchange
JT	Jahn Teller
XRD	X-ray Diffraction
ACS	Alternating Current Susceptometer
TGA	Thermal Gravimetric Analysis
VSM	Vibrating Sample Magnetometer
HMS	Hall Measurement System

CHAPTER 1

INTRODUCTION

1.1 Introduction

Alex Muller and Georg Bednorz discovered the high temperature superconductivity of copper-based oxides in 1989. They were awarded the Nobel Prize in Physics, prompting some scientists to conduct research into the properties of transition metal oxides including manganites compound. Soon after few years of active investigation, a new phenomena namely colossal magnetoresistance effect had been discovered in 1993. A material having magnetoresistance effect when an external magnetic field is applied and its electrical resistivity changes dramatically. Basically, magnetoresistance is defined as:

$$MR(H) = \frac{\rho(H) - \rho(0)}{\rho(H)} \quad (\text{Equation 1.1})$$

Where,

$\rho(H)$ = resistivity with magnetic field

$\rho(0)$ = resistivity without magnetic field, respectively in perovskite manganites.

MR could become positive or negative depend on the type of the material. Because the magnetic field suppresses spin disorder, MR is negative in magnetic materials. (Materials 2016). MR will show a positive value when the resistivity increases. MR will show negative value when the resistivity decreases (Ramirez 1997).

Magnetoresistance is a broad term that encompasses a wide range of phenomena. Positive magnetoresistance in metals, for example, occurs in bulk non-magnetic metals and semiconductors, whereas negative magnetoresistance in ferromagnets, also known as

anisotropic magnetoresistance, occurs in magnetic metals (AMR). Other types of magnetoresistances are ordinary magnetoresistance (OMR), extraordinary magnetoresistance (EMR), anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), tunnelling magnetoresistance (TMR) and colossal magnetoresistance (CMR).

For this research, we will be focusing about Colossal Magnetoresistance (CMR) which can rapidly develop compared to other MR effect due to its ability that can be used widely in magnetic field sensing technologies. The colossal magnetoresistance manganese oxides have a basic perovskite crystal structure with the general formula of LMnO_3 , where L is a lanthanide element like lanthanum (La) or neodymium (Nd). In lanthanum manganite, for example, both the lanthanum and manganese are trivalent cations, La^{3+} and Mn^{3+} , and their emergent charge is entirely equilibrium by the oxygen ion (Ramirez, 1997).

Generally, CMR can be described by using Double Exchange (DE) theory. The electron from 3d orbital of Mn^{3+} can hop to Mn^{4+} and vice versa through the oxygen atom of the Mn-O-Mn bond and create electron movement in the perovskite manganites structure. Nevertheless, this theory is only can be used to low temperature (below T_c) perovskite structure in a ferromagnetic state due to the arrangement of the electron spin in the same direction. CMR materials tend to switch its state from ferromagnetic to paramagnetic if the temperature is above T_c . When the materials in a paramagnetic state, the electron spin is in disorder orientation and fluctuated. Therefore, the double exchange theory become weak. Jahn-Teller theory discover to explain the conducting effect above T_c (Rout, Panda, and Behera 2011).

1.2 Problem Statement

There are a few techniques to prepare the nanoparticle size of the perovskite manganite which is solid state reaction, co-precipitation and sol-gel method. These three methods will give a different result of the electrical properties due to the differences of crystallite size and average grain size formation.

Solid-state reaction method is to prepare the polycrystalline solids from a mixture of solid starting materials. Solids cannot react at room temperature and they need to be heated with higher temperatures to ensure the reaction occurs at a significant rate. However, some compounds might be decomposed due to the high temperature to overcome the lattice energy.

The method of co-precipitating a stoichiometric mixture of soluble metal salts such as hydroxides, citrates, oxalates, or formates is known as co-precipitation. After the mixture has been filtered, dried, and heated, the final product will be made. The regulation of particle size was a problem with this approach, and since blocking temperature is dependent on particle size, a large size distribution might result in non-ideal magnetic behaviour if the particle size was broad. However, grain boundaries are not obvious in co-precipitation (CP) samples, and the sample has low homogeneity and a lot of porosity. (Chand et al., 2010).

In sol-gel method, we called 'sol' that was prepared which is the concentrated solution of the reactant. Gel will be formed by proceeding the concentrated by polymerizing process. The end product will be formed after it was heated to decompose to become oxide. The time taken for this method was short compared to co-precipitation and solid-state method. Besides, many works shown that sol-gel method can synthesize more homogeneous nano-size particles. Hence, we will use sol-gel method to form PSMO. Figure 1.1 shown the Field emission scanning electron microscopy (FESEM) micrographs of Solid-State Reaction (SS), Sol-gel (SG) and co-precipitating (CP) of PSMO.

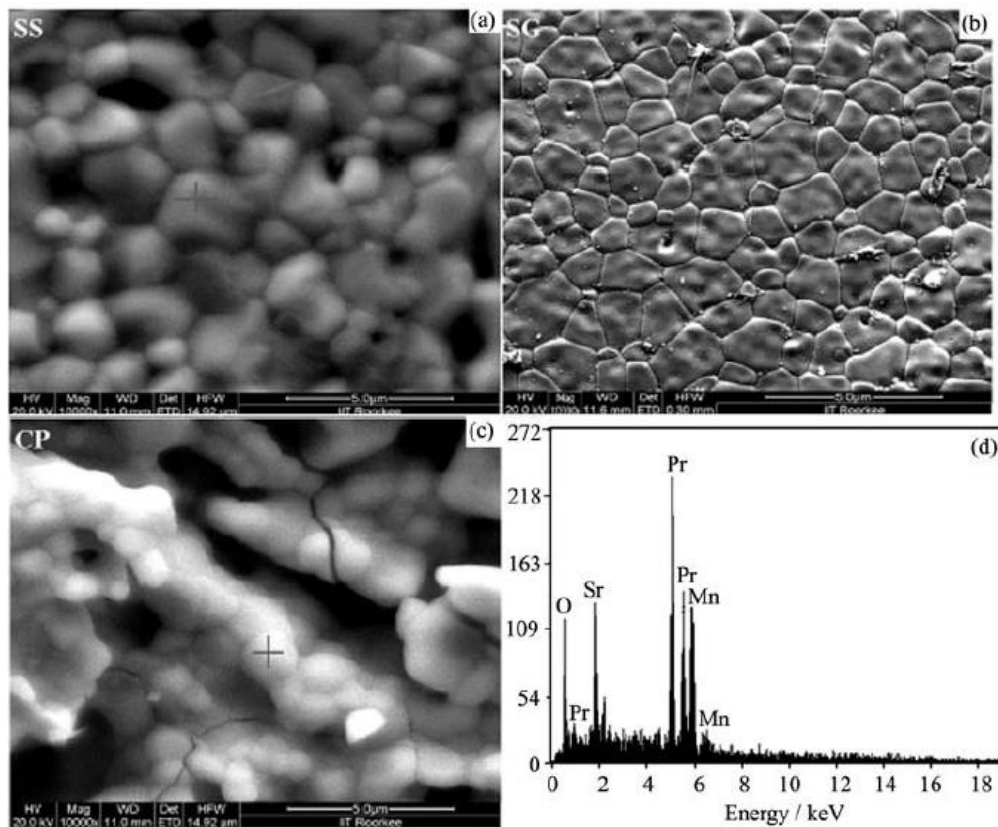


Figure 1.1: FESEM micrographs (a–c) and EDAX spectra (d) of Solid State (SS), Sol-gel (SG) and co-precipitating (CP) of PSMO (Chand et al. 2010).

The grain boundary will give a huge effect to extrinsic magnetoresistance. The intrinsic and extrinsic properties of perovskite manganese oxide have been widely studied since 1950, by some researchers until now. Grain boundary can affect the extrinsic MR, which is the extrinsic MR will increase by adding artificial grain boundary. The effective grain boundary will be adjusted and affect the Low Field Magnetoresistance (LFMR).

Other than grain distribution, the size of particle will also affect its physical properties due to the change of surface over volume of the material can be improved by making the grain size smaller. The smaller the grain size, the higher ration of surface area to volume so it has higher ration of grain boundaries to dislocation. If the grain size decrease, the magnetization and Curie temperature (T_c) will also decrease.

Previous study has shown that wet chemical procedures are more preferred as compared to the conventional solid-state approach for producing greater purity materials with tiny nano-grain size powder at lower temperatures. (Rao et al., 2012). Hence, sol-gel method was used to prepare nanoparticle size of the perovskite manganite to get a crystal clear picture of the effect of grain boundaries and the network of grain structure as a function of sintering temperature (Zhou et al., 2010).

In this research, we will be added oxide to observe the changes in CMR effects. Lim et al. (2020) stated that the mixing of insulating secondary phase into the manganite composites has proven as an effective measure to increase the low field magnetoresistance (LFMR) where we can reach a high value of MR in low magnetic field. Phong et al. (2009) explained that LFMR increases as the Al_2O_3 content increases. Besides, the oxide that we used in this research (Al_2O_3) is a good insulator with high thermal conductivity. Clearly, the effective magnetic anisotropy (K_{an}) decreased due to the presence of Al_2O_3 in the sample (Thanh et al., 2011). Since we want to enhance the CMR effects, many groups have attempted to synthesize CMR-insulators composites, such as LSMO/ CeO_2 (Balcells et al., 1999), LSMO/glass (Gupta et al., 2001) and LSMO/ NiO (Gaur and Varma 2006).

1.3 Objectives

The objectives of this research are:

1. To synthesize nano-size $(1-x) \text{Pr}_{0.6}\text{Sr}_{0.33}\text{MnO}_3 - (x)\text{Al}_2\text{O}_3$ $x = 0, 0.01, 0.03, 0.05 \text{ \& } 0.10$ composite by using sol gel method.
2. To investigate the structure, microstructure, magnetic and magneto-transport properties of $(1-x) \text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 - (x)\text{Al}_2\text{O}_3$ composite.



CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this research, the colossal magnetoresistance (CMR) has been chosen to be focused on. The colossal magnetoresistance (CMR) has their generic formula which is $RE_{1-x}A_xMnO_3$. RE is the trivalent rare earth element while A is a divalent alkaline earth ion. (RE, A) elements occupy the A-site position (corner of a cube) in the perovskite structure, whereas manganese occupies the B-site position (body centre of a cube) (Majumder, Majumder, and Karan, 2013). Rao and Raychaudhuri (1997) stated that manganates are ferromagnetic at or above some values Mn^{4+} content. It becomes metallic when the value is below Curie Temperature (T_c). Theoretical and experimental studies that have looked at perovskite manganites in order to improve their usability in a variety of technological applications. For example, magnetic refrigeration, magneto-resistive transducers, spintronic devices and magnetic sensors (Fkhar et al., 2019). In addition, we need a higher MR at low magnetic field with low electrical resistivity since it will reduce the bit size on the recording media to ensure the data storage capacity will be bigger (Panwar et al., 2010).

2.2 Study of Perovskite and Manganese Oxide Perovskite

The structure of $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ manganite is close to cubic perovskite (ABO_3), as schematically shown in Figure 2.1. The RE trivalent and AE divalent ions occupy the A-site, which has a 12-fold oxygen coordination, while the smaller Mn ion occupies the B-site, which has a 6-fold oxygen coordination. (Kitakaze, 2016).

Because the scale of the relative magnetoresistance in Mn oxides may be quite great, the magnetoresistance is commonly referred to as colossal magnetoresistance, or CMR. which is 99% or more (Sheng et al., 1997) Generally, the octahedron structure in a transition metal and the number of six oxygen atom was exhibited in the cubic perovskite which is act as a building block that was heaped in the cubic structure.

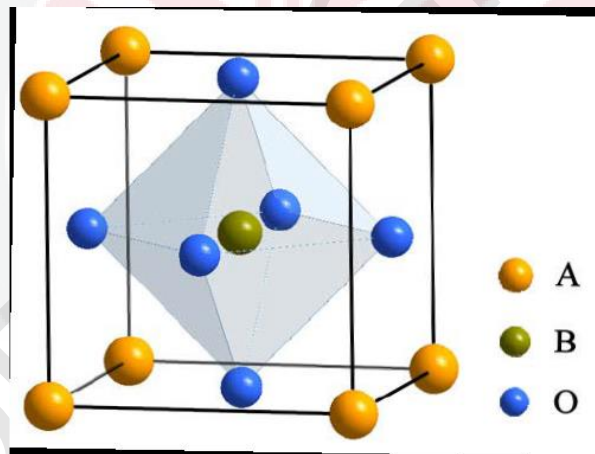


Figure 2. 1: Schematic structure of the cubic perovskite ABO_3 (Kitakaze, 2016)

The RE cation (A-site) was existed at the centre of each octahedron. Each octahedron will go through the shape-deformation by tilting or rotating to ensure the structure will diverge from ideally cubic structure. The shape deformation can be affected with the change of ionic size and external condition such as pressure. The degree of deformation can be described by Goldschmidt tolerance factor which formulated as:

A-O is the bond length between a cation RE and an oxygen ion.

M-O is the bond length between a transition metal ion M and an oxygen ion.

M-O-M bond angle could identify the degree of tilting. In this research, we are going to focus on perovskite manganites Praseodymium Strontium Manganese Oxide ($\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$). The magnetism and conductivity of these manganites are considerably affected by changes in the valence of the perovskite A-site. Boujelben et al. (2001) discovered a direct link between the average ionic radius for the A-site ion $\langle r_A \rangle$ and the Curie temperature T_c in the substituted manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$. The structure of PSMO was shown in figure 2.2.

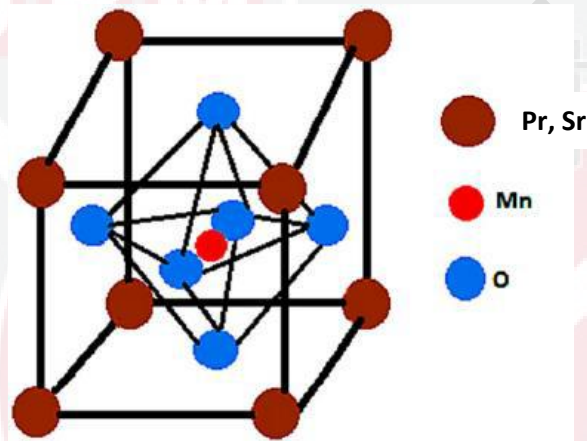


Figure 2.2: The crystal structure of Praseodymium Strontium Manganese Oxide (PSMO)

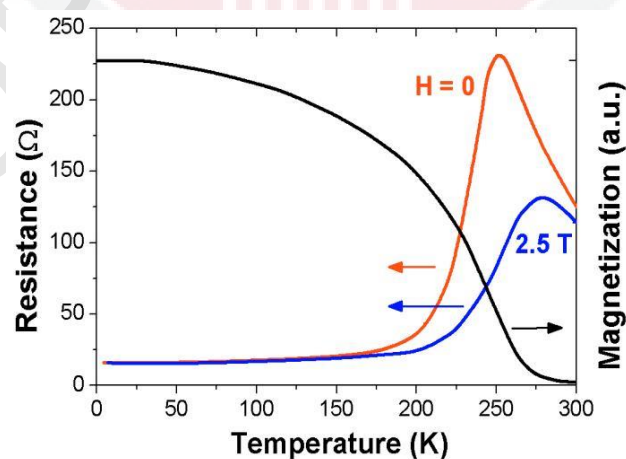


Figure 2.3: magnetization and resistivity of manganite vs temperature. (Retrieved from : <https://www2.cpfs.mpg.de/~wirth/rec/mangint.html>)

Manganites have long been recognised to have ferromagnetic and metallic characteristics. However, it was discovered in 1994 that manganites have a colossal magnetoresistance, meaning that when a magnetic field is applied and the temperature rises, the resistivity rises as well. The resistivity significantly reduces its height till it reaches a particular temperature (Figure 2.3).

