

FABRICATION AND CHARACTERIZATION OF COLOSSAL MAGNETORESISTANCE MANGANITES IN BULK, SINGLE LAYER AND TRILAYER THIN FILMS PREPARED BY PULSED LASER DEPOSITION TECHNIQUE

MANIZHEH NAVASERY

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By MANIZHEH NAVASERY

Thesis submitted to the school of Graduate Studies, Universiti Putra Malaysia, In Fulfillment of the Requirement for the Degree of Doctor of Philosophy

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Dedication

To My Mother

From Earth to Heaven...

The words cannot describe how much I missed her. I lost her at a time when I was studying abroad.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

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By

MANIZHEH NAVASERY

November 2012

Chairman: Abdul Halim Shaari, PhD

Faculty: Science

Electronic and magnetic properties of mixed-valent manganites, $Re_{1-x}M_xMnO_3$ (Re = rare earth, M = alkaline earth), have received a lot of attention in the last decade because of the variety of interesting phenomena exhibited by these materials. This project was aimed at studying the structure and magnetotransport properties of manganites in the form of bulk, single and trilayer thin films prepared by Pulsed Laser deposition (PLD) thechnique by using Nd-YAG laser on different substrates. A comparison study between the bulk and thin film and the effect of substrate type on the structure, morphology and magneto-transport properties of the thin films was studied. In addition the enhancement of magnetoresistance (MR) and phase transition temperature (T_P) on trilayer films are investigated. In the first part, the polycrystalline targets of $La_{2/3}Ca_{1/3}$ MnO₃ (LCMO), $La_{5/8}Sr_{3/8}MnO_3$ (LSMO), $La_{0.7}Na_{0.3}$ MnO₃ (LNMO) and $Pr_{0.7}Ca_{0.3}$ MnO₃ (PCMO) were prepared by solid state

reaction. All samples were characterized by X-ray diffraction (XRD, Philips). The XRD data were analyzed by Rietveld refinement technique. It was found from XRD results that the bulks (same as thin films) were single phase with the orthorhombic Pnma structure for LCMO and PCMO and rhombohedral $R\bar{3}C$ structure for LSMO and LNMO, where no detectable impurities were observed. A four point probe system which is inserted in the liquid nitrogen cryostat was used to measure the phase transition temperature T_P, and magnetoresistance of samples by using Hall effect system. LCMO shows metal-insulator transition at 274 K while PCMO is an insulator. In the case of LSMO and LNMO Transition temperature T_P was above room temperature. The Curie temperature was measured using the CryoBIND T AC Susceptometer. T_C is found from the peak in the $d\chi'/dT$ (where χ' is the real part of the susceptibility) via temperature curve. T_c is 94.18 K for PCMO, 330.4 2 K for LSMO, 319.79 K for LNMO and 285.76 K for LCMO manganite bulks. The PCMO sample is insulating at zero magnetic field, and has a charge ordering transition around 200 K followed by antiferromagnetic and ferromagnetic transitions respectively at 142.21 K and 94.18 K that were obtained from the real and imaginary part of AC susceptibility measurement respectively. Finally, by using the vibrating sample magnetometer (VSM, Lake shore 7400) at the maximum magnetic field (10 KG), the magnetization value was 46.24 emu/g for LSMO, 21.45 emu/g for LNMO, 5.49 emu/g for LCMO and 1.66×10^{-3} emu/g for PCMO bulk manganites . In the second part of this work, the manganite targets of La2/3Ca1/8MnO3 (LCMO), La5/8Ca3/8MnO3, La_{0.3}Na_{0.7}MnO₃ (LNMO) and La_{5/8}Sr_{3/8}MnO₃ (LSMO) were deposited on different substrates such as corning glass (Cg), silicon wafer and MgO by PLD technique. All the

substrates induce in-plane strains on the films, but the lattice mismatch between the manganites and the substrate is much larger for MgO than for other substrates. Thin film samples showed a much higher resistance compared to the bulk. For LSMO/MgO the high Curie temperature of 363 K is one of the high T_C in all LSMO thin films and to the best of our knowledge, it is the highest value that is reported in the literature for MgO substrates with high lattice mismatch parameter. In addition, The Curie temperature of LSMO films is around 352 K, which is one of the high T_C in all LSMO films and it is the highest value that is reported in literature for low cost amorphous substrates such as glass. The Curie temperature, Tc is 292 K for LNMO/Cg, 304 K for LNMO/Si and 286K for LNMO/MgO thin films. The relatively high resistance of the polycrystalline thin film may be caused by crack-like defaults and grain boundaries. Magnetoresistance was measured via fure point probe technique using Hall effect system. The highest MR value obtained was -17.21% for LSMO/MgO film followed by -15.65% for LSMO/Si film at 80 K in a 1 T magnetic field. Transition temperature (T_P) is 224 K for LSMO/MgO and 200 K for LSMO/Si film. The highest MR value obtained was -18.86% for LNMO/MgO film followed by -17.35% for LNMO/Si and 16.59% for LNMO/Cg thin film at 80 K in a 1 T magnetic field. The maximum temperature coefficient of resistance (TCR) (10.42% K^{-1}) occurs at T = 232 K for LNMO/MgO film. To our knowledge, this is the best TCR value obtained for LNMO film deposited on the not well-matched MgO substrate. The Curie temperature, Tc is found from the peak in the $d\chi'/dT$ via the temperature curve that is 275 K for LSMO/Si, 270 K for LCMO/MgO and 292K for LCMO/Cg thin films. The highest MR value was -24.90% for LCMO/Si thin film, -16.77% for LCMO/Cg and -15.40% for LCMO/MgO thin film at 80 K in a 1 T magnetic field. The phase transition temperature (T_P) is 266 K for LCMO/Si,

