**UNIVERSITI PUTRA MALAYSIA**

# STRUCTURAL MAGNETIC AND ELECTRICAL PROPERTIES OF LA0.67CA0.33MN03 PEROVSKITE SYNTHESIZED VIA CONVENTIONAL AND CO-PRECIPITATION METHODS

**HAZAR ALI AHMED ALI SALAMA.**

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**By**

**HAZAR ALI AHMED ALI SALAMA**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

**June 2004**

# DEDICATION

To:

My Parents.......

My Brothers and sisters

My sister, Umyma .....

Anas
It's all for you son...

My beloved new born,
Mohamed

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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**Chairman: Professor Abdul Halim bin Shaari, Ph.D.**

**Faculty : Science and Environmental Studies**

The structural, magnetic and electrical properties of lanthanum manganites having a nominal composition of $La_{0.67}Ca_{0.33}MnO_3$ synthesized via co-precipitation method (COP) following sintering treatments at temperature ranging between 1100°C and 1350°C are reported. XRD pattern showed the monophasic orthorhombic structure of the sample sintered within the above temperature range for a sintering period of 24 hours. The SEM micrographs showed that the grains are well grown and clear grain boundaries are observed. The grain size increased significantly form 1.7μm to 10.3μm as the sintering temperature increases and were well compacted. Large grains growth with layered features is observed in samples sintered at higher temperature. Ferromagnetic-paramagnetic phase transition were observed in the $\chi$'-temperature curves for all the sintered samples. The Curie temperature, $T_c$ shifts to lower temperature as the sintering temperature, $T_s$ increases. All the samples show the typical ferromagnetic-paramagnetic

phase transition, $T_c$ in the range 267.9 K~259.7 K. The transport properties show the transition of semiconducting to metallic conductivity at $T_p$, the transition occurs within the range 276 K ~ 288 K which is higher compared with the data reported earlier. Based on the semiconducting model, $Ln(R) \propto \left(-E_a/K_BT\right)$ it was observed that the Activation energy, $E_a$ value ranges from 100.40 to 118.73 meV. The colossal magnetoresistance effect appears at low temperature and the highest value of CMR effect was observed at temperature approaching $T_p$. The highest CMR value was observed near the insulator–metal transition. The maximum MR with a value of ~68.2% for H = 1.06 T is obtained in the sample prepared at 1200°C.

The specimens of $La_{0.67}Ca_{0.33}MnO_3$ prepared via COP method were compared to the specimen prepared by Conventional Powder method (CPM) for samples sintered at 1300°C. XRD spectrum for the samples exhibit orthorhombic distorted and single-phase perovskite structures. The Curie temperature, $T_c$ and the metal-insulator transition temperature, $T_p$ were obtained by ac susceptibility and four- point probe techniques. The results showed that $T_c$ and $T_p$ were 260 K and 276 K respectively for the COP specimen, which is higher than the results obtained by specimen prepared by CPM with $T_c$ and $T_p$ 245 K and 246 K respectively. These results are due to the high chemical homogeneity and high density for the COP specimen as compared to the CPM specimen. The CMR for the (COP) specimen is observed near the insulator- metal transition with the value of ~ 56% for H = 1.06 T while for the CPM the CMR value of ~34%

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**STRUKTUR, SIFAT MAGNETIK DAN ELEKTRIKAL $La_{0.67}Ca_{0.33}MnO_3$ PEROVSKITE YANG DISEDIAKAN MELALUI KAEDAH PEMENDAKAN**

Oleh

**HAZAR ALI AHMED ALI SALAMA**

**Jun 2004**

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Struktur, sifat magnet dan elektrik bagi lanthanum manganites dengan komposisi nominal $La_{0.67}Ca_{0.33}MnO_3$ yang disediakan melalui kaedah pemendakan diikuti dengan persinteran pada suhu di antara 1100°C ke 1350°C dilaporkan. Keputusan XRD menunjukkan struktur fasa tunggal orthorombik pada sampel yang disinter pada suhu tersebut pada kadar 24 jam. Mikrograf SEM menunjukkan saiz butiran yang jelas pembesaranaya dan sempadan butiran yang jelas. Saiz butiran bertambah secara signifikan dari 1.7μm ke 10.3μm berkadar langsung dengan suhu persinteran dan semakin padat. Butiran yang besar dan berlapis kelihatan pada sampel yang disinter pada suhu yang lebih tinggi. Peralihan fasa ferromagnet-paramagnet kelihatan pada lengkungan suhu $\chi'$ untuk semua sampel yang disinter. Suhu Curie,$T_c$ beranjak ke suhu yang lebih rendah berkadar songsang dengan suhu persinteran,$T_s$. Semua sampel menunjukkan fasa peralihan feromagnet-paramagnet,$T_c$ yang tipikal pada julat