Mn ion contain insufficient d-shell ($[Ar]3d^5 4s^2$). Hund's rule stated that the the unpaired electrons spin in the 3d orbitals have to be in parallel respectively (Figure 2.4) to decrease the energy. In consequence, only five of the d shells correlate to the spin are obtainable.

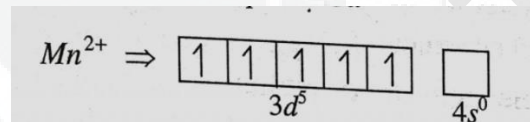


Figure 2.4: Electronic configuration of 3d orbital of Mn ion

The Coulomb repulsion is one of the two interactions implicit by Hund's rule that create the electron spin to be indifferent d-orbital and the Hund's coupling that ensure the electron spins being parallel among them. Although there are five degenerate d-orbitals, they are divided into two groups which is $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ in e_g while in t_{2g} , there are three degenerate into three which are d_{xy} , d_{zx} and d_{yz} . The symmetry cubic in which manganites crystallised causes this splitting. Because the e_g orbitals are aligned with p-oxygen and generate a stronger Coulomb repulsion than other directions, the energy in e_g is higher compared to when the energy in t_{2g} .

In Mn^{4+} , the three t_{2g} levels have three localised electrons in the outer shell of the d-shell, but the other two electrons from the e_g levels are vacant. Mn^{3+} ions, unlike Mn^{4+} ions, have an additional electron that can fill the e_g level. According to Tokura (1999), the e_g level is known to be the one that is active for conductivity. Because levels that hybridise with oxygen p-levels

cause the conduction band to exist, manganites are dubbed half-metal (conduction band is mainly filled up in one orientation spin). The eg orbitals that overlap with the Mn and the p-level oxygen determine the conduction band bandwidth.

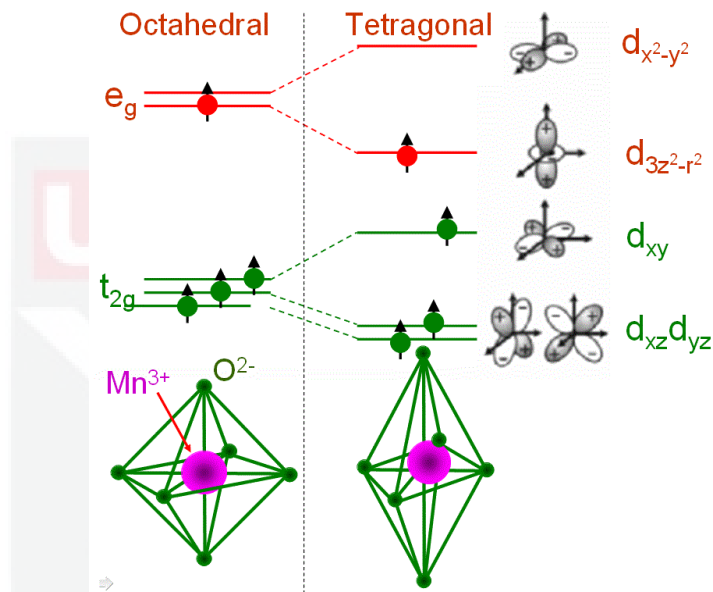


Figure 2.5: The outer shell of Mn is 3d. The five of the 3d level are split in e_g, whereas in e_g, there are two degenerate levels which is d_{x²-y²} and d_{3z²-r²} while in t_{2g}, there are three degenerated levels which are d_{xy}, d_{zx} and d_{yz}.

This occur due to the cubic crystal field. The Jahn-Teller distortion, which interacts on the Mn³⁺ ion, caused further level splitting.

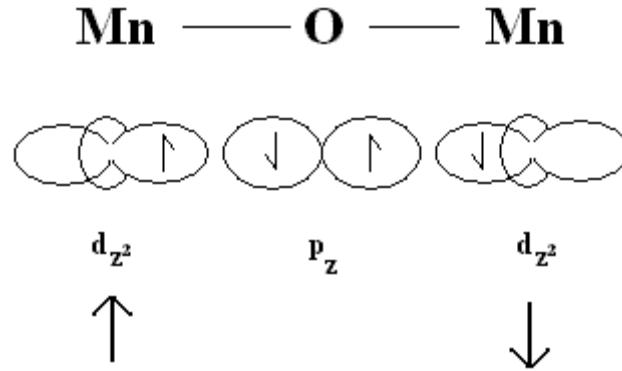


Figure 2.6: Double exchange mechanism of Mn-O-Mn

The charge transfer from electrons is explained by the conduction electron hopping to the Mn site. This can occur only when the electron spin is parallel to the moment of the site. Figure 2.6 shows two concurrent movement happen from Mn^{3+} to the oxygen and then to the Mn^{4+} ion. Double exchange is the term that being used to explain this movement since the electron moves to the other through oxygen ion.

The secondary phase of Al_2O_3 behave as energy barrier for the conduction electron. This energy barrier will increase the magnetic inhomogeneity and local spin disorder at grain boundaries and rise the magnetic domain scattering. Therefore, results in rise of LCMO composites' resistivity which is High Filed Magnetoresistance (HFMR). On the other hand, there is the enhancement if magnetoresistance at a lower temperature, which we call Low Field Magnetoresistance (LFMR). The polarized spin tunnelling of the electron at the grain boundaries make the magnetoresistance increase (Zhou, Zhu, and Li, 2017).

The increases of resistivity happened because of the double exchange mechanism that happens at T_c between Mn^{3+} , O^{2-} and Mn^{4+} ions. The material shows ferromagnetic characteristics and metallic behaviour due to electron hopping from Mn to other Mn ions. Nevertheless, after at specific temperature, the resistivity display reduced in its height, this is what happens when Jahn-Teller distortion occur. As the temperature rises, the lattice begins to vibrate. The energy levels of lattice vibrations are quantized, and a phonon is a quantum of

vibrations. The electron will have a difficulty jumping across the Mn-O-Mn due to the phonon effect. Extrinsic features include grain size, grain borders, and the presence of a secondary phase. As the boundary between two adjacent ferromagnetic LCMO grains gets bigger than the coupling length of two adjacent ferromagnetic LCMO grains, the magnetoresistance decreases (Siwach et al. 2009).

2.3 Intrinsic and Extrinsic Effect in CMR

There are two types of CMR effect which is intrinsic MR (due to grain) and extrinsic MR (due to grain boundary) (Panwar et al., 2010). The intrinsic MR of manganites might refer to the reducing in resistance because of the reduction of spin fluctuation in the applied magnetic field. In this case, the intrinsic CMR can be elucidated by using Double Exchange (DE) mechanism and Jahn-Teller (JT) mechanism that could be perceived near Curie temperature (T_c) in a high magnetic field (Nasri et al., 2013).

The intra-grains transport of conduction electron that manage the intrinsic CMR will be affected by a double exchange mechanism in a single crystal structure. Other than that, intrinsic properties also can be described by using spin fluctuations that happened directly below the magnetic critical transition temperature T_c (Uozu et al., 2006). Besides, the CMR effect is the highest when $T=T_M$ in metal-insulator temperature and $T=T_c$ in paramagnetic to ferromagnetic transition concurrently. The MR value will be reduced if the sample temperature is decreased. This state can be noticed in both single-crystal bulk and epitaxial film. A few Tesla of the magnetic field is needed in the single crystal to show the effectiveness of MR effect.

However, in composites, extrinsic MR (MR mainly dominant by effective grain boundary layer at low temperatures) reduces (Panwar et al., 2010). Besides, this extrinsic MR could also observed when there are chemical or structural inhomogeneities element exists

between the intergranular grains or even within each intragranular grain (Lisboa-Filho et al., 2004).

As the conduction electrons pass the grain boundaries, the extrinsic low field magnetoresistance (MR) effect is induced by spin polarised tunnelling (SPT) or spin-dependent scattering (SDS) (Siwach, Singh, and Srivastava, 2005).

The extrinsic MR, due to the existence of intergrain spin-polarized tunnelling or spin-dependent scattering among the grain boundaries in the presence of an external magnetic field, would be increased if the particle is decreasing or other elements are added into manganites.

There are many external factors that can give a significant influence on grain boundaries, for example the method of preparation, sintering temperature and particle morphology which are the major causes for the extrinsic MR effect. It also has a main role to enhance the room temperature of magnetoresistance and raise low field magnetoresistance (LFMR) because it acts as a transport function between ferromagnetic particles (FM). LFMR happens at a low magnetic field at a range of temperatures and depend on polycrystalline manganites extrinsic properties like the method of preparation. A bigger extrinsic MR effect than intrinsic CMR, as evidenced by the structural and magnetic inhomogeneities in manganite (Belevtsev et al., 2005). If the extrinsic inhomogeneities are shown to be unavoidable even in a single crystal sample, the intrinsic effects will become very weak and almost not exist in all cases.

2.4 Aluminium Oxide Doping of LSMO

2.4.1 XRD pattern

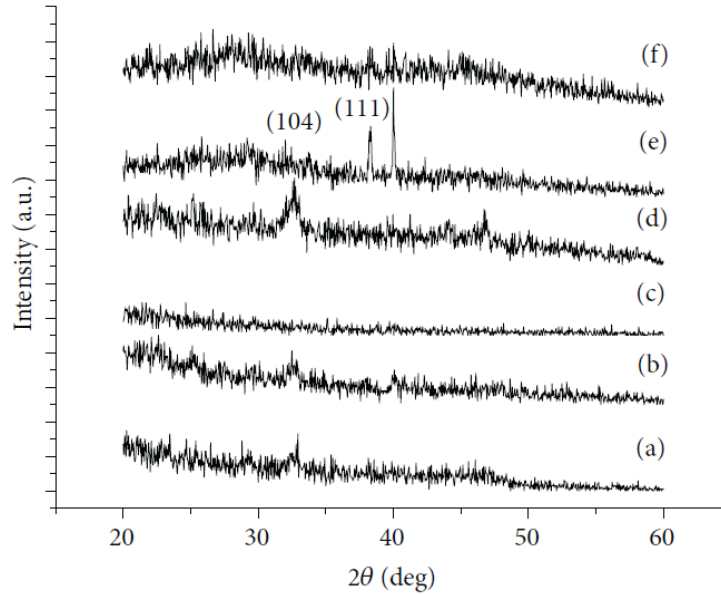


Figure 2.7: XRD patterns of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ with different concentrations of (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$, and (f) $x = 0.25$ (Abdullah et al., 2014)

Figure 2.7 shows the XRD pattern of the samples with different concentrations. According to Abdullah et al., (2014), there was no clear formation of single phase with rhombohedral distorted perovskite structure by observing the XRD graph pattern. When the concentration of x increased, the intensity of the width diffraction will decrease. This can be determined that the crystal structures of the LSMAO sample were effected since the level of doping increased.

2.4.2 Morphological structure

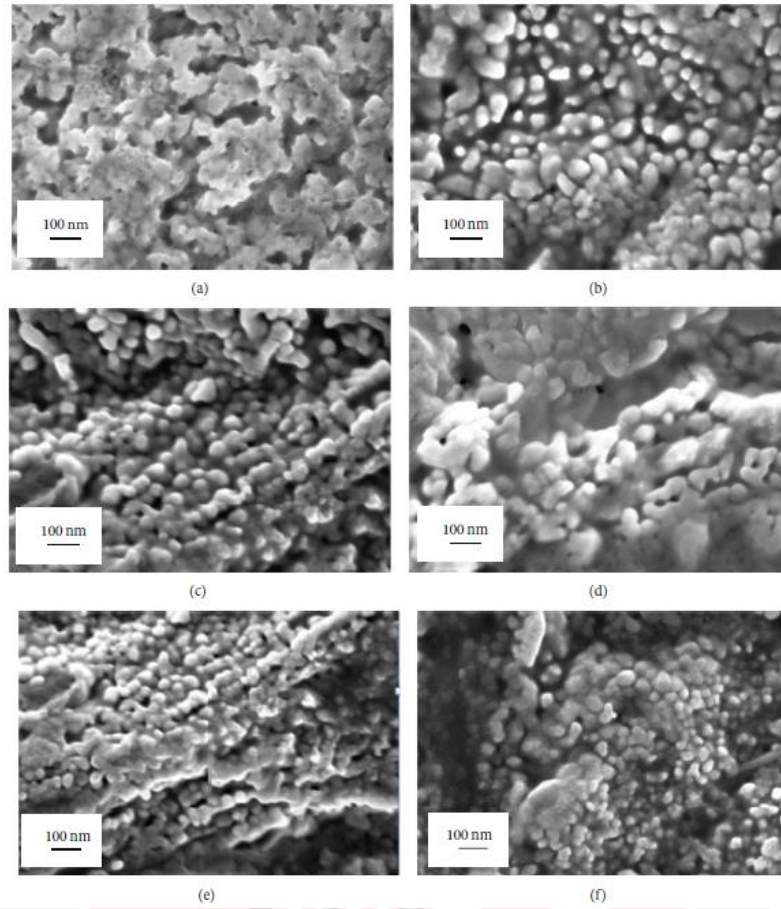


Figure 2.8: FESEM image of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ with different concentrations of (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$, and (f) $x = 0.25$ (Abdullah et al., 2014)

Figure 2.8 shown the FESEM image of the samples with different concentrations. The size of grain decreased when the concentration of x is increased. Abdullah et al. (2014) stated that when the concentration of x increased, the structural morphology of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ samples become more compact and homogenous. Al^{3+} will be substituted in Mn^{3+} or Mn^{4+} ion because Al^{3+} ion is smaller compared to $\text{Mn}^{3+}/\text{Mn}^{4+}$. Hence, the size of Al will be reduced.

2.4.3 Electrical properties

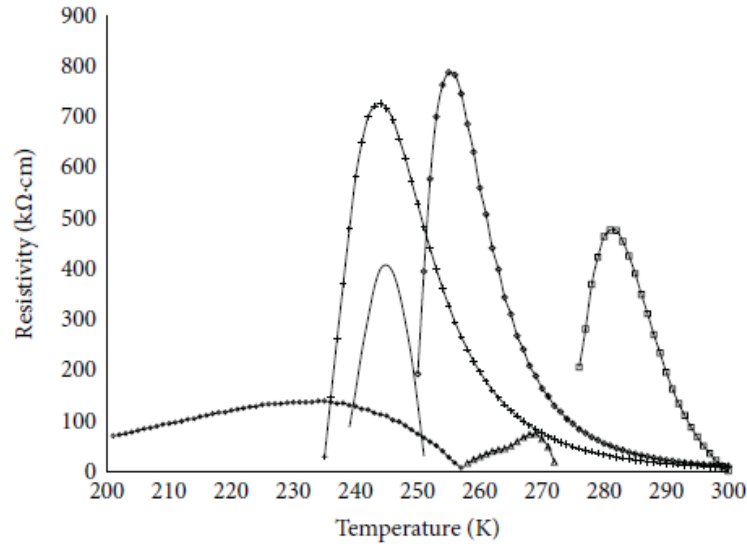


Figure 2.9: Temperature dependence of resistivity for $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ with different concentrations of (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$, and (f) $x = 0.25$ (Abdullah et al., 2014)

Figure 2.9 shows that the resistivity value decreases when the temperature increases. A semiconducting behavior was indicated and the samples follow the metal-insulator transition (T_{MI}) at T_p . From the graph, T_p should shifted at lower temperature for samples $x = 0.00$ and $x = 0.05$, but different for sample $x = 0.10, 0.20$ and 0.25 .

2.4.4 Magnetic properties

TABLE 3: Value of magnetization with concentration of Al at 10 kOe, measured at room temperature.

Concentration x	Magnetization (emu/g)
0.00	0.0457
0.05	0.1855
0.10	0.0287
0.15	0.1293
0.20	0.0537
0.25	0.0717

Table 2.1: Value of magnetization with concentration of Al at 10kOe, measured at room temperature. (Abdullah et al., 2014).