209K for LCMO/MgO and 231 K for LCMO/Cg thin film. The significant observation in this study is the enhancement of magnetoresistance (MR) up to 36% in the LCMO/ PCMO /LCMO trilayer films. The reason for the enhanced MR suggested that it is due to the induced double exchange mechanism in PCMO by applying the magnetic field. The melting of the charge ordered state is associated with a huge CMR effect.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

FABRIKASI DAN PENCIRIAN MAGNETORINTANGAN KOLOSAL MANGANIT-MANGANIT DALAM PUKAL, SATU LAPISAN DAN TIGA LAPISAN FILEM NIPIS YANG DISEDIAKAN MENGGUNAKAN TEKNIK PEMENDAPAN LASER BERDENYUT

Oleh

MANIZHEH NAVASERY

November 2012

Pengerusi: Abdul Halim Shaari, PhD

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Elektronik dan magnet bagi manganit valentoercompur, $RE_{1-x}M_xMnO_3$ (Re = nadir bumi, M = alkali bumi) telah menerima banyak perhatian dalam dekad yang lalu kerana pelbagai fenomena menarik yang dipamerkan oleh bahan-bahan ini. Projek ini bertujuan untuk mengkaji struktur dan sifat magneto-pengangkutan manganite-manganite dalam bentuk pukal, filem nipis tunggal dan tiga lapisan yang disediakan oleh teknik pemendapan Laser berdenyut (PLD) ke atas substrat-substrat yang berbeza. Satu kajian perbandingan antara filem nipis dan pukal dan kesan jenis substrat ke atas struktur, morfologi dan sifat magneto-pengangkutan filem nipis telah dikaji. Selain itu, peningkatan suhu magnetorintangan (MR) dan fasa peralihan (T_P) pada filem tiga lapisan turut diselidik. Dalam bahagian pertama polihablur La_{2/3}Ca_{1/3} MnO₃ (LCMO), La_{5/8}Sr_{3/8}MnO₃ (LSMO), La_{0.7}Na_{0.3} MnO₃ (LNMO) dan Pr_{0.7}Ca_{0.3} MnO₃ (PCMO) telah disediakan dengan kaedah



tindak balas keadaan pepejal. Keputusan XRD menunjukkan bahan pukal dan juga filem nipis adalah fasa tunggal dengan struktur ortorombik Pnma bagi LCMO dan PCMO dan struktur rombohedral R3C bagi LSMO dan LNMO, dimana tiada bendasing dijumpai. LCMO menunjukkan peralihan logam-penebat pada 274 K, manakala PCMO adalah penebat. Dalam kes LSMO dan LNMO, T_p adalah di atas suhu bilik. Suhu Curie, Tc, maganit pukal didapati dari puncak dalam $d\chi'/dT$ melalui keluk suhu iaitu 94.18K untuk PCMO, 330.42 K untuk LSMO, 319.79 Kuntuk LNMO dan 285.76 K untuk LCMO. Sampel PCMO berpenebat pada medan magnet sifar, dan mempunyai tertiban caj peralihan sekitar 200 K yang diikuti oleh peralihan antiferromagnet dan feromagnet pada 142.21 K dan 94.18 K yang diperolehi dari bahagian nyata dan khayalan pengukuran kerentanan AC masing. Akhir sekali, pada medan magnet maksimum (10 kG), nilai kemagnetan manganit pukal adalah 46.24 emu/g untuk LSMO, 21.45emu/g untuk LNMO, 5.49 emu/g untuk LCMO dan 1.66×10^{-3} emu/g untuk PCMO. Dalam bahagian kedua kerja ini, manganit La_{2/3}Ca_{1/8}MnO₃ (LCMO), La_{5/8}Ca_{3/8}MnO₃ La_{0.3}Na_{0.7}MnO₃ (LNMO) dan La_{5/8}Sr_{3/8}MnO₃ (LSMO) telah dienapkan di atas substrat yang berbeza seperti kaca Corning, wafer silikon dan MgO dengan menggunakan teknik Pemendapan Laser Berdenyut (PLD). Semua substrat mendorong terikan dalam pelan yang luas di atas filem, tetapi ketidakpadanan kekisi di antara manganit-manganit dan substrat adalah lebih besar bagi MgO berbanding substrat lain. Sampel filem nipis menunjukkan rintangan yang lebih tinggi berbanding sampel pukal. Suhu Curie yang tinggi untuk LSMO/MgO iaitu 363 K adalah salah satu T_C yang tinggi dalam semua filem nipis LSMO dan sebagaimana pengetahuan kami, nilai T_C ini adalah nilai tertinggi yang dilaporkan dalam kajian literatur untuk substrat MgO dengan