267.6 K ~ 259.7 K. Sifat pengangkutan menunjukkan peralihan semikonduktor ke sifat logam pada $T_p$, peralihan terhasil pada julat 276 K ~ 288 K di mana ia lebih tinggi daripada data yang sebelumnya. Berdasarkan model semikonduktor, $Ln(R) \propto (-E_a/K_BT)$ kelihatan nilai tenaga teruja, $E_a$ pada julat 92.40 ke 118.73 meV. Nilai-nilai ini adalah lebih tinggi dengan signifikan daripada yang didapati. Kesan raksaksa magnetorintangan muncul pada suhu rendah dan nilai yang tertinggi untuk kesan CMR kelihatan pada suhu menghampiri $T_p$. Nilai CMR yang paling tinggi kelihatan menghampiri peralihan penebat-logam. Nilai MR maksimum dengan nilai ~68.2% pada H = 1.06 T diperolehi pada sampel yang disediakan pada suhu 1200°C.

Sampel $La_{0.67}Ca_{0.33}MnO_3$ yang disediakan melalui kaedah pemendakan dibandingkan dengan sampel yang disediakan dengan kaedah tindakbalas pepejal untuk sampel-sampel yang disinter pada suhu 1300°C. Spektrum XRD bagi sampel mempamerkan penyerotan orthorombik dan struktur perovskit fasa tunggal. Suhu Curie, $T_c$ dan suhu peralihan logam-penebat, $T_p$ diperolehi dengan kaedah kerintangan a.u dan teknik penduga empat titik. Keputusan menunjukkan $T_c$ dan $T_p$ adalah 260 K dan 276 K masing-masing untuk sampel COP, di mana nilainya adalah lebih tinggi daripada keputusan yang diperolehi oleh sampel CPM dengan $T_c$ dan $T_p$ adalah 245 K dan 246 K masing-masing. Keputusan ini adalah berkaitan dengan homogeniti dan ketumpatan tinggi pada sampel COP dibandingkan dengan sampel CPM. CMR pada sampel COP diperhatikan menghampiri peralihan penebat-logam dengan nilai ~ 56% untuk H = 1.06 T dan nilai CMR sampel CPM bernilai ~ 34%.

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# LIST OF ABREVIATIONS AND KEY WORDS

| | |
|---|---|
| <A> | Average ionic radius |
| a, b, c | Lattice Parameter |
| AFI | Antiferromagnetic insulator |
| AFM | Antiferromagnetic |
| AMR | Anisotropic Magnetoresistance |
| CMR | Colossal Magnetoresistance |
| COP | Co precipitation |
| CPM | Conventional Powder Method |
| DE | Double exchange |
| $d_{hkl}$ | Distance between atom and selected 2θ |
| $d_{La\text{-}O}$ | La-O bond distance |
| $d_{Mn\text{-}O}$ | Mn-O bond distance |
| $E_a$ | Activation energy |
| EMR | Extraordinary Magnetoresistance |
| f | Frequency. |
| FMI | Ferromagnetic insulator |
| GMR | Giant Magnetoresistance |
| H | Applied magnetic field |
| hkl | Miller indices |
| JT | Jahn-Teller |
| $k_B$ | Boltzman constant |

| | |
|---|---|
| LCMO | La-Ca-Mn-O system |
| M | Magnetization |
| MI | Metal to insulator |
| MIT | Metal-insulator transition |
| MR | Magnetoresistance |
| PMI | Paramagnetic insulator |
| R (0) | The resistance in zero magnetic field |
| R (H) | The resistance in the magnetic field |
| S | Spin electron |
| SEM | Scanning Electron Microscope |
| T | Temperature in Kelvin |
| t | Tolerance factor |
| $T_c$ | Curie temperature |
| TMR | Tunnelling Magnetoresistance |
| $T_p$ | Phase transition temperature. |
| $T_s$ | Sintering temperature. |
| VLMR | Very Large Magnetoresistance |
| XRD | X-ray diffraction |
| $\Theta$ | Paramagnetic Curie point |
| $\chi$ | Susceptibility |