Based on the table 2.1, samples $x = 0.05$ and 0.15 obtained the highest value of magnetization compared to others which indicated weak ferromagnetic properties. The magnetic properties will show a good ferromagnetic behavior at room temperature.

2.5 Phase exist in the perovskite manganites

In this research, the material that will be focused is PSMO. Al_2O_3 was added to the pure PSMO with different molar ratio, x which were 0, 0.01, 0.03, 0.05 & 0.10. When x is low, it will separate less in grain boundary meanwhile, if x is increased, it will separate more at the grain boundary and also influence the transport properties (Das et al., 2004). The function of Al_2O_3 is to insulate barrier at grain boundaries, reducing spin disorder. The purpose of this research is to observe on how varied Al_2O_3 compositions after PSMO nanocomposites' structural, magnetic and magnetotransport properties (Lim et al., 2020).

2.5.1 PSMO manganites

Ng et al. (2018) investigated about the structure surface morphology, electrical, magnetotransport and magnetic properties prepared by sol-gel method by heat treatment at 600-1000°C. From the XRD pattern in figure 2.10 (a), a single-phase orthorhombic crystal structure was formed at 600°C (PSS6).

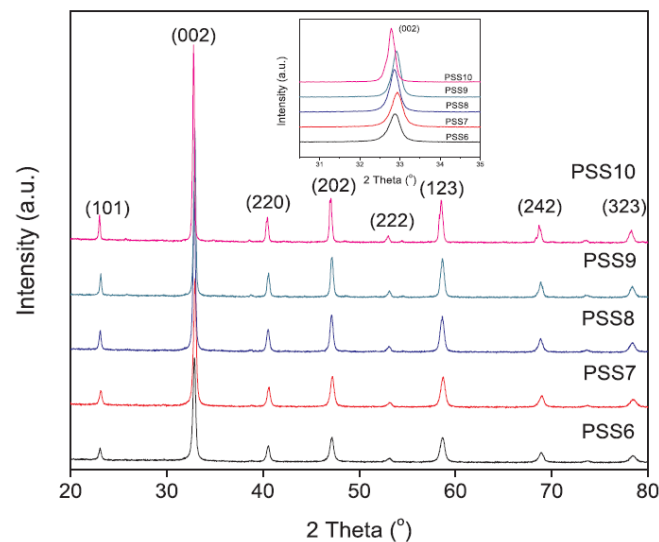


Figure 2.10 (a): XRD pattern for PSMO samples at temperatures 600-1000°C (Ng et al., 2018)

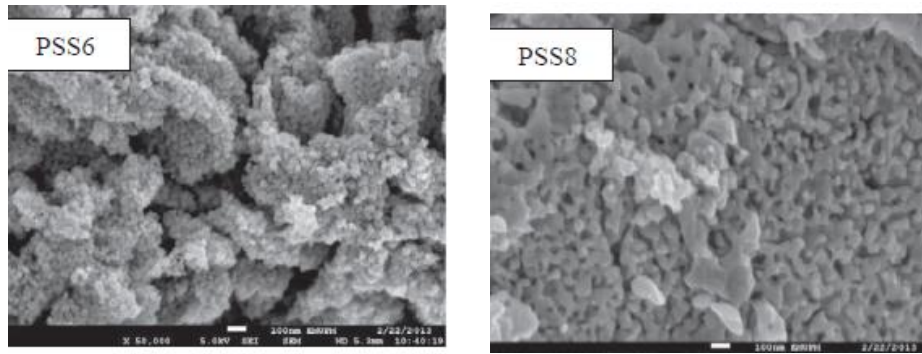


Figure 2.10 (b): Surface morphology for samples PSS6 and PSS8 (Ng et al., 2018)

Figure 2.10 (b) showed the surface morphology of the samples by using emission scanning electron microscopy. PSS6 displayed a microstructure where homogenous round shape particles were observed. The grain started to join together and their grain boundaries are hard to be observed. The grain size and crystallite size increased when the sintering temperature increase because of the congregation effect.

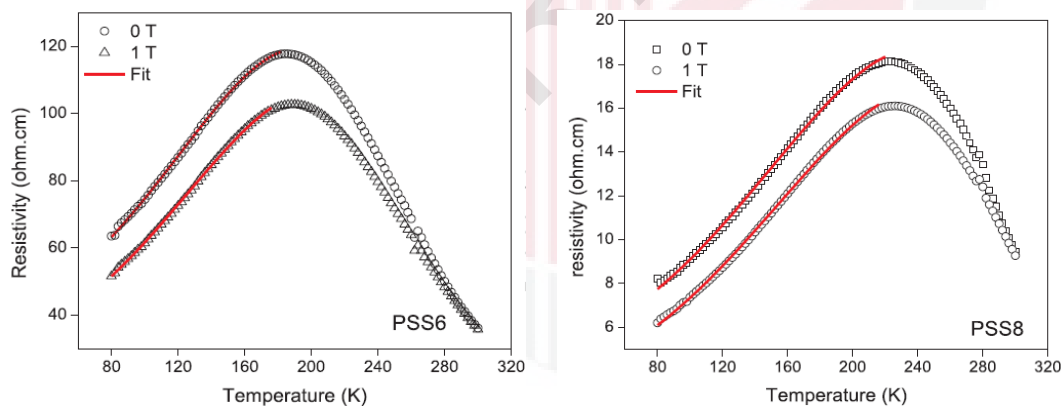


Figure 2.10 (c) : The temperature dependence of resistivity at 0 T and 1 T for $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ samples for PSS6 and PSS8 (Ng et al., 2018)

Figure 2.10 (c) showed the temperature dependence of resistivity at zero magnetic fields in the temperature range of 80-300 K. The increasing of grain size will make the resistivity

decreasing. Metal-insulator transition temperature (T_p) is defined as the temperature at the highest resistivity value. All samples showed a metallic behaviour at low temperature ($T < T_p$) and become insulator-like ($T > T_p$) above the T_p . Metal-insulator transition temperature (T_p) can be explained as the temperature at the highest resistivity value. In addition, both paramagnetic-ferromagnetic (T_c) and metal-insulator (T_p) transition temperature increase with the grain size.

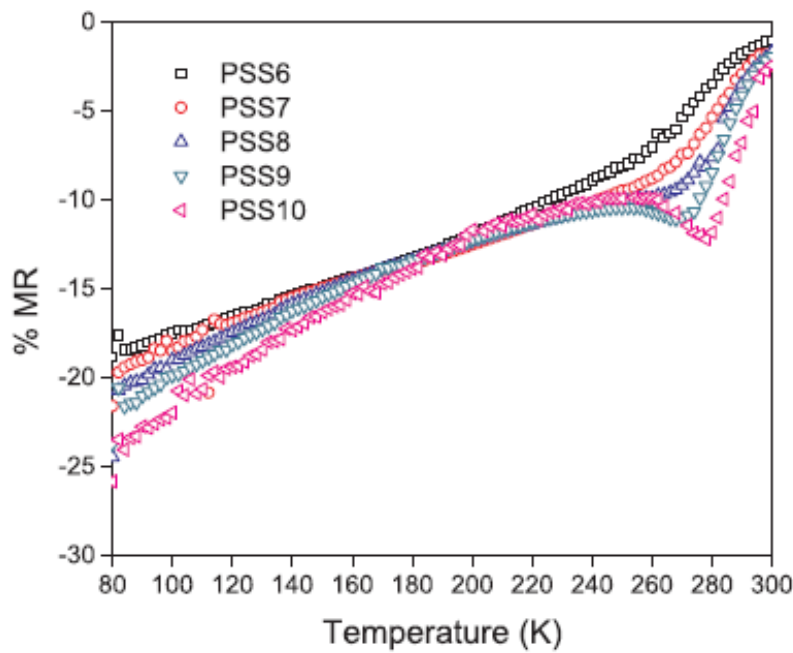


Figure 2.10 (d): %MR against Temperature for PSMO that sinter at different temperature at 1T (Ng et al., 2018)

The temperature decrease makes the %MR increase which obtained a value at -26% as shown in figure 2.10 (d). The intrinsic MR is described a relatively steep drop near the transition temperature (T_p or T_c) while the extrinsic MR will be increase as the temperature decrease. From the curve, the extrinsic MR is dominated for lower sintering sample with weak intrinsic MR. Nevertheless, the intrinsic MR effect appeared and showed a small drop of %MR around T_c when the grain size is increased.

2.5.2 NSMO manganites

Figure 2.11 showed the XRD pattern of NSMO manganites and all NSMO samples are polycrystalline in nature and degree of crystallinity remains constant since Sr concentration does not affect it. All the samples are well crystallized in single phase orthorhombic structure and slight shift in peak position with dopant (Sr) concentration is observed.

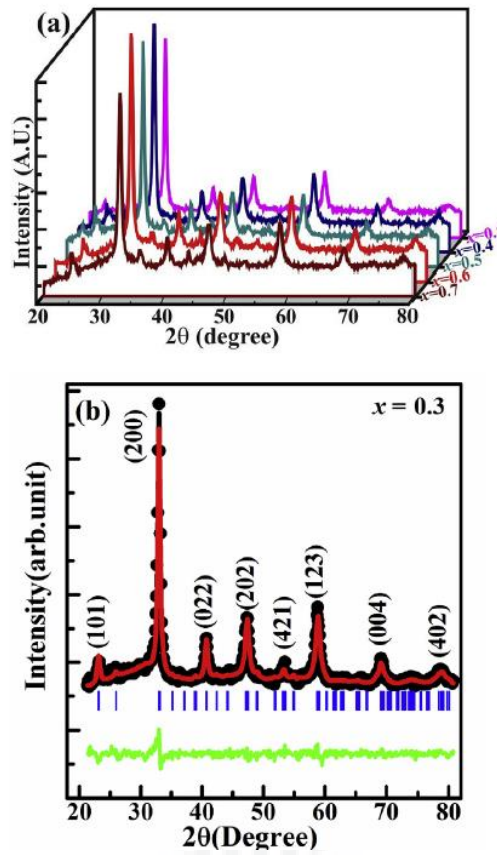


Figure 2.10 (a): XRD pattern of NSMO, (b) Rietveld refinement for $x = 0.3$ (Thombare et al., 2019)

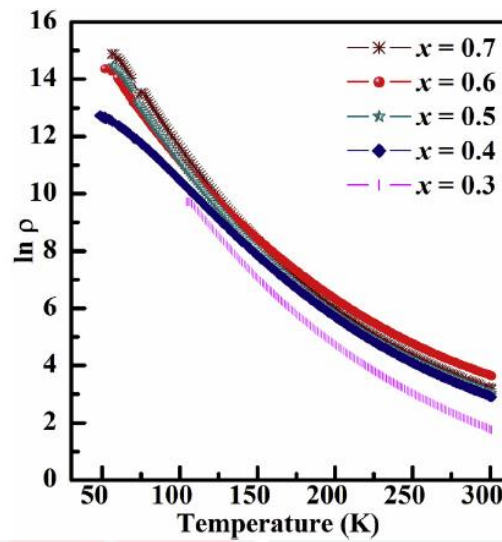


Figure 2.11 (b): Temperature dependent resistivity for NSMO

Figure above displayed variation of resistivity for NSMO in the temperature range 5-300 K with zero magnetic field. The resistivity value is beyond the range of resistivity below 70 K. In addition, the resistivity of with $x = 0.3$ showed reduce with the higher temperature.

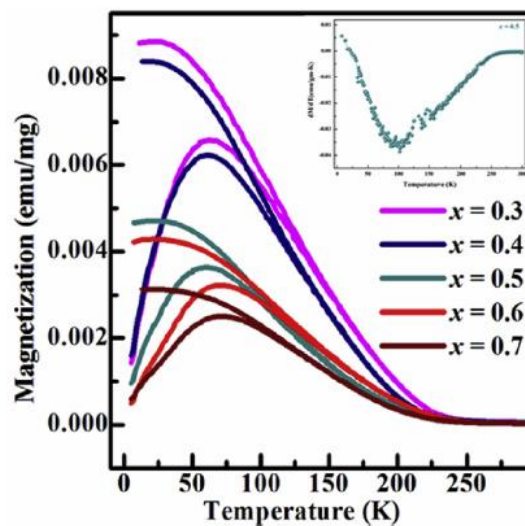


Figure 2.11 (c): Field dependent magnetization (M-H) loops at 5 K

NSMO particles have been observed at 5 K and 300K as shown in figure 2.11 (c). At 300 K, all samples exhibit paramagnetic nature. All samples show ferromagnetic (FM) behavior and unsaturated moment at 5 K even at higher applied field up to 7 Tesla. This is because the short-range ferromagnetic interactions within antiferromagnetic regions and hard spins in the surface layer are not aligned even at higher fields. NSMO shows ~100% MR at low temperatures.

2.5.3 LCMO/Al₂O₃ composites

According to the research that had been made by Phong *et al.* (2009), they observed that the Al₂O₃ phase was found but as a second phase in the LCMO composite compound. Figure 2.12 (a) shows the result for SEM micrograph of LCMO/Al₂O₃ composites with $x = 0.01$ and 0.04 . The interfaces between LCMO and Al₂O₃ can be differentiated clearly. It also proved by Energy-Dispersive X-Ray (EDX) spectra of the doped composites shows the aluminium peak along with La, Ca, Mn and O peaks which support the presence of Al₂O₃ in the doped composites. However, the Al₂O₃ did not go into the LCMO lattice but only located at the grain boundaries of the LCMO composites. There is no new phase that can be observed except for LCMO and Al₂O₃ phases. Besides, there is also no reaction between LCMO and Al₂O₃ compound.

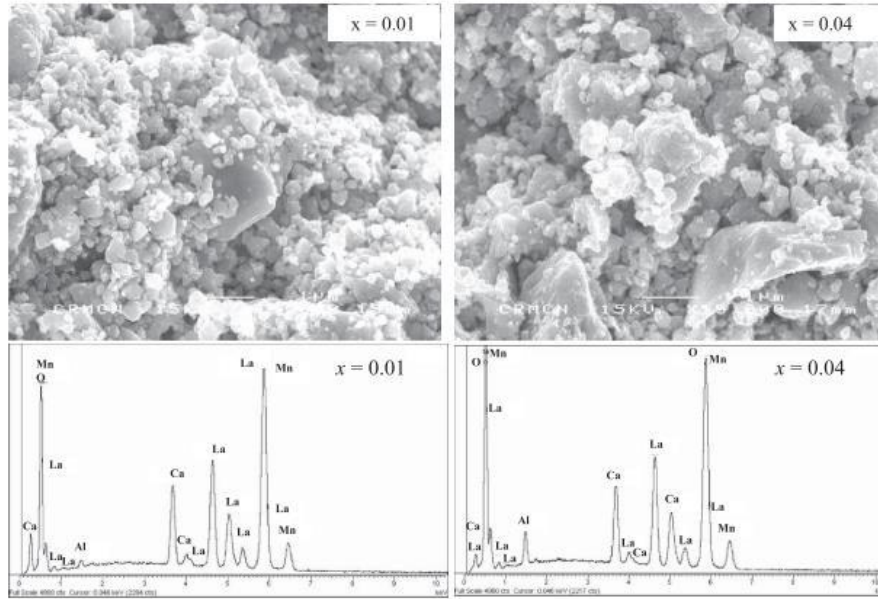


Figure 2.11 (a) Scanning Electron Microscope Micrographs and EDX spectra of LCMO/Al₂O₃ composite sample with $x=0.01$ and 0.04 (Phong et al., 2009).