ketidaksepadanan parameter kekisi yang tinggi. Disamping itu, suhu Curie filem LSMO adalah sekitar 352 K, yang merupakan salah satu T_C yang tinggi dalam semua filem-filem LSMO dan sebagaimana pengetahuan kami, nilai T_C ini adalah nilai tertinggi yang dilaporkan dalam kajian literatur untuk substrat amorfus kos rendah seperti kaca. Suhu Curie, Tc, untuk filem-filem nipis LNMO/Cg adalah 292 K, 304 K untuk LNMO/Si dan 286 K untuk LNMO/MgO. Rintangan yang tinggi untuk polihablur filem nipis adalah disebabkan kemungkinan seperti retak dan sempadan butiran. Nilai MR tertinggi diperolehi adalah -17.21% untuk filem LSMO/MgO yang diikuti oleh -15.65% untuk filem LSMO/Si pada 80 K dalam medan magnet 1 T. Suhu peralihan (T_P) adalah 224 K untuk LSMO/MgO dan 200 K untuk filem LSMO/Si. Nilai MR tertinggi diperolehi adalah -18.86% untuk filem nipis LNMO/MgO yang diikuti oleh -17.35% untuk LNMO/Si dan 16.59% untuk filem nipis LNMO/Cg pada 80 K dalam medan magnet 1 T. Pekali suhu rintangan maksimum (TCR) (10.42% K^{-1}) berlaku pada T = 232 K untuk filem LNMO/MgO. Ini adalah nilai TCR terbaik yang diperolehi bagi filem LNMO yang dienapkan di atas substrat MgO yang tidak sepadan. Suhu Curie, Tc, filem nipis didapati dari puncak dalam $d\chi'/dT$ melalui keluk suhu iaitu 275 K untuk LSMO/Si, 270 K untuk LCMO/MgO dan 292 K untuk LCMO / Cg. Nilai MR tertinggi adalah -24.90% untuk filem nipis LCMO/Si, -16.77% untuk filem nipis LCMO/Cg dan -15.40% untuk filem nipis LCMO/MgO pada 80 K dalam medan magnet 1T. Suhu fasa peralihan (T_P) bagi filem nipis LCMO/Si adalah 266 K, 209 K untuk LCMO/MgO dan 231 K untuk LCMO/Cg. Pemerhatian penting dalam kajian ini adalah peningkatan magnetorintangan (MR) sehingga 36% dalam filem tiga lapisan LCMO/PCMO/LCMO. Alasan bagi peningkatan MR dicadangkan berpunca dari pengaruhan mekanisme tukarganti berganda dalam PCMO

dengan menggunakan medan magnet. Kecairan keadaan tertib caj adalah dikaitkan dengan kesan CMR yang besar.



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I certify that a Thesis Examination Committee has met on 5 September 2012 to conduct the final examination of Manizheh Navasery on her thesis entitled "Fabrication and Characterization of Colossal Magnetoresistance Manganites in Bulk, Single layer and Trilayer Thin Films Prepared by Pulsed Laser Deposition Technique" in accordance with the Universities and University College Act 1971 and the Constitution of Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.



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LIST OF ABREVATIONS /NOTATIONS/GLOSSARY OF TERMS

*

AFM	Antiferromagnetic, Atomic Force Microscopy
AFI	Antiferromagnetic Insulating
CMR	Colossal Magnetoresistance
CE	Charge Exchange
со	Charge Ordering
CAF	Canted Antiferromagnetic
DE	Double Exchange Mechanism
FWHM	Full Width Half Maximum
GB	Grain Boundary
GMR	Giant Magnetoresistance
RE	Rare Eearth element
PM	Paramagnetic
PLD	Pulsed Laser Deposition
MR	Magnetoresistance
FE-SEM	Field Emission- Scanning Electron Microscope
VSM	Vibration Sample Magnetometer
LAO	LaAlO ₃
JT	Jahn-Teller distortion
T_P	Phase Transition Temperature
T _C	Curie temperature

- T_N Neel Temperature
- FMI Ferromagnetic Insulator
- FMM Ferromagnetic Metallic
- $LSMO \qquad \qquad La_{1-x}Sr_xMnO_3, \ La_{5/8}Sr_{3/8}MnO_3$
- LNMO La_{1-x}Na_xMnO₃, La_{0.7}Na_{0.3}MnO₃
- $LCMO \qquad La_{1-x}Ca_xMnO_3, La_{2/3}Ca_{1/3}MnO_3$
- PCMO Pr_{1-x}Ca_xMnO₃, Pr_{0.7}Ca_{0.3}MnO₃
- T_{MI} Metal-Insulator Temperature
- STO SrTiO₃
- XPD X-ray Diffraction
- AMR Anisotropic magnetoresistance
- TMR Tunnelling magnetoresistance
- Cg Corning glass