# CHAPTER I

# INTRODUCTION

Since the discovery of high $T_c$ superconductivity in copper oxides, in 1986, transition-metal oxides of perovskite structure are receiving much attention. A few years after the initial discovery, in 1993, more excitement greeted reports that certain manganese oxides showed a huge change in electrical resistivity when a magnetic field was applied. This effect is generally known as magnetoresistance, but the resistivity change observed in these oxides was so large that it could not be compared with any other forms of magnetoresistance. The effect observed in these materials "the manganese perovskites" was therefore dubbed "colossal" magnetoresistance to distinguish it from the giant magnetoresistance (GMR) observed in magnetic multilayers and granular films.

The discovery; first reported by researchers at Siemens in Germany and a little later by a group at Bell Labs in New Jersey raised expectations of a new generation of magnetic devices and sensors, and launched a frenetic scientific race to understand the cause of the effect. Today, the promise of great strides in technology remains a challenge, but the perovskites are receiving a lot of attention in their own right (Fontcuberta, 1999).

One reason for this growing interest is the rare-earth manganese oxides, the manganites. In the beginning of the 1990's it was found that some manganites could exhibit a magnetic phase transition close to room temperature, which were accompanied by a magnetic field driven metal-insulator transition (Chahara et al, 1993, Helmolt et al, 1993, Jin et al, 1994).

In general, magnetoresistance is a measure of the change in electrical resistance as function of the magnetic field *H* and is usually calculated as:

$$MR\% = \frac{R(H) - R(0)}{R(0)} \times 100 \qquad 1.1$$

where R(*H*) denotes the field dependent resistance and R(0) the resistance at zero magnetic field.

There can be many different physical effects causing magnetoresistance; some of the most common ones are shown in Figure. 1.1. In the mid 19$^{th}$ century it was pointed out that the electric resistance in magnetic materials depends on the orientation of an applied magnetic field relative to the orientation of the crystal itself, (Thomson, 1857). A phenomenon given the name anisotropic magnetoresistance is shown in Figure. 1.1a. On the other hand, the ordinary magnetoresistance (Figure 1.1b), which is related to the Hall Effect, originates from the impact of the Lorentz-force on moving charge carriers. In absolute numbers, the magnitudes of the anisotropic and the ordinary magnetoresistances are moderate and typically not more than a few percent. In the end of the 1980's it was discovered that multi-layers of magnetic and nonmagnetic metallic materials could show a magnetoresistance of much higher magnitude than previously observed (Baibich et al., 1988). The prefix giant was then used to describe the magnetoresistance (Figure 1.1c). Only about half a decade later it was discovered that doped rare-earth manganese oxides by themselves could possess even higher magnetoresistance (in some cases close to 100%) (Chahara et al., 1993; Helmolt et al., 1993; Jin et al., 1994) The physical origin of the magnetoresistance in manganites was completely different from the giant magnetoresistance effect, and hence the term *colossal* was used to describe the effect. The general behavior of colossal magnetoresistance is shown in Figure. 1.1d.

In magnetic tunnel junctions there is another type of magnetoresistance, known as tunnelling magnetoresistance or sometimes junction magnetoresistance, Figure 1.1e and Figure 1.1f. The resistance of a magnetic tunnel junction is lower when the magnetization of the electrodes is parallel than in the antiparallel configuration. It is the ability to switch between these two configurations that is the origin of the tunnel magnetoresistance.