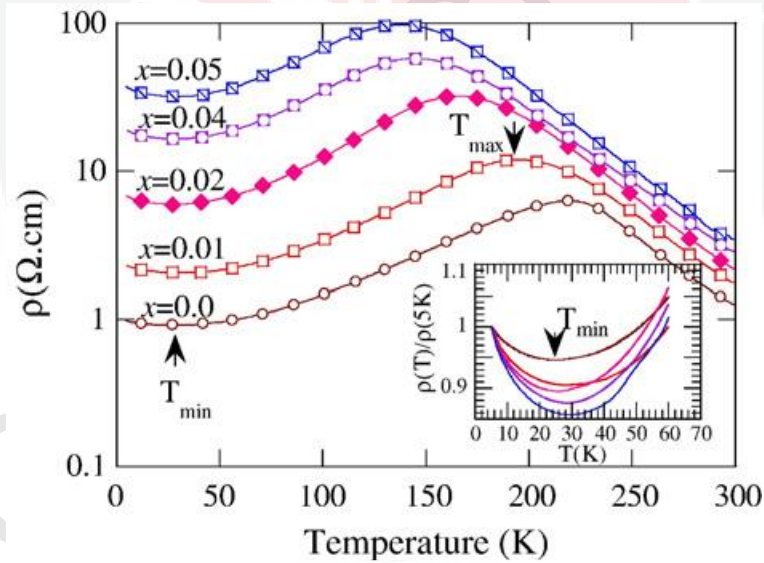


Figure 2.12 (b): $\rho(T)$ for $(1-x)\text{LCMO}/x\text{ Al}_2\text{O}_3$ composite samples down to 5 K. Inset distinct resistivity upturn at low temperature ($T \sim 50$ K) in the normalized resistivity vs. temperature curve (Phong et al., 2009).

Based on the figure 2.12 (b), all the composites display a distinct metal-insulator transition with reducing temperature because of the increasing concentration of Al₂O₃, and,

therefore, the resistivity increase simultaneously. Al_2O_3 acts contrastingly at different concentrations. The graph shows the paramagnetic (PM) to Ferromagnetic (FM) phase transition temperature T_c was determined from the peak of dM/dT . In the pure LCMO samples, the electrical transport was noticed between a direct contact through the LCMO grains while the electrical channel homogeneous between the inter-grains of LCMO. The ferromagnetic (FM) proportion cluster showed a reducing trend since the intergrain separation became more noticeable than the electron hopping, hence, the magnetotransport will be diminished (Zhou et al., 2017).

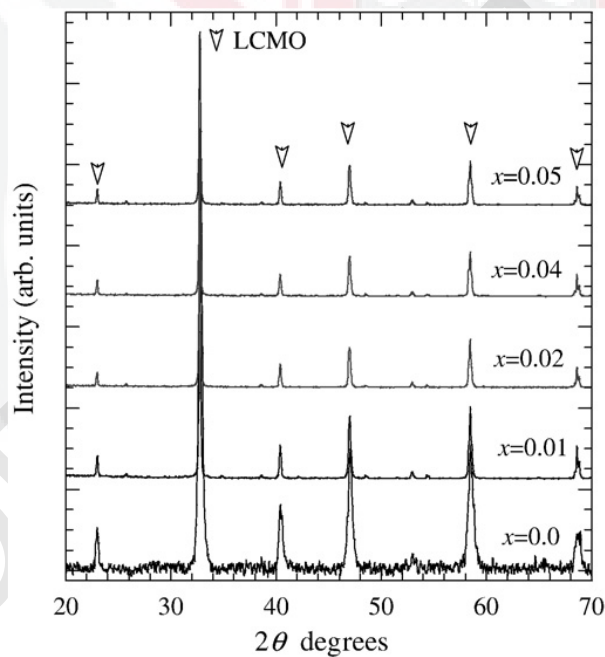


Figure 2.12 (c): XRD pattern of $(1-x)$ LCMO/ $x\text{Al}_2\text{O}_3$ composites (Phong et al., 2009).

Figure 2.12 (c) shows the result of XRD pattern for the composited of LCMO that was added with different composition of Al_2O_3 . It shows the perovskite phase of LCMO is maintained at all different composition of Al_2O_3 . The results shown that there was coexistence of two phases in the composites. Moreover, the addition of Al_2O_3 did not change

the position of the peaks of LCMO phase, which implies that Al_2O_3 is distributed at the grain boundaries and on the surface of the LCMO grains.

2.5.4 PSMO/ Al_2O_3

Figure 2.9 (a) shows the result of 3D Micrograph of PSMO/ Al_2O_3 composites with $x = 0.00$ and 0.20 . The particle size of manganites increases as Al_2O_3 in composite increases. The particle size also increases as the $(x)\text{Al}_2\text{O}_3$ composition increases.

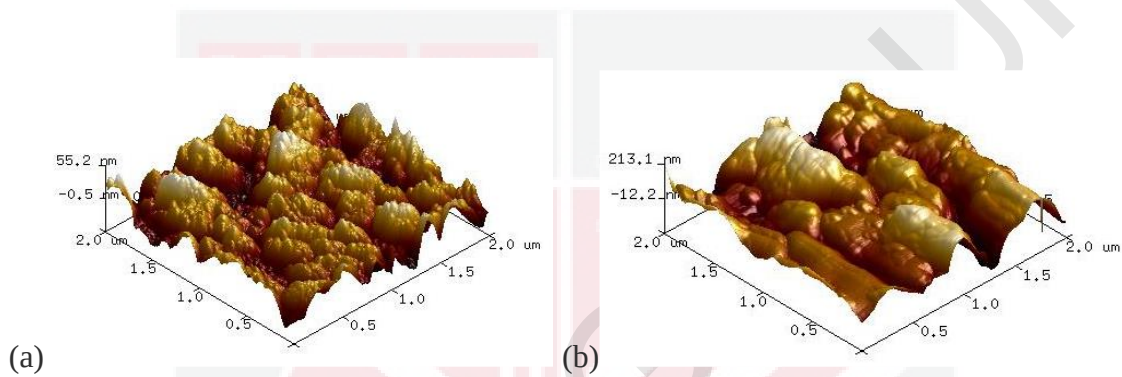


Figure 2.12 (a): 3D Micrograph of PSMO: Al_2O_3 (a) $x = 0.00$, (b) $x = 0.20$

Figure 2.13 (b) shows the magnetization, M as a function of magnetic field, H for PSMO samples. The composites are not completely paramagnetic behaviour. The samples exhibit minor ferromagnetic hysteresis loop with a very weak spin alignment. By using the vibrating sample magnetometer (VSM), the results displayed that the composites do not possess the paramagnetic behavior.

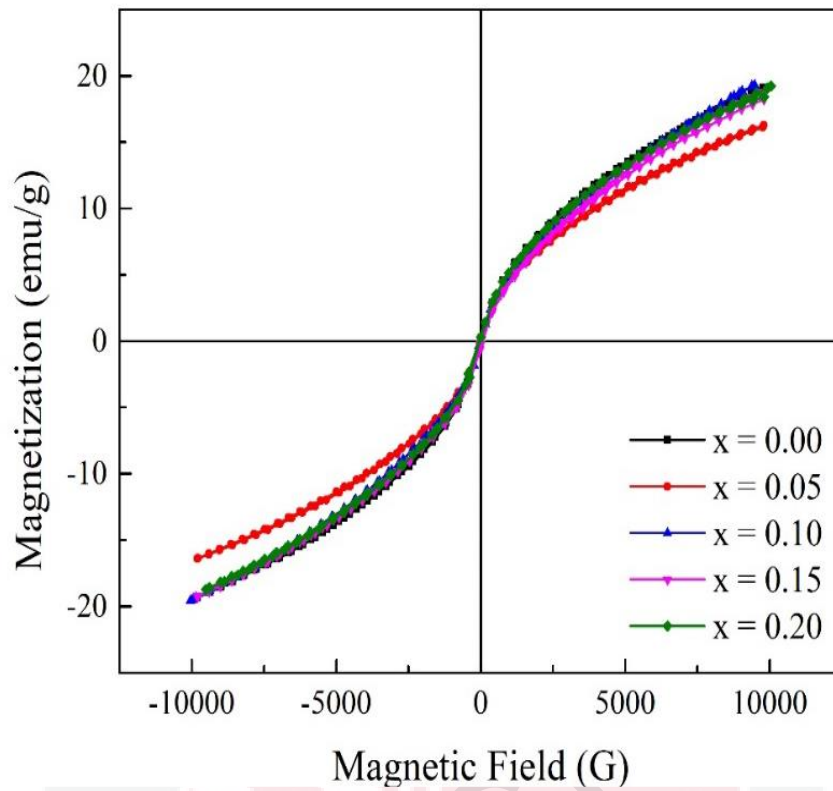


Figure 2.13 (b): Magnetization, M against magnetic field, H of PSMO composites

Figure 2.13 (c) shows the XRD pattern of PSMO/ Al_2O_3 with x 0.00, 0.05, 0.10, 0.15 and 0.20 composites. It shows the single perovskite structure of the PSMO and Al_2O_3 pattern, there were no new phase observed. This means that PSMO and Al_2O_3 coexist in the composited and there was no chemical interaction during sintering process. When Al_2O_3 increase, the peak intensity also increases.

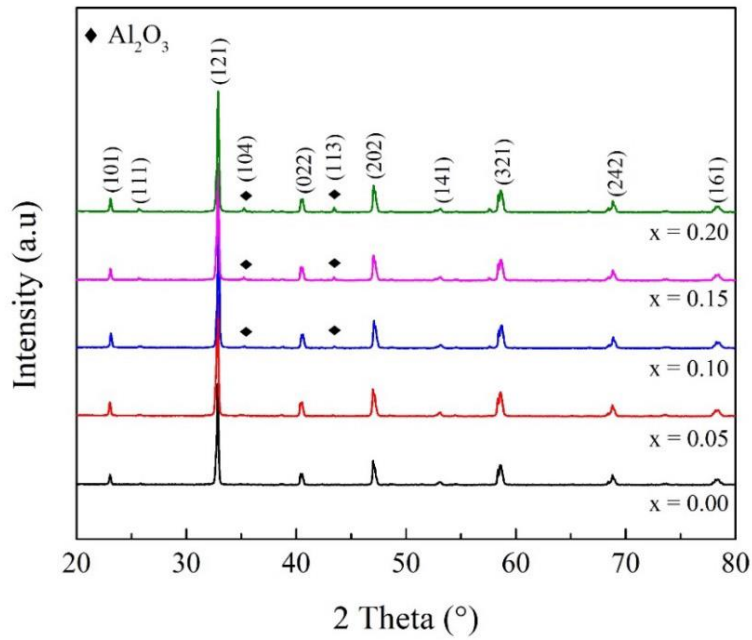


Figure 2.13 (c): XRD patterns for $(1-x) \text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3: x\text{Al}_2\text{O}_3$ composites with $x = 0.00, 0.05, 0.10, 0.15, 0.20$

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this experiment, Praseodymium Strontium Manganese Oxide (PSMO) were prepared by using the sol-gel method, five different compositions of Aluminium Oxide nanoparticles were added into five PSMO samples. 0, 0.01, 0.03, 0.05 & 0.10 of the compositions will be added into pure sample respectively. After all the synthesis were done, all of the samples will be characterized.

3.2 Sample Preparation

3.2.1 Starting Materials

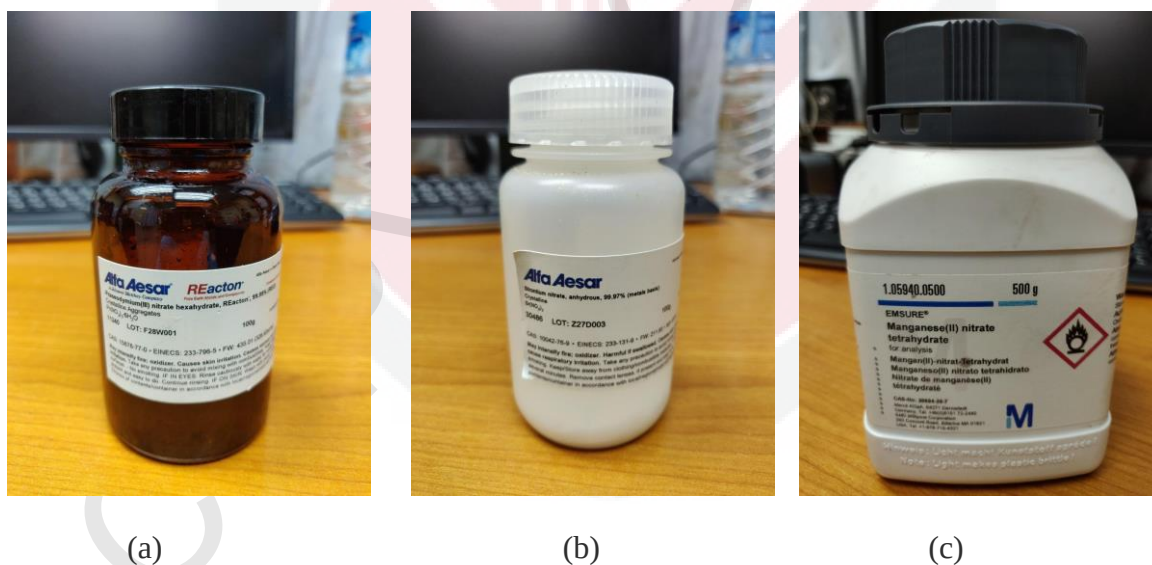


Figure 3.1 (a) Praseodymium (III) nitrate hexahydrate, (b) Strontium nitrate and (c) Manganese (II) nitrate tetrahydrate

The sample material such as praseodymium nitrate, strontium nitrate and manganese nitrate were weighed by using the electronic weight-scaling machine (Figure 3.2). The sample

is then mixed and stirred with 70°C in order to turn into gel form. After the sample turned into gel form, the sample was put into an oven for 24 hours. First one hour, the temperature of the oven was raised from 70°C to 90°C. After an hour, the temperature once again raised to 110°C and let it dried for 24 hours. The sample will be turn into dried brown colour bird nest like structure. Then it will be grinded then undergoes calcination and sintering process. After that, different composition of Aluminium Oxide will be added into the pure sample. These samples will be grinded again then pressed to pallet form.



Figure 3.2: Electronic weigh-scaling machine

3.2.2 Mixing Process

The starting material was mixed using distilled water according to the amount required to achieve crystal clear solution. Then, it will be stirred by using stirring machine in the fume hood. The revolution per minute is in moderate speed so that the solution will not split out by putting a magnetic stirrer inside the solution in the beaker. The magnetic stirrer was required to put at the centre of the axis just to ensure the solution will be stirred evenly. The solution was stirred for 30 minutes before adding citric acid to make sure the material equally mixed to form homogenous solution before adding the acid.

3.2.3 Titrating Process

The citric acid was dissolved into distilled water before adding into the solution. Adding the citric acid is to ensure to form a complex metal solution. The vapour was existed at the beaker because of the endothermic reaction with the distilled water. After 30 minutes, the citric acid added was added into the solution by titration. The purpose of titration was to mix the citric acid and the solution homogeneously (Figure 3.3). After the titration process, the solution was proceeded by stirring for 30 minutes.



Figure 3.3: Titration process by adding citric acid

3.2.4 Heating Process

After 30 minutes stirring the citric acid, ethylene glycol was added to the solution and stirred for one hour. The purpose of adding ethylene glycol was to form a polymer chain of metal complex. After an hour, the solution was heated up to 70°C and stirred until the solution turn from green liquid to green viscous glassy gel form (Figure 3.4). The estimate duration for the stirring process is around 24 hours. The beaker must be covered using a paper to avoid the sample being contaminated. The volume of solution decreased and viscosity increases, thus the magnetic stirrer will rotate slowly (250 rpm). When the magnetic stirrer was hard to rotate, then it shown that the solution has turned into gel form.