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

In the last 20 years, two classes of materials have defined and dominated the landscape condensed matter physics study of oxide materials: high-temperature of superconductivity in doped cuprates and doped manganites. Figure 1.1 typically shows Normalized resistance via temperature for superconductor (YBCO) and manganite (LCMO) at zero magnetic field. The research in the field of spintronics contents phenomena such as giant magnetoresistance (GMR), colossal magnetoresistance (CMR), spin-tunneling in junctions (STJ), spin coherence and spin dephasing have attracted more attention. The spintronics (Daughton et al., 1999; Gregg et al., 2002; Wolf et al., 2001; Žutić et al., 2004) is defined as the branch of electronics that utilizes the spin degree of freedom of the electron together with its charge, to store and transmit information. The discovery of negative magnetoresistance (MR) in rare-earth manganates, $RE_{1-x}A_xMnO_3$ (RE = rare earth, A = alkaline earth) with the perovskite structure, has attracted wide attention. The magnitude of MR in these materials can be very large, more than of 100%. For this reason, many workers prefer to call this colossal magnetoresistance (CMR), as distinct from gaint magnetoresistance (GMR) in layered or granular metallic materials. In metallic multilayers or granular alloys, the mechanism involves spin-polarized transport. In the manganates also, spinpolarized transport is responsible for the large negative MR, but it is distinctly different from what happens in the metallic multilayers.

The properties of manganites compounds with a Mn³⁺/Mn⁴⁺ mixed valence keep attracting attention from both experimentalists and theorists. The rich phase diagram with entangled insulating, metallic, ferromagnetic (FM), antiferromagnetic (AFM) and paramagnetic phases, reveals a strong coupling between the lattice, spin and electronic degrees of freedom. These called double exchange mechanism assuming the oxygen mediated electron exchange between neighboring Mn^{3+}/Mn^{4+} sites is only a starting point of modelling (Haghiri-Gosnet and Renard, 2003). The mobility of the conduction electron between Mn^{3+}/Mn^{4+} pairs is greatly enhanced when the magnetic moments on adjacent Mn ions are aligned. The mixed valence also leads to the formation of small polarons, arising from Mn^{3+}/Mn^{4+} valence changes and to Jahn-teller distortion involving Mn that leads to incoherent hopping and high resistivity in the insulating phase. The Mn³⁺-O²⁻-Mn⁴⁺ bond lengths and angles play a crucial role in determining the magnetotransport in manganites (Teplykh et al., 2004). Moreover, an applied magnetic field enhances the FM order, thus reduces the spin scattering and produces a so-called negative colossal magnetoresistance (CMR) peak.

1.2 Applications of CMR materials

The manganite materials are especially interesting since they present large electronic correlations leading to a strong competition between lattice, charge, spin, and orbital degrees of freedom. These manganese-based perovskite oxides exhibit half-metallic character and CMR response rendering them as the ideal materials to develop novel concepts of oxide-electronic devices and for the study of fundamental physical interactions. Due to the close similarity between kinetic energy of charge carriers and Coulomb repulsion, tiny perturbations caused by small changes in temperature, magnetic or electric fields, strain and so forth may drastically modify the magnetic and transport properties of these materials. In addition, the half metallic character may find applications in spintronics. The simplest type of application is the spin-valve device: an insulating tunnel barrier is sandwiched between magnetic metal. Due to the high spin-polarization of carriers in half-metallic manganites, the spin dependent tunneling between two ferromagnetic manganites electrodes across a thin insulating barrier should produce a large magneto-resistance response.

Moreover, because these materials should allow true on-of operations, they would be very appropriate for sensor elements of non-volatile devices. Unfortunately, the CMR effect currently requires very high magnetic fields and low temperatures for most materials making them impractical for use in devices. Therefore, currently, high magnetoresistance at room temperature and under low magnetic field are more interested. Magnetoresistance (MR) is important in many technological applications, such as magnetic data storage, read - write heads, magnetic - bolometric sensors, magnetic tunnel junction (MTJ) and magnetoresistive random access memory (MRAM).

In summary, few applications of CMR materials are listed below:

- 1. Magnetic field sensors
- (a) Using the CMR effect in a film
- (b) Using a spin valve structure
- (c) As a microwave CMR sensor
- 2. Electric field effect devices
- (a) Using a SrTiO₃ gate
- (b) Using a ferroelectric gate
- 3. Bolometric uncooled infrared (IR) sensors using the metal -insulator transition at Curie temperature
- 4. Low temperature hybrid HTS-CMR devices
- (a) Flux focused magnetic transducers
- (b) Spin polarized quasi-particle injection devices

The industrial requirements for a magnetic sensor can be summarized as follows.

- 1. Operation at room temperature and up to 100 K above room temperature.
- 2. At least a 20% response at a field of 100 Gauss
- 3. Temperature independent CMR values over 50-350 K
- 4. Acceptable noise values
- 5. Retention of magneto-transport properties in patterned films at dimensions

approaching sub-1000Å scales. (The current thinking is that oxide-based CMR sensors will have maximum impact only on memory systems approaching densities of 100 Gb/cm²).