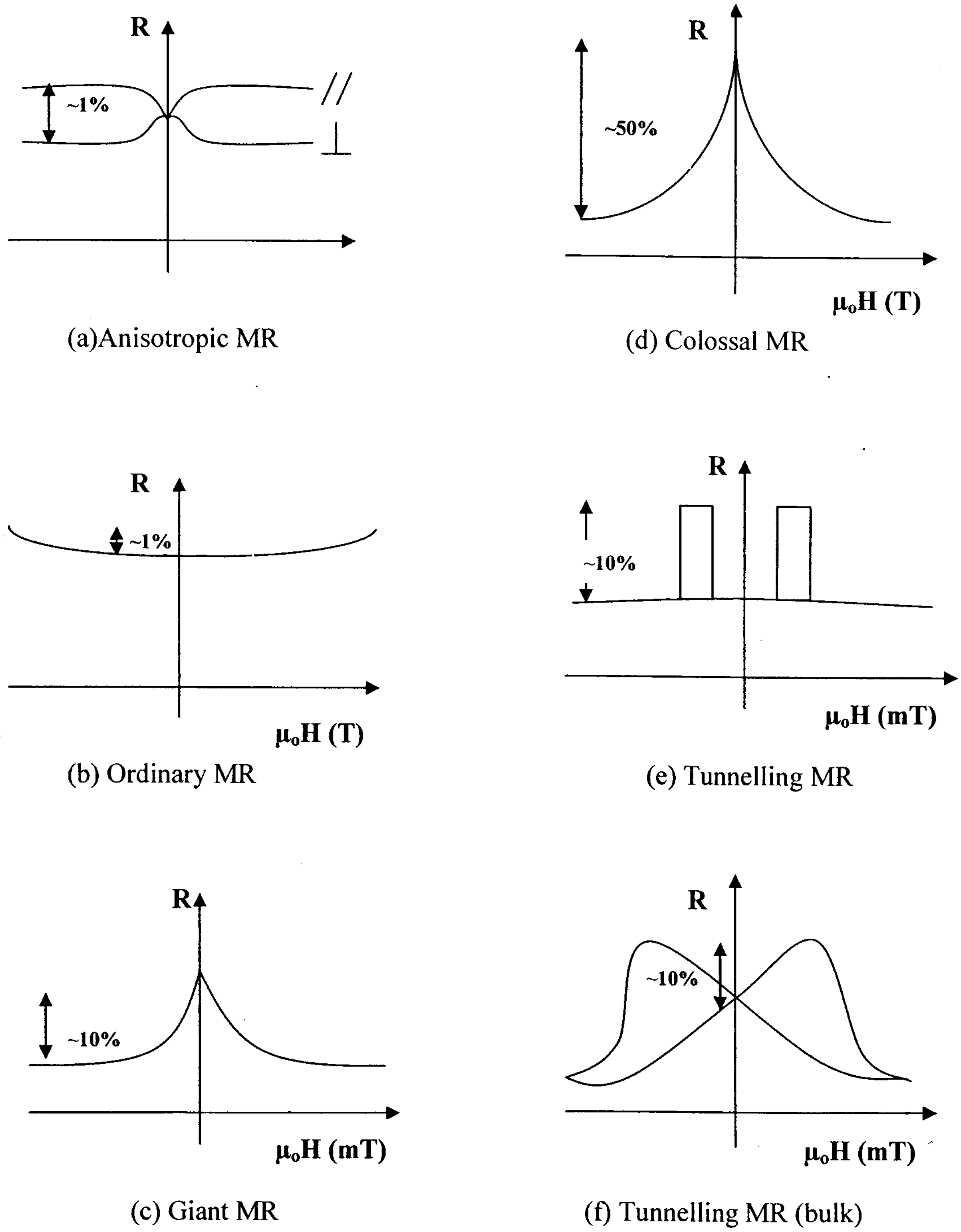


Figure 1.1: A summary of the most common types of magnetoresistance (MR). The anisotropic, ordinary and colossal MR can be considered as intrinsic effects of the material, while giant and tunnelling MR depend on extrinsic parameters. The tunnelling MR in e) appears in magnetic tunnel junctions, so called spin-valves, while intergrain tunneling in powder and polycrystalline bulk causes a smearing as shown in panel f). Note the different magnitude of the scales.

Anisotropic Magnetoresistance (AMR) measure the change in resistance seen when the current flowing through a sample changes from being parallel to internal magnetization to being perpendicular to it. The materials that exhibit AMR include Permalloy (NiFe) and iron filings. The Tunneling Magnetoresistance (TMR) affect a large change in the electrical resistance upon the application of a magnetic field of two magnetic layers separated by an insulating layer. The Giant Magnetoresistance (GMR) which describes the behavior of materials that have alternating layers of ferromagnetic and nonmagnetic materials deposited on an insulated substrate. The very Large Magnetoresistance (VLMR) effect is seen in homogenous material, and is very similar to GMR.

**Table1.1: Comparison of MR Types**

| Type of MR | Increase in Resistance % |
|---|---|
| MR | 1 |
| AMR | 20 |
| GMR | 200 |
| CMR | 100,000 |