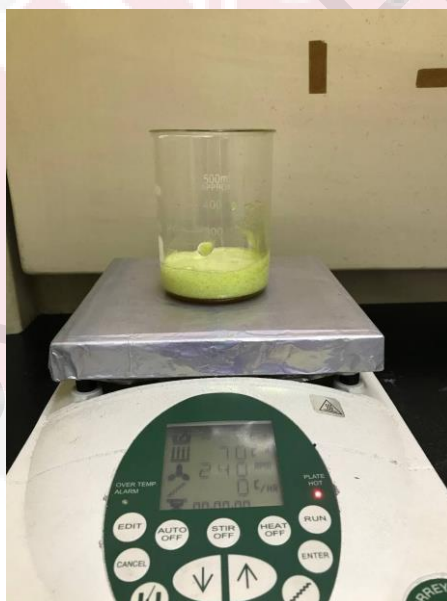


Figure 3.4: Stirring the solution for 24 hours at 70°C by using stirring machine

3.2.5 Drying Process

The gel form compound is then dried in the oven at 70°C. For each hour, the temperature of the oven needed to increase 20°C until it reached 110°C. So, the first hour is 70°C, next 1 hour is 90°C, and last an hour is 110°C. After it has been heated for 24 hours, it was cooled down until 40°C before taking out from the oven. The purpose of drying is to transform gel form into dry nest compound. (Figure 3.5).



Figure 3.5 Gel form heating by using oven

3.2.6 Grinding Process

The dried nest compound formed was then grinded using a mortar and mould into a smaller size of powder form (Figure 3.6). The grinding process was 30 minutes until the shining crystal inside the powder disappear and it is truly grinded. The process must be done carefully to avoid the sample spill out which can make the amount of the sample reduce. Then, the plastic spatula was used to taken out the sample to ensure the scratch of the mortar. 1g of the sample was kept in the weighing paper to submit to TGA characterization.

The grinding process was made just to ensure the size of particle reduce which it can obtain homogenous particle size distribution. The decreased size of the grain will contribute larger surface area for powder and much more space that are ready for reaction. Hence it will produce more reaction site.



Figure 3.6: Grinding dried bird nest by using mortar

3.2.7 Calcination Process

Firstly, the grinded material was put into the ceramic boat before it goes through the calcination process. The mixture will undergo an initial heat treatment in a furnace at 500°C for 5 hours. The furnace heating rate is 2°C per minutes so it took 3 hours 55 minutes in order to increase its temperature until 500°C. After 5 hours heating, it took 3 hours 55 minutes too to cool down the furnace temperature. The temperature of furnace needs to drop until around 50°C before it can be taken out. The purpose of calcination is by converting the material into more simple reactants so it can react with other component to form a new compound. It helps the material to attain more stable state at room temperature and reduce the grain size to obtain the nano scale particle. Besides, it may help to eliminate others foreign particles which are volatile. The schematic for heating and cooling process is shown in figure 3.7.

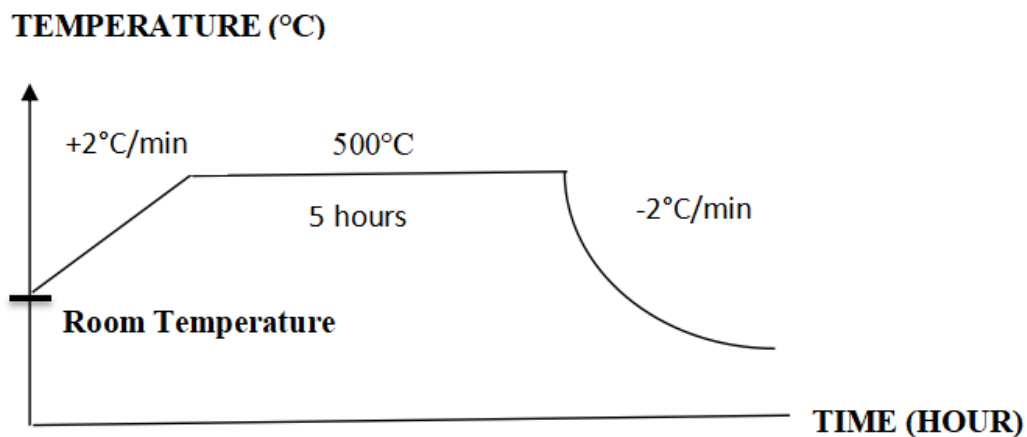


Figure 3. 7: Temperature setting for calcination process



Figure 3.7(a): Sample after calcine at 500°C for 5 hours



Figure 3.7(b): Powder weight after calcination

3.2.8 Grinding and Adding of Aluminium Oxide

The sample was cooled down to a room temperature and it will be grinded again. This process is to secure the mixture to be thoroughly well mixed. Besides, the aluminium oxide was added with different concentration which is 0, 0.01, 0.03, 0.05 & 0.10. The sample was grinded for 45 minutes for each one of them.

3.2.9 Pelleting

By using a manual hydraulic compressor, the sample was pelleted with applied pressure 5k Newton at room temperature. Three pieces of round pellet were acquired with two of them weighted for 0.4g and 0.7g. The 0.4g was sent to ACS and HMS analysis while 0.7g was sent to XRD analysis. Figure 3.8 showed a hydraulic compressor.



Figure 3.8: hydraulic compressor

3.2.10 Sintering

Lastly, the round pellet sample were sintered in the furnace at 800°C for 6 hours. The heating and cooling rate were set 2°C/min. This final sintering process was to ensure the sample obtain a high purity compound and guarantee the sample was dense which can decrease the volume in grain boundaries and remove pores from the starting material. Figure 3.9 shown the temperature settings for final sintering process.

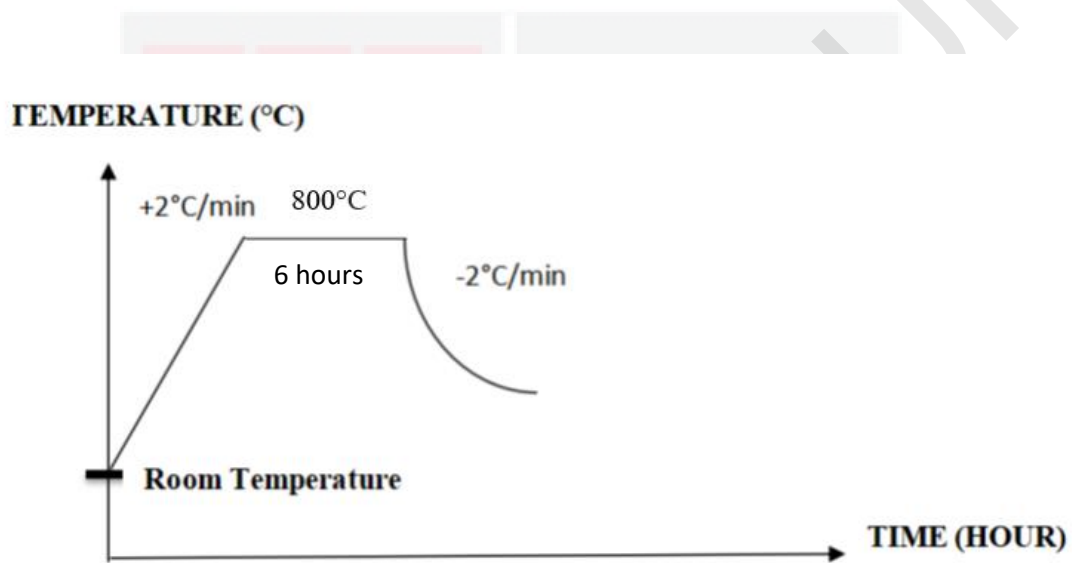


Figure 3.9: Temperature settings for final sintering process

3.3 Sample Characterization

The samples were sent to laboratory to characterize their structural, magnetic and magnetotransport properties by using X-ray Diffraction (XRD) Method, Hall Measurement System (HMS). Alternating Current Susceptometer (ACS) and Thermal Gravimetric Analysis (TGA) and Vibrating Sample Magnetometer (VSM).

3.3.1 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is utilised in this study to detect whether weight or mass loss has altered. It is a method in which the mass of a sample is measured versus time and temperature to determine if it has decomposed, oxidised, or lost volatiles. The oxygen stoichiometry of the sample may also be determined using this TGA. It consists of a precision balance with a sample pan located inside a furnace with a programmable control temperature. The thermal reaction can take place in various of atmospheres, including ambient air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapours of liquids, or "self-generated atmosphere"; and pressures such as high vacuum, high pressure, constant pressure, or controlled pressure. There are a lot of applications of TGA which are to obtain temperature and weight change of decompositions reactions, allows determination of Curie temperatures of magnetic transitions by measuring the temperature at which the force exerted by a nearby magnet disappears on heating or reappears on cooling. Next, can be used to determine the evaporations rates such as to measure the volatile emissions of liquid mixture. It also can determine the purity of a mineral, organic material or inorganic compound.

3.3.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a method that used to establish and look into the phase identification of crystalline material. This technique is based on the dual wave or particles to disclose detail information about the structure of crystalline material. Besides, XRD can measure the lattice parameter, orientation, crystallite size and phase identification of the crystalline materials.

Bragg's Law may be used to describe the relationship between the angle at which a beam of X-rays of a specific wavelength diffracts off a crystalline surface and the angle at which it diffracts. The Bragg's Law equation is:

$n\lambda = 2d_{hkl} \sin \theta$, where;

n = integer representing the order of the diffraction peak

λ = wavelength of the x-ray

d_{hkl} = inter-plane distance of atoms, ions or molecule

θ = Bragg angle or scattering angle

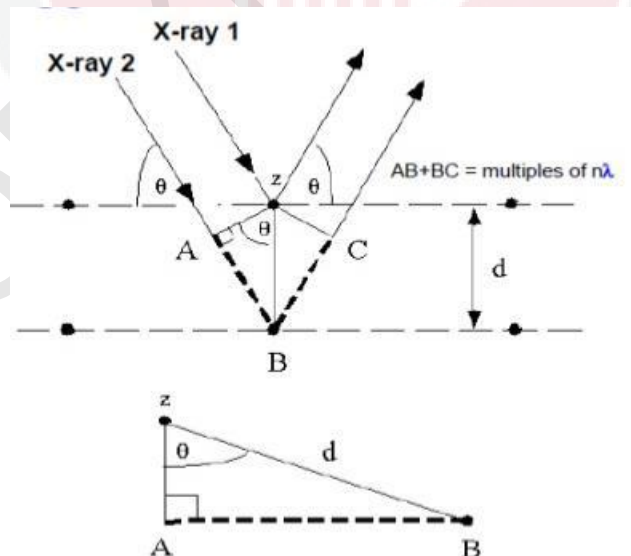


Figure 3.10(a): Schematic diagram for Bragg's Law (Source: Bragg's Law and Diffraction: How waves reveal the atomic structure of crystal. Retrieved from: <https://www.classe.cornell.edu/~dms79/xrd/Bragg-sLaw-and-Diffraction-applet.htm>)

Generally, the Bragg's Law described the angles under the n order reflection occur where $n = 1, 2, 3, 4, \dots$. When the wavelength increases, the reflection on the same plane will also increase. Otherwise, when the spacing value increase, the glancing angle will be decreased. All of the diffracted x-rays will be discovered, processed and enumerate due to distinguish a crystalline structure. By scanning the sample through a range of 2θ angles, the direction of diffraction of the lattice can be achieved. Identification of a material can be attained through converting the diffraction peak to d-spacing because each material had its unique set of d-spacing. Basically, the d-spacing will be compared with standard reference pattern.

A single crystal and polycrystalline or powder will be determined in x-ray diffraction work. Every each of the unit cells in a single crystal were line up in a perfect extended pattern. Hence, it can be explained that the single crystal was a perfect crystal. Polycrystalline has a variety of solid material mixed and thus it is pivotal to have a sample with a smooth surface. Therefore, the grinding process will be done.

For a certain condition, there will be a random distribution of all possible h, k, l . Conversely, crystallites would have h, k, l reflecting planes oriented parallel to the specimen surface to provide to the reflected intensities. In order to have an equal number of crystallites contributing it, each possible reflection from h, k, l planes are required. All feasible reflection may be produced via the glancing angle θ . Intending to satisfy the Bragg's Law condition, the different d-spacing in polycrystalline material was deemed. It can yield by varying the angle θ . The angular positions and intensities of the resultant diffracted peaks provide a pattern that will display the characteristics of the sample. The different phase mixtures are exhibited in that

particular material if the resultant diffractogram shows the addition of individual patterns.

Figure 3.10 (b) shown the schematic diagram of XRD.

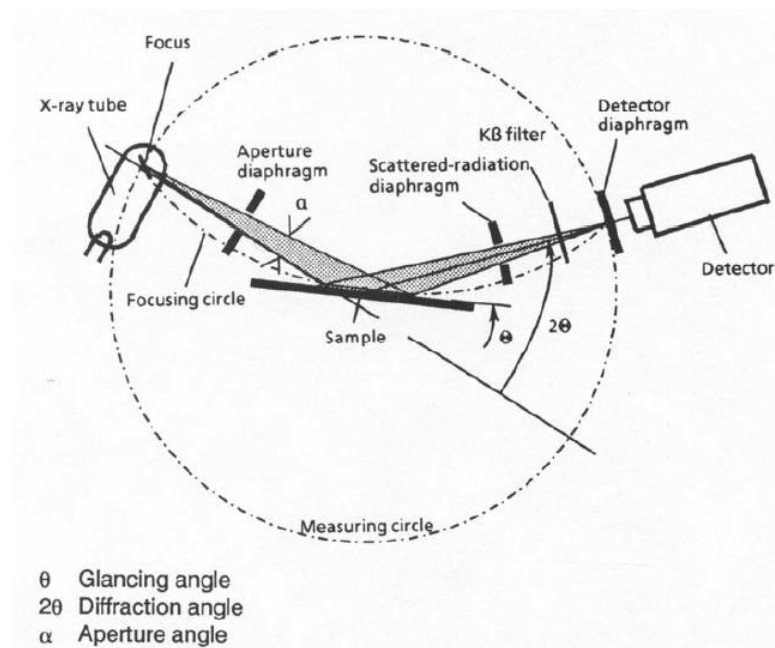


Figure 3.10(b) : Schematic diagram of XRD (Diffraction, 2007)

3.3.3 Vibrating Sample Magnetometer (VSM)

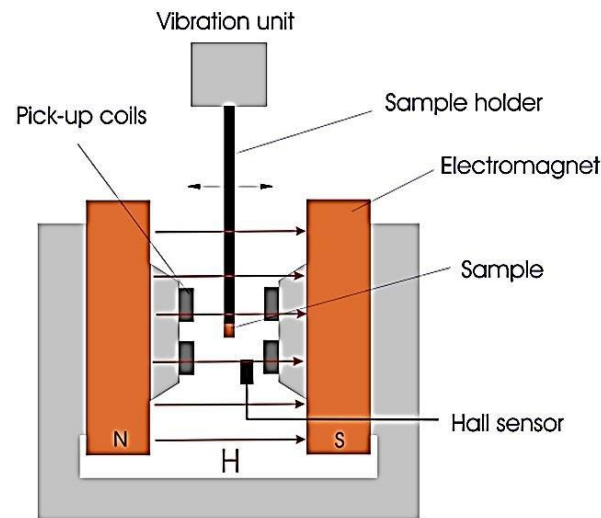


Figure 3.12: Schematic Diagram for Vibrating Sample Magnetometer

The Vibrating Sample Magnetometer (VSM) was a scientific apparatus used to investigate a material's magnetic characteristics as a function of magnetic field, temperature, and time. Powdered materials, solids, liquids, single crystals, and thin films could very well be easily facilitated in a VSM. The fundamental theory of the vibrating sample magnetometer (VSM) was based on Faraday's Law of Induction, which indicated that adjusting the magnetic field may generate an electric field. When material is put in a uniform magnetic field H , a magnetic moment, m , is induced in the sample. In VSM, the sample is usually inserted within the detecting coil to induce sinusoidal motion and a magnetic flux will occur, changing the induced voltage in the sensor coil. It was expected to be proportional to the sample's magnetic moment. To create a magnetic field, an electromagnet or a superconducting magnet can be utilised. It is able to quantify the induced electric field, which reveals information about the changing magnetic field. As a reason, we can also declare that VSM can be used to predict the behaviour of magnetic materials. The sample will be placed in the VSM to investigate the continuous magnetic field. If the sample is magnetic, the constant magnetic field will magnetise it, revealing either the alignment of magnetic domains or the individual magnetic spins in

combination with the field. Strong constant fields can be used to achieve large magnetization. By varying the magnetic field, Faraday's Law of Induction states that an electric field will be induced in the pick-up coil. The induced current was proportional to the sample's magnetization, implying that as the magnetization rose, so did the induced current. Using control and monitor software, the system can interpret the number of magnetised samples and determine the magnetization value, which is dependent on the intensity of the continuous magnetic field.