Figure 1.1: Normalized resistance via temperature for superconductor (YBCO) and manganite (LCMO) at zero magnetic field (The results are taken from my research work at UPM).

1.3 Problem Statement

Currently manganite research is one of the research topics in solid state condensed matter physics, aiming to improve the understanding of the behavior of electrons in crystals. There are two main reasons interesting to the manganites as background of this study. The first reason is the unexpectedly large magnetotransport properties of these materials. By application of relatively small magnetic fields, the resistivity changes by several orders of magnitude. A second motivation to study the manganites is contained in their rich phase diagram, exhibiting a variety of phases, with unusual spin, charge, lattice and orbital order. On the other hand, the high Curie temperature and especially high magnetoresistance of these materials making the multilayer study of manganites is important as it has a direct application in electronic devices and industry.

Currently, important issues in manganite namely are; How could the magnetoresistance in manganite film and polycrystals be improved? How could the room temperature and metal-insulator transition temperature in these materials be increased? What is the effect of substrate type on physical and magneto-transport properties of these materials? What is the effect of insulator manganite if sandwiched between two metallic manganites?

In order to address these questions, we have studied $La_{2/3}Ca_{1/3}MnO_3$ (LCMO), $La_{5/8}Sr_{3/8}MnO_3$ (LSMO), $La_{0.7}Na_{0.3}MnO_3$ (LNMO) and $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) polycrystalline bulk manganites in the form of bulk and thin films that are deposited on different substrates. In addition a LCMO/PCMO/LCMO trilayer is fabricated to study the effect of multilayers on the enhancement of magnetoresistance.

1.4 Objective of Thesis

This thesis is focused on fabrication and characterization of LCMO, LSMO, LNMO and PCMO polycrystalline manganites in the form of bulk, single and trilayer thin films deposited on different substrates by Pulsed Laser Deposition (PLD) technique.

The objectives of this work are presented as follow:

- To prepare and characterize high quality La_{2/3}Ca_{1/3}MnO₃ (LCMO), La_{5/8}Sr_{3/8}MnO₃ (LSMO), La_{0.7}Na_{0.3}MnO₃ (LNMO) and Pr_{0.7}Ca_{0.3}MnO₃ (PCMO) polycrystalline bulk manganites via solid state reaction method.
- To prepare and characterize high quality La_{2/3}Ca_{1/3}MnO₃ (LCMO), La_{5/8}Sr_{3/8}MnO₃ (LSMO), La_{0.7}Na_{0.3}MnO₃ (LNMO) single layer thin films grown on different substrates by PLD technique.
- 3) To investigate the magnetoresistance enhancement in LCMO/PCMO/LCMO trilayers films grown on Si-wafer by PLD method.

1.5 Plan of Thesis

The thesis is arranged in the following way:

In Chapter 1, general introduction of manganites, motivation and objectives of thesis are included.

In Chapter 2, a summary of pervious work and literature review of manganites are given.

In Chapter 3, an overview of theory of manganites, thin film growth methods and fundamental of laser ablation are described.

In Chapter 4, an overview of sample preparation and the deposition process are described. In addition, the basic instruments used to fabricate and characterize the samples were introduced.

Chapter 5 describes the characterization and measurement details of bulk manganites, single layer and trilayer thin films. Finally the analysis and discussion of results are presented.

In Chapter 6 conclusions and suggestions are included.

REFERENCES

- Adams, C., Lynn, J., Smolyaninova, V., Biswas, A., Greene, R., W Ratcliff, I., Cheong, S., Mukovskii, Y., & Shulyatev, D. (2004). First-order nature of the ferromagnetic phase transition in (LaCa) MnO₃ near optimal doping. *Physical Review B*, 70(13), 134414-134425.
- Alessandri, I., Malavasi, L., Bontempi, E., Mozzati, M., Azzoni, C., Flor, G and Depero, L. (2004). Synthesis and characterisation of $La_{1-x}Na_xMnO_{3+\delta}$ thin films manganites. *Materials Science and Engineering: B*, 109(1), 203-206.
- Amaral, V., Araújo, J., Pogorelov, Y. G., Sousa, J., Tavares, P., Vieira, J., Algarabel, P and Ibarra, M. (2003). Tricritical points in La-based ferromagnetic manganites. *Journal of Applied physics*, 93(10), 7646-7648.
- Anderson, P., and Hasegawa, H. (1955). Considerations on double exchange. *Physical Review*, 100(2), 675-681.
- Anjana Dogra, Sudhindra Rayaprol, Babu, P. D., G., R. K and Gupta, S. K. (2010). Influence of chemical pressure on the magnetism of $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ (x = 0.0–0.3). *Journal of Alloys and Compounds, 493*, L19-L24.
- Awana, V., Tripathi, R., Balamurugan, S., Kishan, H and Takayama-Muromachi, E. (2006). Magneto Transport of high TCR (temperature coefficient of resistance) La_{2/3}Ca_{1/3}MnO₃: Ag Polycrystalline Composites. *Arxiv preprint cond-mat*, 0609364.
- Banerjee, A., Pal, S., and Chaudhuri, B. (2001). Nature of small-polaron hopping conduction and the effect of Cr doping on the transport properties of rare-earth manganite LaPbMnCrO. *The Journal of Chemical Physics*, *115*, 1550-1558.
- Bao, Y., Gao, J., and Gawne, D. T. (2010). Crack formation and its prevention in PVD films on epoxy coatings. *Surface and Coatings Technology*, 205(1), 15-21.
- Bebenin, N., Zainullina, R., Bannikova, N., Ustinov, V and Mukovskii, Y. M. (2008). Magnetic phase transition and electronic transport in single-crystalline La_{0.7} Ca_{0.3} MnO₃. *Physical Review B*, 78(6), 064415-064422.
- Bebenin, N., Zainullina, R., Chusheva, N., Ustinov, V and Mukovskii, Y. M. (2006).
 Hall effect and conductivity in La_{1-x}B_xMnO₃single crystals. *Journal of Magnetism and Magnetic Materials*, 300(1), e111-e113.
- Beschoten, B., Johnston-Halperin, E., Young, D., Poggio, M., Grimaldi, J., Keller, S., DenBaars, S., Mishra, U., Hu, E and Awschalom, D. (2001). Spin coherence and dephasing in GaN. *Physical Review B*, 63(12), 121202-121206.