3.3.4 Alternating Current Susceptometer (ACS)

For low magnetic signal, ACS characterization is applied to manage the domain wall. It may also determine magnetic phase and evaluate magnetic susceptibility ($M = \chi H$) which becomes indispensable, especially for the determine the phase transitions and magnetic relaxations in paramagnetic salts, spin glass, super paramagnetism, low dimensional magnets and superconductivity materials. In a material, ACS analysed paramagnetic, diamagnetic, ferromagnetic, and superconductor properties. In the AC susceptibility measurement, each of these magnetization processes exhibits a strong response. AC susceptibility studies of solids, powders, and liquids, as well as dynamic magnetic analysis in the field of magnetic nanoparticles (MNPs) are the examples of ACS applications. Curie temperature is defined as the temperature at which a material's magnetic properties rapidly change.

3.3.3 Hall Measurement System (HMS)

Hall Measurement system was used to measure the resistivity changed in the material when there is a presence of external magnetic field.

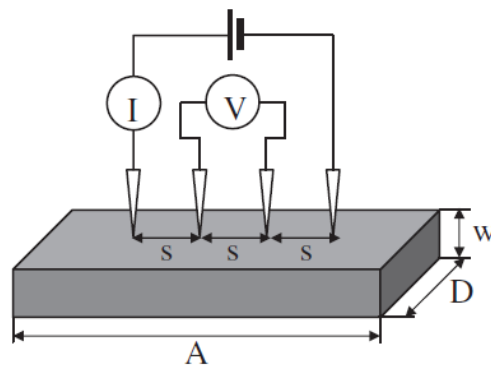


Figure 3.11: Four-point probe resistivity test (Mironov et al., 2007)

The four-point probe method involves in measuring which can be divided pairs of current carrying and voltage sensing electrode. In advance, four probe method is more accurate compared to two probe method. In four probe, a pair is used as a current carrying meanwhile another pair is used to measure voltage. Along with a four-point collinear probe, the instrumentation used for this test involve a DC current source and a sensitive voltmeter. The contact resistance will be get rid as a result of separating current and voltage electrode. Four equivalently will be in contact with material which obtained unknown resistance by using this technique. A different connection of the probe will produce a different type of way in obtaining resistivity. Consequently, the measurement of the substrate resistivity can be obtained by passing a current along two outer probes and the inner probes functioned as measuring the voltage.

Resistance of the top emitter layer is known as sheet resistivity. When current pass along the outer probes, a voltage can be induced in the inner probe. There are some precautions that we need to take note when using four-point probe. The drive current adjustment was required to be done depend on the resistivity of the sample to ensure an authentic reading can be obtained. Current was reduced if the resistivity sample high to secure the voltage at that time will not become too high. It is effortless to measure if the resistivity of the sample is low since the contact with silicon is ohmic.

Commonly, the current will be increased and voltmeter will be modified to low scale.

The volume resistivity can be calculated by using:

$$\rho = \frac{2\pi}{\frac{1}{s_1} + \frac{1}{s_3} - \frac{1}{s_2 + s_3} - \frac{1}{s_1 + s_2}} R$$

Where,

s_1, s_2, s_3 = Separation distances between four probes

R = resistance

The %MR can be calculated by using the equation 1.1.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to identify the material's thermal stability and to observe the weight changes of the material since it went through heating process at a constant rate. The weight percent against temperature was obtained from the TGA analysis. Before calcine process were happened on the sample, the sample was submitted to undergo TGA analysis.

In case to prepare PSMO compound by using sol-gel method, citric acid and ethylene glycol were added into the precursor solution to help PSMO to form, since the ethylene glycol will behave as polymerization of metal ions and citric acid will act as a chelating agent (Lau, 2020). Figure 4.1 shown the TGA result for PSMO sample. There were 2 stages of the weight loss of the PSMO precursor. The first weight loss obtained from TGA analysis is the decrease of - 83.3% from the temperature 55.43°C to 692.51°C. This is due to the water removed from the compound during the heating process was done as the water boiling point its 100°C and also the decomposed of precursor impurities in PSMO compound such as nitrares and ethylene glycol that had been obtained from the date. Lastly, the last stage is the stable change of weight from 693.14°C to 995.41°C. Hence, 693.14°C might be the starting point of formation of PSMO phase which is all oxides have reacted for this temperature range.

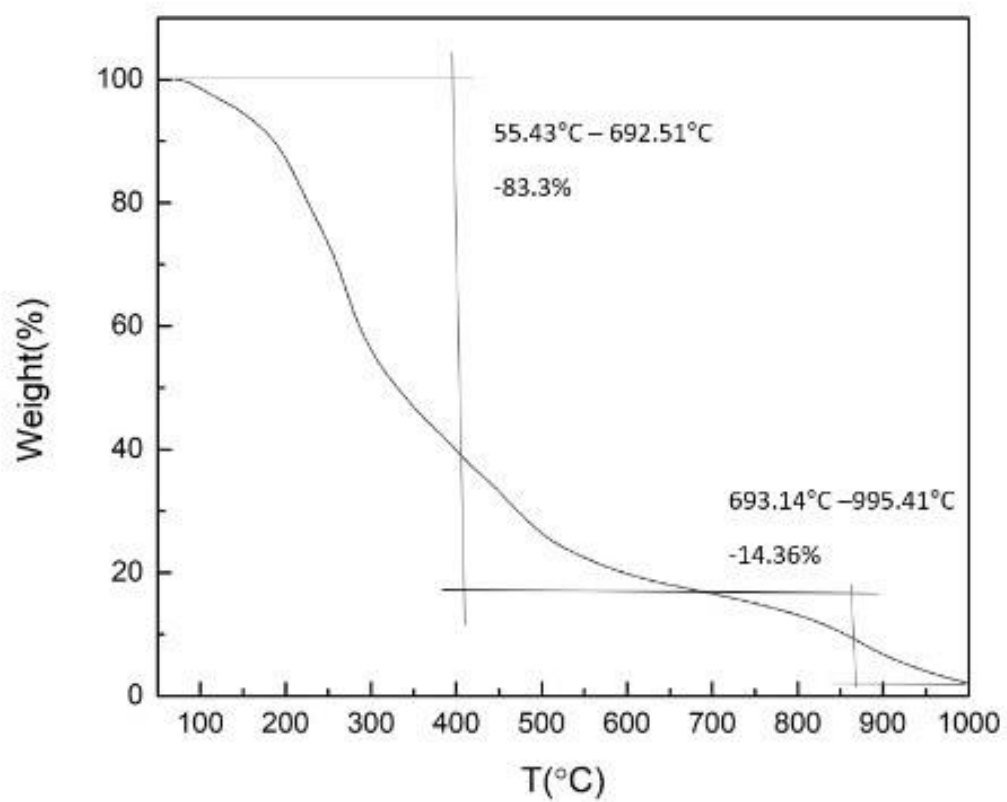


Figure 4.1: Thermogravimetric Analysis graph result.

4.2 XRD Analysis

For this research, we had prepared sample of PSMO with the addition of different composition of Al_2O_3 in nano-sized to form composite compound by using sol-gel method. The crystallographic properties of PSMO/ Al_2O_3 composite were analyzed which is all the samples were scanned by using X-ray diffraction and then the obtained XRD data were analyzed by using Rietveld Refinement method. Figure 4.2 shows the XRD spectrum of PSMO and Al_2O_3 with the ratio of 0%, 1%, 3%, 5% and 10%. There were 7 XRD peaks corresponding to the PSMO phase and the patterns displayed that all the samples are single-phase without any detectable impurity or secondary phase. This was may due to the Aluminium Oxide that were added were evaporate or react with PSMO which is substitution occur in Mn site.

In table 4.1, all XRD spectrum already refinement using Highscore has been tabulate. The pure PSMO has unit cell with lattice parameters $a = 5.4521 \text{ \AA}$, $b = 7.7044 \text{ \AA}$ and $c = 5.4809 \text{ \AA}$. All sample indexed according to an orthorhombic perovskite structure with $Pnma$ space group. The lattice parameters remain almost the same and the bond angle and bond distance also does not change.

As the radii size of Al^{3+} ions ($0.053 \text{ \AA}$) are smaller than Mn^{3+} ions ($0.067 \text{ \AA}$), this indicated that more Al^{3+} will take place of Mn^{3+} in $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ (Abdullah and Zulfakar, 2013).

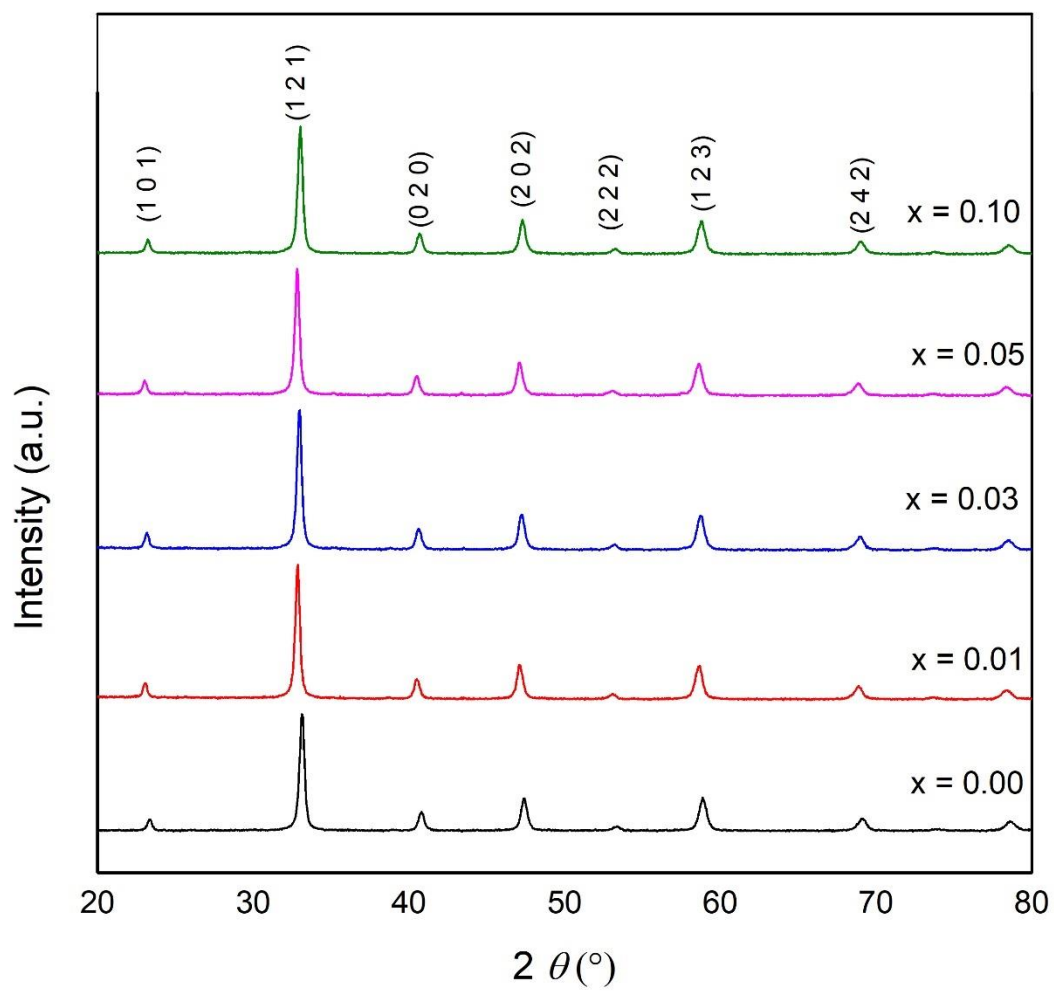


Figure 4.2: XRD Spectrum for all samples of PSMO composites.

Table 4.1: Refinement result of PSMO and Al₂O₃

Sample code	PSMO				
Sample	Pr _{0.6} Sr _{0.33} MnO ₃				
Ref code	98-006-7110				
Structure type	Orthorhombic				
Space group	P n m a				
Al ₂ O ₃ composition	0%	1%	3%	5%	10%
a/Å	5.4521	5.4475	5.4490	5.4462	5.4531
b/Å	7.7044	7.6974	7.6996	7.6945	7.7044
c/Å	5.4809	5.4766	5.4765	5.4744	5.4735
Volume/Å ³	230.225	229.638	229.762	229.408	229.956
Mn1-O1(Å)	1.943	1.941	1.941	1.940	1.942
Mn1-O1(Å)	1.952	1.951	1.951	1.950	1.951
Mn1-O2(Å)	1.948	1.947	1.947	1.946	1.948
Mn1-O2(Å)	1.948	1.947	1.947	1.946	1.948
ΔMn1-O1-Mn(°)	165.89	165.89	165.89	165.89	165.9
ΔMn1-O2-Mn(°)	162.65	162.65	162.65	162.65	162.7
Crystallite size (nm)	27.4	30.7	29.8	30.1	28.0
R _{exp} (%)	3.57653	3.4634	3.3790	3.5028	3.4612
R _p (%)	2.92811	2.7917	2.6663	2.9604	2.8412
R _{wp} (%)	3.71389	3.6317	3.5065	3.8128	3.5897
Goodnees of fit	1.07829	1.0995	1.0769	1.1849	1.0756

4.3 Vibrating Sample Magnetometer

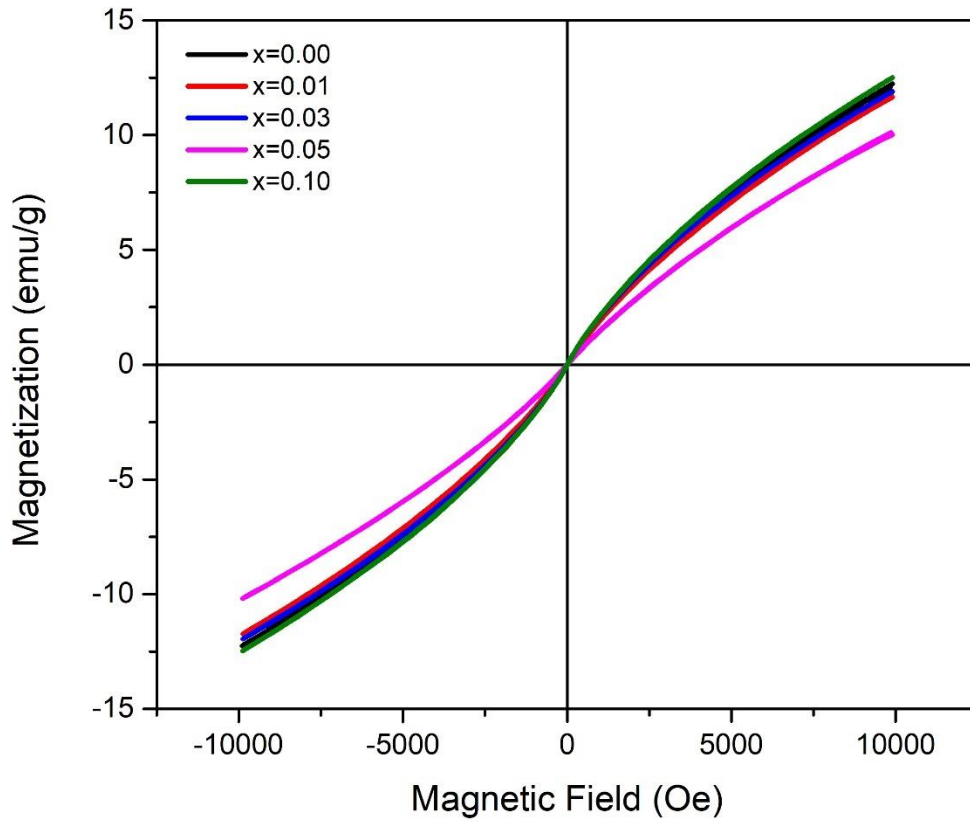


Figure 4.3: Magnetic hysteresis loop for all samples with various Al_2O_3 contents

By using vibration sample magnetometer, the magnetometer property was investigated at room temperature. Figure 4.3 shows the hysteresis curve graph pattern for the sample with concentration $x = 0.00, 0.01, 0.03, 0.05$ and 0.10 . Since the T_c of PSMO is estimated between 200 K to 305 K, it shown that at room temperature, the magnetic material still behaves as a ferromagnetic but a weak ferromagnetic. Based on table 4.2, it indicates that the highest value of magnetization is samples $x = 0.00$ and 0.10 where the values are 12.1678 emu/g and 12.4593 emu/g. Samples $x = 0.00$ and 0.10 show the highest value of magnetization which shows weak ferromagnetic properties.