- Billinge, S. J. L. (2006). Structure determination and phase analysis by the use of neutron diffraction. JOM Journal of the Minerals, Metals and Materials Society, 58(3), 47-51.
- Biškup, N., De Andres, A., Martinez, J and Perca, C. (2005). Origin of the colossal dielectric response of Pr_{0.6}Ca_{0.4}MnO₃. *Physical Review B*, 72(2), 024115.
- Bowen, M., Barthélémy, A., Bibes, M., Jacquet, E., Contour, J. P., Fert, A., Ciccacci, F., Duo, L and Bertacco, R. (2005). Spin-polarized tunneling spectroscopy in tunnel junctions with half-metallic electrodes. *Physical Review Letters*, 95(13), 137203-137207.
- Chatterji, T., Ouladdiaf, B., Mandal, P., Bandyopadhyay, B and Ghosh, B. (2002). Jahn-Teller transition in La_{1-x} Sr_x MnO₃ in the low-doping region. *Physical Review B*, 66(5), 054403-054411.
- Chen, Y., and Wu, T. (2008). Thickness dependent transport properties and percolative phase separation in polycrystalline manganite thin films. *Applied physics letters*, 93(22), 224104-224107.
- Cheong, S.W., and Hawang, H.Y.(2000). ferromagnetism vs.charge/orbital ordering in mixed-valent manganites. colossal magnetoresistance Oxides, 237-280.
- Choi, S. G., Reddy, A. S., Yu, B. G., Yang, W. S., Cheon, S. H and Park, H. H. (2010). Effect of high temperature post-annealing of La_{0.7}Sr_{0.3}MnO₃ films deposited by radio frequency magnetron sputtering on SiO₂/Si substrates heated at low temperature. *Thin Solid Films*, *518*(15), 4432-4436.
- Coey, J., Viret, M and Von Molnar, S. (1999). Mixed-valence manganites. Advances in physics, 48(2), 167-293.
- Coey, J. M. D., Viret, M., Ranno, L and Ounadjela, K. (1995). Electron localization in mixed-valence manganites. *Physical Review Letters*, 75(21), 3910-3913.
- Collado, J., García-Muñoz, J and Aranda, M. (2010). Effects of the A-site cation number on the properties of Ln_{5/8}M_{3/8}MnO₃ manganites. *Journal of Solid State Chemistry*, 183(5), 1083-1089.
- Dan Liu, W. L. (2011). Growth and characterization of epitaxial (La_{2/3}Sr_{1/3})MnO₃ films by pulsed laser deposition. *Ceramics International*, *37*, 3531-3534.
- Daoudi, K., Tsuchiya, T and Kumagai, T. (2008). Growth and characterization of epitaxial La_{0. 7}Ca_{0. 3}MnO₃ thin films by metal-organic deposition on (LaAlO₃) 0.3-(SrAlTaO6) 0.7 substrates. *Thin Solid Films*, *516*(18), 6325-6329.
- Daughton, J., Pohm, A., Fayfield, R., and Smith, C. (1999). Applications of spin dependent transport materials. *Journal of Physics D: Applied Physics*, 32, R169.