Concentration, x	Magnetization (emu/g)
0.00	12.1678
0.01	11.6820
0.03	11.9149
0.05	10.0957
0.10	12.4593

Table 4.2: Value of magnetization with concentration $x = 0.00, 0.01, 0.03, 0.05, 0.10$ which are measured at room temperature.

4.4 AC Susceptibility

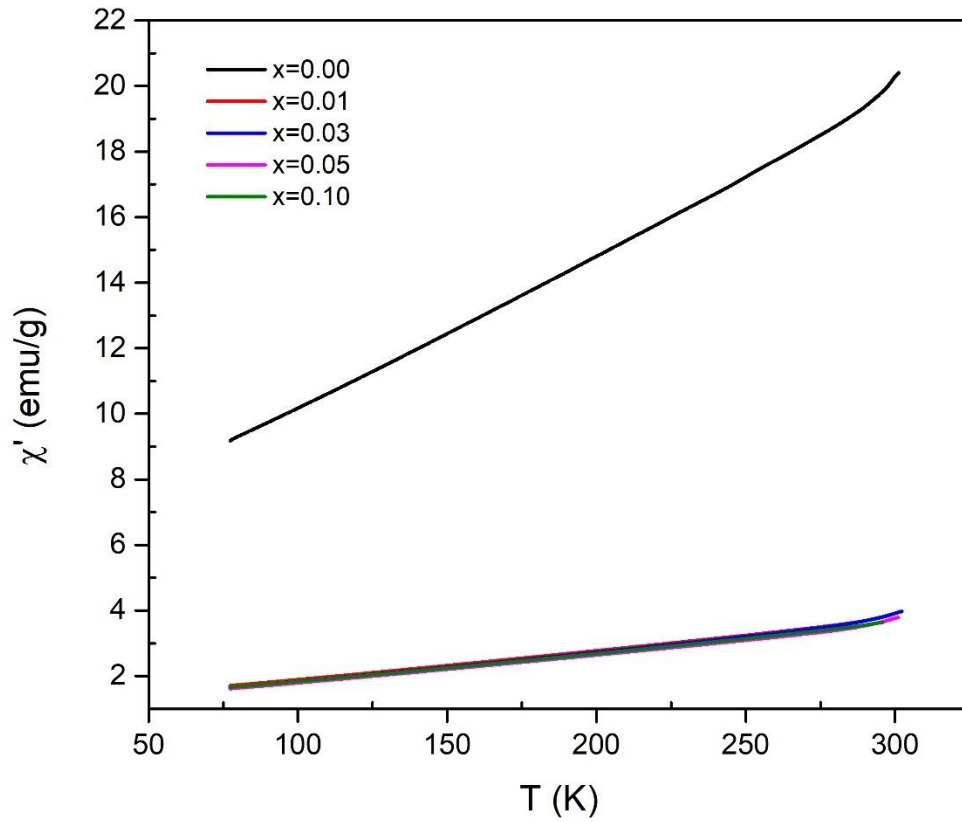


Figure 4.4: Temperature dependence of the real part of ac susceptibility for samples in ac field for PSMO/Al₂O₃ samples

Figure 4.4 shows the graph of susceptibility against temperature. The results shown that as the secondary oxide was added, the magnetization drop drastically. Hence, the magnetic property was changed and has been weakened which is there must be a modification towards the sample. From the XRD results, we cannot find the peaks of aluminium oxide. Obviously, the assumption of substitution of Al³⁺ in Mn³⁺ does occur because this is due to the disturbance of PSMO system. Until room temperature, they are still in ferromagnetic state.

4.5 HALL MEASUREMENT SYSTEM (FOUR POINT PROBE)

The electrical properties of the sample were observed by using four-point probe via hall measurement system. 3 types of graphs have been plotted in order to observe more about the differences between the samples on their electrical properties with range 80 K until 300 K.

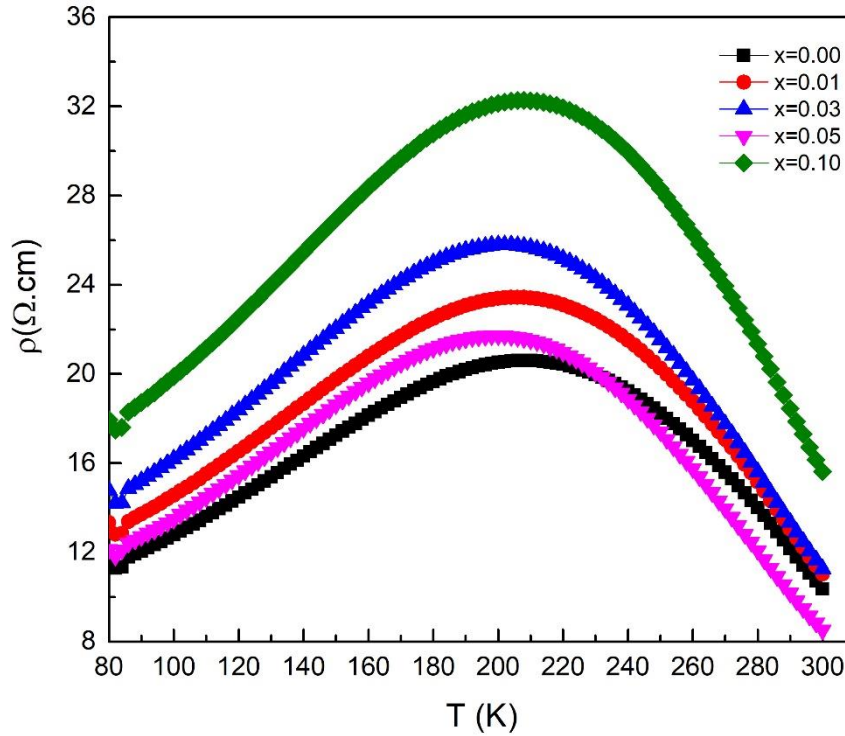


Figure 4.5: Graph of resistivity against Temperature

From figure 4.5, the results were observed as the temperature increases starting from 80 K, the resistivity increased until it reached to a maximum temperature which called as metal-insulator temperature (T_{MI}). The maximum peak of the graph is called the T_{MI} . The sample act as a metallic behaviour before T_{MI} . This is because resistance increases with temperature and double exchange interaction mechanism is dominant at the region upon reaching T_{MI} . It has been displayed that the temperature shifted to a higher temperature which might cause by magnetic

field of other factors. Increasing the concentration of Al_2O_3 will lead to shift T_{MI} to a lower temperature.

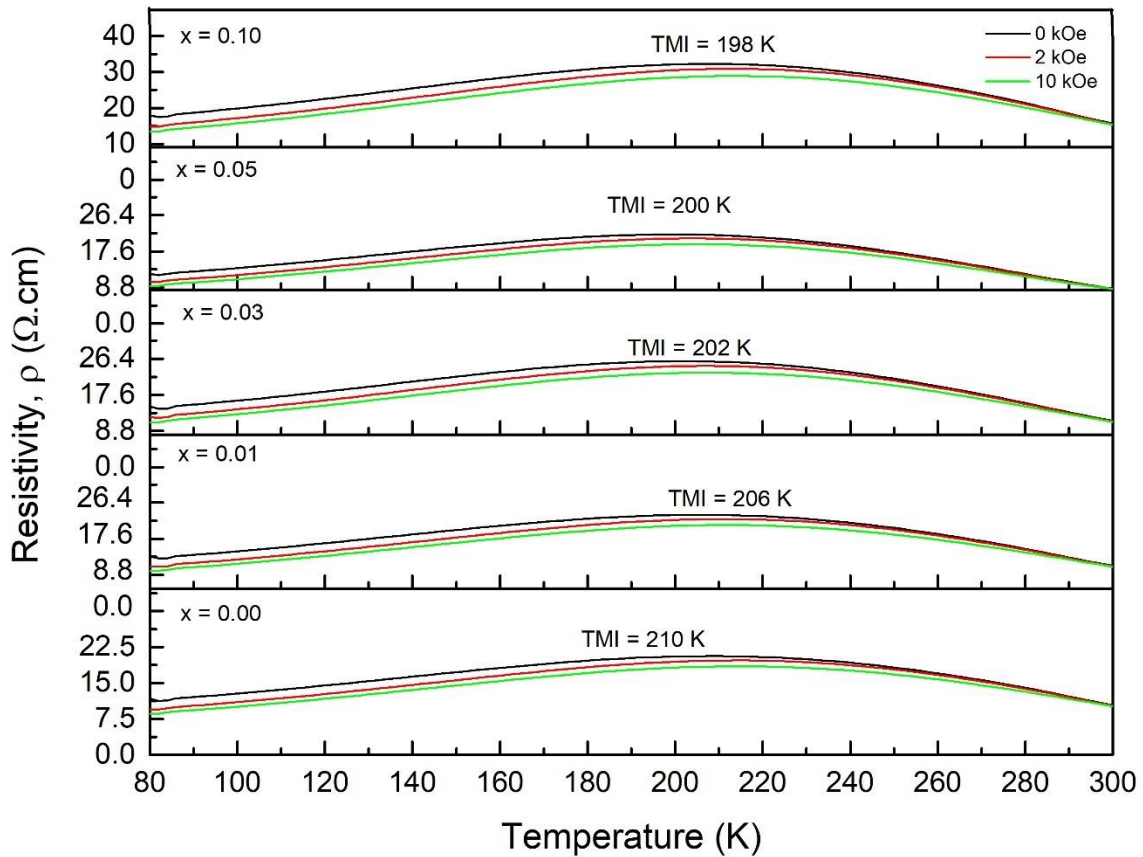


Figure 4.6: Resistivity curve as a function of Temperature for sample $x = 0.00, 0.01, 0.03, 0.05$ and 0.10 of Al_2O_3 in pure PSMO

Figure 4.6 shows the resistivity graph decreases as the magnetic field was applied throughout the temperature range and T_{MI} shifts slightly to the left where to the lower temperature. There is an enhancement of magnetoresistance shown from the graph. The MR enhanced with low concentration at higher temperature. However, as the concentration of Al_2O_3 increases, the MR enhanced at low temperature.

The region is considered as metallic behavior below T_{MI} and is explained by double exchange (DE) mechanism. In DE mechanism, the electron in e_g orbital at Mn^{3+} atom is hopping to the

Mn^{4+} site through the oxygen. Ideally, the resistivity should be increases with increasing of the temperature. However, the resistivity drops back after TMI, which follow the insulating behavior. Hence, DE cannot be use to explain this phenomenon. Hence, Jahn Teller effect was introduced at the region. The phonon effect has a significant impact on the electrical transport mechanism in this region, and the Jahn teller effect has been enhanced as a result of the phonon effect in this region, which is the region following the T_{MI} . therefore, the resistivity drops when temperature increased.

In order to see more clearer image of the enhancement of magnetoresistance, the graphs of MR against magnetic field were plotted.

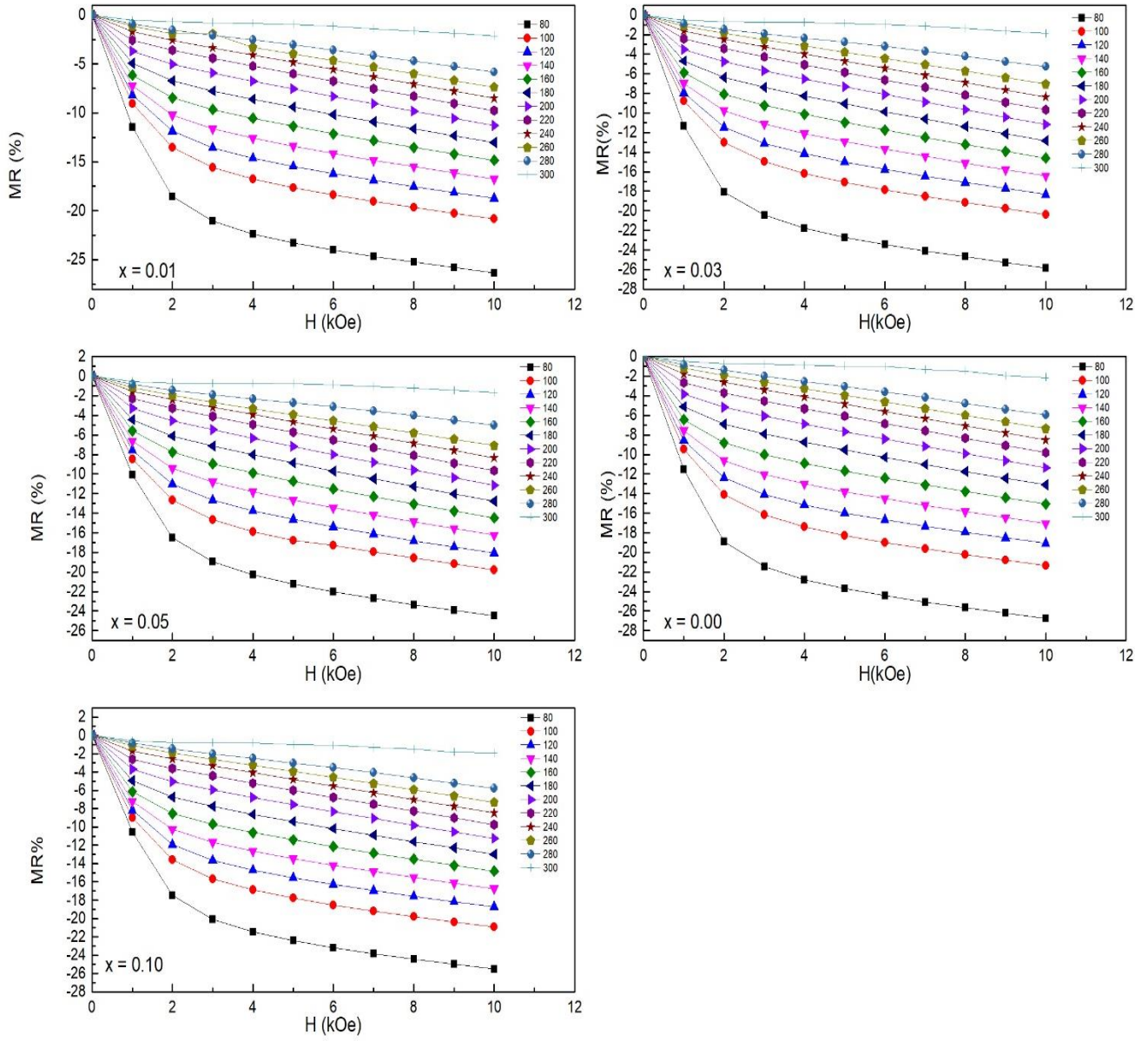


Figure 4.7: %MR curve as a function of magnetic field in various temperatures for sample $x = 0.00, 0.01, 0.03, 0.05$ and 0.10 of Al_2O_3 in pure PSMO

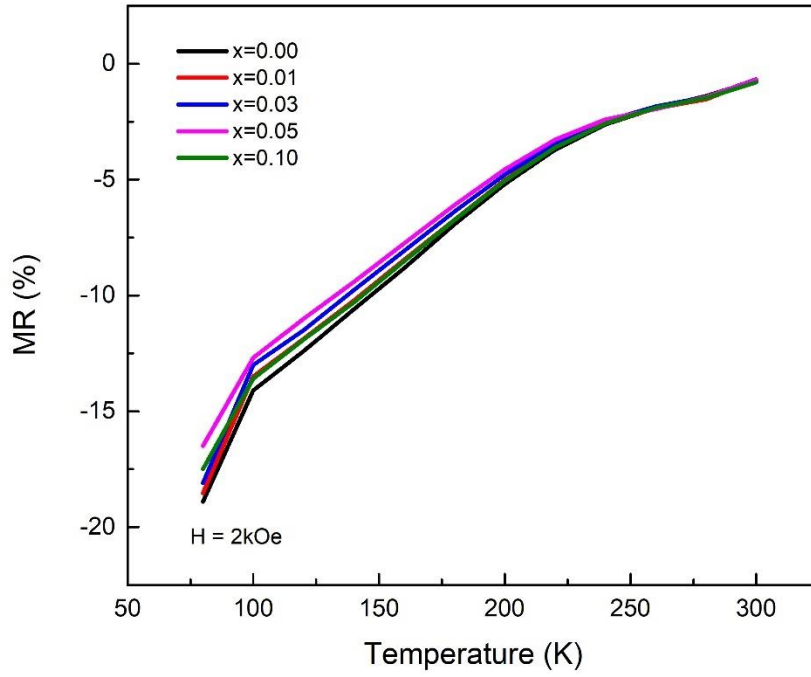


Figure 4.8: MR curve as a function of Temperature at 2kOe

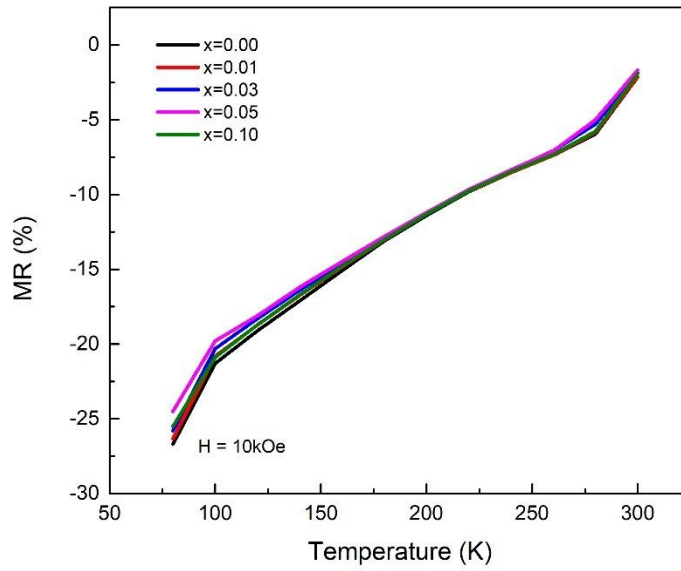


Figure 4.9: MR curve as a function of Temperature at 10kOe

Based on figure 4.8, the intrinsic effect and extrinsic effect for the sample at low field was displayed. The addition of Al_2O_3 into PSMO system has suppressed the intrinsic effect at low

temperature. The extrinsic effect is bigger for the samples with the concentrations instead of the pure PSMO at lower temperature. The extrinsic effect in pure PSMO is smaller at lower temperature. According to the definition of magnetoresistance, the value of MR will be increase if the resistivity also increased.

Figure 4.8 and 4.9 show the magnetoresistance characteristics under an applied field of 2kOe and 10kOe as a function of temperature for the samples in this research. The graphs display a significant maximum MR peak close to the value of T_c . This behavior normally related to the intrinsic MR behavior where typically maximum MR occurred near T_c . The %MR keep going to increase after T_c . For typical extrinsic MR behavior at low temperature, the MR will be increasing as in the graph. Hence, from this study, addition of secondary oxide does enhance the LFMR.

CHAPTER 5

CONCLUSION

5.0 Summary

As a conclusion, $\text{Pr}_{0.6}\text{Sr}_{0.33}\text{MnO}_3$ nanocomposites have been prepared by using sol gel reaction method and various composition (0%, 1%, 3%, 5% and 10%) of Al_2O_3 were added into pure PSMO in order to determine the structure, electrical and magnetotransport properties of the sample.

For XRD analysis, the results show that all the samples are single-phase without any detectable impurity or secondary phase was observed. The lattice parameter, bond angle and bond length are almost the same for all the samples.

Next the magnetic behavior of PSMO is ferromagnetic in room temperature since the curie temperature of PSMO is estimated to be between 200K to 305K. Based on the results from XRD, ACS and also VSM, the secondary oxide was actually substituted into the parent compound.

Other than that, the presence of Al_2O_3 enhance the low-field magnetoresistance and the shifting of T_{MI} to the lower temperature. This is because of the suppression of DE effect and JT distortions were used after T_{MI} .

5.1 Recommendations for future work

In this project, the structure, electrical and magnetotransport properties by addition of different composition of Aluminium Oxide into pure PSMO perovskite manganite in nano powder via sol gel reaction method had been done. However, there are some researches can be done in order to improve the study of colossal magnetoresistance in the following ways:

1. Different synthesize techniques can be used to obtain different particles distribution such as solid-state method and co-precipitation.
2. Used a different sintering temperature to study the effect of grain size on affecting the extrinsic MR.

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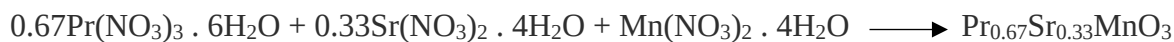
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APPENDICES

Chemical Balance Equation



Mass of each element

$$0.67\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} = 291.4567\text{g}$$

$$0.33\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} = 69.8379\text{g}$$

$$1 \text{ mole } \text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} = 251.01\text{g}$$

$$\text{Total mass of reactant} = 612.3046\text{g}$$

Desired weight to produced 20g of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

$$[\text{Pr}] = \frac{291.4567}{612.3046} \times 20\text{g} = 9.5199905\text{g}$$

$$1 \text{ mole of } [\text{Pr}] = \frac{9.5199905}{435.01} = 0.021884 \text{ mole}$$

$$[\text{Sr}] = \frac{69.8379}{612.3046} \times 20\text{g} = 2.281148\text{g}$$

$$1 \text{ mole of } [\text{Sr}] = \frac{2.281148}{211.63} = 0.010778 \text{ mole}$$

$$[\text{Mn}] = \frac{251.01}{612.3046} \times 20\text{g} = 8.19886\text{g}$$

$$1 \text{ mole of } [\text{Mn}] = \frac{8.19886}{251.01} = 0.032663 \text{ mole}$$

$$\text{Molar Ratio} = \frac{[\text{CA}]}{[\text{MI}]} = 3$$

$$\begin{aligned} [\text{CA}] &= 3 \times 0.06532 \text{ mole} = 0.19596 \times 192.13 \\ &= 37.6497\text{g} \end{aligned}$$

$$[\text{EG}] = \frac{[\text{CA}]}{[\text{EG}]} = 3$$

$$\begin{aligned} &= 0.06532 \times 62.07 \\ &= \frac{4.0544}{1.11} \\ &= 3.6526 \text{ cm}^3 \end{aligned}$$

Name and formula

Reference code: 98-006-7110

Compound name: Praseodymium Strontium Manganese Oxide (0.6/0.4/1/3) - Lt
Chemical name: Praseodymium Strontium Manganese Oxide (0.6/0.4/1/3) - Lt
Common name: Praseodymium Strontium Manganese Oxide (0.6/0.4/1/3) - Lt
ICSD name: Praseodymium Strontium Manganese Oxide (0.6/0.4/1/3) - Lt

Chemical formula: $\text{Mn}_1\text{O}_3\text{Pr}_{0.6}\text{Sr}_{0.4}$
Second chemical formula: $(\text{Pr}_{0.6}\text{Sr}_{0.4}) (\text{MnO}_3)$

Crystallographic parameters

Crystal system: Orthorhombic
Space group: $P n m a$
Space group number: 62

a (Å): 5.4270
 b (Å): 7.6510
 c (Å): 5.4680
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 90.0000

Calculated density (g/cm³): 6.51
Volume of cell (10⁶ pm³): 227.04
Z: 4.00
RIR: 9.07

Subfiles and quality

Subfiles: ICSD Pattern
Inorganic
Quality: Calculated (C)

Comments

ICSD collection code: 94984
Creation Date: 1/1/1970
Modification Date: 1/1/1970
Calculated Pattern Original Remarks: Magnetic structure available in fulltext
Structures: GdFeO₃
Original ICSD space group: PNMA
ICSD Collection Code: 94984

Original ICSD space group: PNMA

At least one temperature factor missing in the paper.

No R value given in the paper

Structure type: GdFeO₃

Temperature in Kelvin: 10

Rietveld profile refinement applied

The structure has been assigned a PDF number (calculated powder diffraction data): 01-070-8803

Neutron diffraction (powder)

Magnetic structure available in fulltext

Structure type: GdFeO3

Recording date: 10/1/2003

Modification date: 8/1/2008

ANX formula: ABX3

Z: 4

Calculated density: 6.51

Pearson code: oP20

Wyckoff code: d c2 b

TRANS Origin 0 0 1/2

Publ. title: Neutron diffraction, NMR and magneto-transport properties in the Pr_{0.6} Sr_{0.4} Mn O₃ perovskite manganite

References

Primary reference:

Dubourdieu, C. Shimizu, K. Yelon, W.B. Cai, Q. Pierre, J. Cheikhrouhou, A. Ellouze, M. Boujelben, W., *Journal of Alloys Compd.*, 334, 1, (2002)

Peak list

No.	h	k	l	d [Å]	2Theta [deg]	I [%]
1	0	1	1	4.44867	19.942	0.0
2	1	0	1	3.85188	23.072	7.6
3	0	2	0	3.82550	23.233	4.0
4	1	1	1	3.44047	25.876	0.0
5	0	0	2	2.73400	32.729	19.1
6	1	2	1	2.71432	32.973	99.4
7	2	0	0	2.71350	32.983	100.0
8	2	1	0	2.55742	35.060	0.0
9	1	0	2	2.44166	36.780	0.1
10	2	0	1	2.43066	36.952	0.0
11	1	1	2	2.32609	38.678	0.4

12	2	1	1	2.31657	38.843	0.2
13	0	3	1	2.31130	38.936	0.4
14	0	2	2	2.22433	40.523	9.6
15	2	2	0	2.21325	40.735	10.1
16	1	3	1	2.12648	42.476	0.0
17	1	2	2	2.05817	43.958	0.1
18	2	2	1	2.05157	44.107	0.1
19	2	0	2	1.92594	47.151	25.2
20	0	4	0	1.91275	47.496	12.7
21	2	1	2	1.86768	48.716	0.0
22	2	3	0	1.85837	48.976	0.0
23	0	1	3	1.77305	51.501	0.1
24	1	3	2	1.76368	51.794	0.1
25	2	3	1	1.75952	51.926	0.1
26	1	0	3	1.72782	52.952	1.2
27	2	2	2	1.72023	53.204	2.1
28	3	0	1	1.71745	53.297	1.2
29	1	4	1	1.71316	53.441	2.0
30	1	1	3	1.68538	54.394	0.0
31	3	1	1	1.67575	54.732	0.1
32	1	2	3	1.57466	58.574	15.6
33	0	4	2	1.56727	58.877	19.6
34	3	2	1	1.56680	58.897	20.8
35	2	4	0	1.56338	59.038	7.2
36	2	3	2	1.53693	60.158	0.0
37	2	0	3	1.51302	61.210	0.0
38	3	0	2	1.50865	61.406	0.0
39	1	4	2	1.50574	61.538	0.0
40	2	4	1	1.50315	61.655	0.0
41	2	1	3	1.48428	62.527	0.0
42	0	3	3	1.48289	62.592	0.0
43	3	1	2	1.48015	62.721	0.1
44	0	5	1	1.47359	63.032	0.1
45	1	3	3	1.43045	65.163	0.0
46	3	3	1	1.42455	65.467	0.0
47	1	5	1	1.42209	65.594	0.0
48	2	2	3	1.40698	66.390	0.0
49	3	2	2	1.40346	66.578	0.0
50	0	0	4	1.36700	68.596	3.2
51	2	4	2	1.35716	69.164	16.2
52	4	0	0	1.35675	69.187	14.7
53	4	1	0	1.33591	70.425	0.0
54	2	5	0	1.33287	70.609	0.0
55	1	0	4	1.32559	71.056	0.0
56	4	0	1	1.31682	71.602	0.0
57	1	1	4	1.30613	72.279	0.1
58	2	3	3	1.30126	72.593	0.1
59	3	3	2	1.29847	72.774	0.0
60	4	1	1	1.29774	72.822	0.0
61	1	5	2	1.29661	72.895	0.0
62	2	5	1	1.29496	73.003	0.1
63	0	2	4	1.28728	73.510	0.3
64	3	0	3	1.28396	73.731	0.6
65	1	4	3	1.28216	73.852	1.0
66	4	2	0	1.27871	74.084	0.8
67	3	4	1	1.27791	74.139	1.0
68	0	6	0	1.27517	74.325	0.3
69	3	1	3	1.26625	74.938	0.0
70	1	2	4	1.25253	75.903	0.0
71	4	2	1	1.24512	76.436	0.0
72	2	0	4	1.22083	78.242	2.5

73	3	2	3	1.21723	78.518	5.9
74	4	0	2	1.21533	78.665	2.8
75	1	6	1	1.21056	79.036	5.5
76	2	1	4	1.20558	79.426	0.0
77	4	1	2	1.20028	79.847	0.0
78	2	5	2	1.19808	80.024	0.0
79	4	3	0	1.19780	80.046	0.0
80	2	4	3	1.18665	80.953	0.0
81	3	4	2	1.18454	81.128	0.0
82	1	3	4	1.17620	81.825	0.1
83	0	5	3	1.17195	82.186	0.0
84	4	3	1	1.17006	82.347	0.0
85	2	2	4	1.16304	82.953	1.5
86	4	2	2	1.15828	83.370	1.7
87	0	6	2	1.15565	83.603	0.7
88	2	6	0	1.15409	83.742	0.8
89	3	3	3	1.14682	84.394	0.0
90	1	5	3	1.14554	84.510	0.0
91	3	5	1	1.14250	84.787	0.0
92	1	6	2	1.13031	85.922	0.0
93	2	6	1	1.12921	86.025	0.0
94	0	4	4	1.11217	87.674	3.0
95	4	4	0	1.10663	88.227	3.1
96	2	3	4	1.10117	88.779	0.0
97	4	3	2	1.09713	89.193	0.0
98	3	0	4	1.09063	89.868	0.0
99	1	4	4	1.08952	89.984	0.0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0.26620	0.02610	0.73270	0.5000	1.0000	8d
2	O2	O	0.49410	0.25000	0.05330	0.5000	1.0000	4c
3	MN1	Mn	0.00000	0.00000	0.50000	0.5000	1.0000	4b
4	SR1	Sr	0.00360	0.25000	0.99770	0.5000	0.4000	4c
5	PR1	Pr	0.00360	0.25000	0.99770	0.5000	0.6000	4c

Stick Pattern