- De Gennes, P. G. (1960). Effects of double exchange in magnetic crystals. *Physical Review*, 118(1), 141-154.
- De Teresa, J. M., Barthélémy, A., Fert, A., Contour, J. P., Montaigne, F and Seneor, P. (1999). Role of metal-oxide interface in determining the spin polarization of magnetic tunnel junctions. *Science*, 286(5439), 507-509.
- Dirks, A., and Leamy, H. (1977). Columnar microstructure in vapor-deposited thin films. *Thin Solid Films*, 47(3), 219-233.
- Dong, W., Zhu, X., Tao, R and Fang, X. (2006). Properties of (h 00)-oriented $La_{1-x}Na_xMnO_3$ films (x= 0.1, 0.15 and 0.3) prepared by chemical solution deposition method. *Journal of Crystal Growth*, 290(1), 180-184.
- Dorsey, P., Bushnell, S., Seed, R and Vittoria, C. (1993). Epitaxial yttrium iron garnet films grown by pulsed laser deposition. *Journal of Applied physics*, 74(2), 1242-1246.
- Eason, R. (2007). Pulsed laser deposition of thin films: applications-led growth of functional materials: Wiley-Blackwell.
- Emin, D., and Holstein, t. (1976). Adiabatic theory of an electron in a deformable continuum. *Physical review Letters*, 36(6), 323.
- Eerenstein, W., Wiora, M., Prieto, J., Scott, J and Mathur, N. (2007). Giant sharp and persistent converse magnetoelectric effects in heterostructures. *Nature materials*, 6(5), 348-351.
- Fang, S., Zhiyong Pang, F. W., Liang Lin and Shenghao Han (2011). Annealing Effect on Transport and Magnetic Properties of La_{0.67}Sr_{0.33}MnO₃ Thin Films Grown on Glass Substrates by RF Magnetron Sputtering. J. Mater. Sci. Technol, 27(3), 223-226.
- Fontcuberta, J., Martinez, B., Seffar, A., Pinol, S., Garcia-Munoz, J and Obradors, X. (1996). Colossal magnetoresistance of ferromagnetic manganites: Structural tuning and mechanisms. *Physical Review Letters*, 76(7), 1122-1125.
- Gajek, M., Bibes, M., Fusil, S., Bouzehouane, K., Fontcuberta, J., Barthélémy, A and Fert, A. (2007). Tunnel junctions with multiferroic barriers. *Nature materials*, 6(4), 296-302.
- Geohegan, D., Chrisey, D and Hubler, G. (1994). Pulsed laser deposition of thin films. eds DB Chrisey, GK Hubler, John Wiley and Sons, Inc, 613.
- Geohegan, D. B. (1992). Fast intensified-CCD photography of YBa₂Cu₃O_{7-x} laser ablation in vacuum and ambient oxygen. *Applied physics letters*, 60(22), 2732-2734.

Goldschmidt, V. (1926). The laws of crystal chemistry. *Naturwissenschaften*, 14, 477-485.

- Gomes, I., Almeida, B., Lopes, A., Araújo, J., Barbosa, J and Mendes, J. (2010). Structural and magnetic characterization of LaSrMnO₃ thin films deposited by laser ablation on MgO substrates. *Journal of Magnetism and Magnetic Materials*, 322(9), 1174-1177.
- Gregg, J., Petej, I., Jouguelet, E., & Dennis, C. (2002). Spin electronics-a review. Journal of Physics D: Applied Physics, 35, R121.
- Gupta, A., Gong, G., Xiao, G., Duncombe, P., Lecoeur, P., Trouilloud, P., Wang, Y., Dravid, V and Sun, J. (1996). Grain-boundary effects on the magnetoresistance properties of perovskite manganite films. *Physical Review B*, 54(22), 15629-15632.
- Gupta, A., and Sun, J. (1999). Spin-polarized transport and magnetoresistance in magnetic oxides. *Journal of Magnetism and Magnetic Materials*, 200(1), 24-43.
- Haghir-Gosnet, A., and Renard, J.(2003). CMR maganites: Physics, thin film and devices, *Journal of physics D: Applied physics*, 36, R127-R150
- Holstein, T. (1959). Studies of polaron motion: Part II. The "small" polaron. Annals of *Physics*, 8(3), 343-389.
- Huang, Q., Santoro, A., Lynn, J., Erwin, R., Borchers, J., Peng, J., Ghosh, K., and Greene, R. (1998). Structure and magnetic order in La_{1-x}Ca_xMnO₃ (0< x<= 0.33). *Physical Review B*, 58, 2684-2691.
- Hwang, H., Cheong, S., Ong, N and Batlogg, B. (1996). Spin-Polarized Intergrain Tunneling in La_{2/3}Sr_{1/3} MnO₃. *Physical Review Letters*, 77(10), 2041-2044.
- Hwang, H., Cheong, S., Radaelli, P., Marezio, M and Batlogg, B. (1995). Lattice Effects on the Magnetoresistance in Doped LaMnO₃. *Physical Review Letters*, 75(5), 914-917.
- Ishii, Y., Yamada, H., Sato, H., Akoh, H., Ogawa, Y., Kawasaki, M and Tokura, Y. (2006). Improved tunneling magnetoresistance in interface engineered (La, Sr) MnO junctions. *Applied physics letters*, 89, 042509-042514.
- Jahn, H. A., and Teller, E. (1937). Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 161*(905), 220-235.

- Jin, S., Tiefel, T. H., McCormack, M., Fastnacht, R., Ramesh, R and Chen, L. (1994). Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O films. *Science*, 264(5157), 413-415.
- Jonker, G., and Van Santen, J. (1950). Ferromagnetic compounds of manganese with perovskite structure. *Physica*, *16*(3), 337-349.
- Ju, H. G., J.;Peng, JL;Li, Q.;Xiong, GC.;Venkatesan, T.;Greene, RL (1995). Dependence of giant magnetoresistance on oxygen stoichiometry and magnetization in polycrystalline La_{0.67} Ba_{0.33}MnO_z. *Physical Review B*, 51(9), 6143-6146.
- Kalyana, L.Y., and Venugopal, R.P., (2009). Influnce of sintering temperature and oxygen stoichiometry on electrical transport properties of La_{0.67}Na_{0.33}MnO₃ manganites. Journal of Alloy and compounds, 470(1), 67-74.
- Kramers, H. (1934). L'interaction entre les atomes magnétogènes dans un cristal paramagnétique. *Physica*, 1, 182-192.
- Lebedev, O., Van Tendeloo, G., Amelinckx, S., Leibold, B., and Habermeier, H. U. (1998). Structure and microstructure of La _{1-x} Ca_x MnO_{3-δ} thin films prepared by pulsed laser deposition. *Physical Review B*, 58(12), 8065-8074.
- Leufke, P. M., and Ajay Kumar Mishra, A. B., Di Wang, Christian Kübel, Robert Kruk , Horst Hahn (2012). Large-distance rf- and dc-sputtering of epitaxial La_{1-x}Sr_xMnO₃ thin films. *Thin Solid Films*, 520(17), 5521-5527.
- Leung, Y., and Wong, K. (1998). Low temperature processing of epitaxial La_{1-x}Ca_xMnO₃ thin films by pulsed laser deposition. *Applied Surface Science*, 127, 491-495.
- Li, H., Fang, Q and Zhu, Z. (2002a). Preparation and colossal magnetoresistance in a trilayer La_{0.67}Sr_{0.33}MnO₃/La_{0.75}MnO₃/La_{0.67}Sr_{0.33}MnO₃ device by dc magnetron sputtering. *Materials Research Bulletin*, *37*(5), 859-866.
- Li, H., Sun, J and Wong, H. (2002b). Enhanced low-field magnetoresistance in La_{2/3}Ca_{1/3}MnO₃/Pr_{2/3}Ca_{1/3}MnO₃ superlattices. *Applied physics letters*, 80(4), 628-630.
- Li, P., Yuan, S., Liu, L., Wang, X., Wang, Y., Tian, Z., He, J., Yuan, S., Liu, K., Ying, S and Wang, C. (2008). Effect of grain boundary on electrical, magnetic and magnetoresistance properties in La_{2/3}Ca_{1/3}MnO₃/CuMn₂O₄ composites. *Solid State Communications*, 146, 515-521.

- Licci, F., Turilli, G., Ferro, P and Ciccarone, A. (2003). Low-Temperature Synthesis and Properties of LaMnO_{3±d} and La_{0.67}R_{0.33}Mn_{O3±d} (R= Ca, Sr, Ba) from Citrate Precursors. *Journal of the American Ceramic Society*, 86(3), 413-419.
- Liu,D., and Liu,W. (2012).Room temperature ultrahigh magnetoresistance nanostructure La_{2/3}Sr_{1/3}MnO₃ films on SrTiO₃ substrate. *Ceramics International*, *38*(*3*), 2579-2581
- Lu, W., Luo, X., Hao, C., Song, W and Sun, Y. (2008). Magnetocaloric effect and Griffiths-like phase in La_{0.6}7Sr_{0.33}MnO₃ nanoparticles. *Journal of Applied physics*, *104*(11), 113908.
- Ma, X., Zhang, H., Xu, J., Niu, J., Yang, Q., Sha, J and Yang, D. (2002). Synthesis of La_{1-x}Ca_xMnO₃ nanowires by a sol-gel process. *Chemical physics letters*, 363(5), 579-582.
- Maity, S., Dhar, A., Ray, S., & Bhattacharya, D. (2011). Role of growth temperature and oxygen partial pressure on the structural and electrical properties of pulsed laser deposited La_{1-x}Sr_xMnO_{3-x} thin films. *Journal of Physics and Chemistry of Solids*, 72, 804-809.
- Majumdar, S., H. Huhtinen, H. S. M., P. Paturi (2012). Stress and defect induced enhanced low field magnetoresistance and dielectric constant in La_{0.7}Sr0.3MnO3 thin films. *Journal of Alloys and Compounds*, *512*, 332-339.
- Malavasi, L., Mozzati, M. C., Alessandri, I., Affronte, M., Cervetto, V., Azzoni, C. B and Flor, G. (2004). Thin films of sodium-doped lanthanum manganites: role of substrate and thickness on the magnetoresistive response. *Solid state ionics*, 172(1), 265-269.
- Mao, S. S., Mao, X., Greif, R and Russo, R. E. (2000). Initiation of an early-stage plasma during picosecond laser ablation of solids. *Applied physics letters*, 77, 2464-2466.
- Martin, L., Chu, Y. H and Ramesh, R. (2010). Advances in the growth and characterization of magnetic, ferroelectric, and multiferroic oxide thin films. *Materials Science and Engineering: R: Reports, 68*(4), 89-133.
- Metev, S. (1994). Process characteristics and film properties in pulsed laser deposition. *Pulsed Laser Deposition of thin films*, 229-254.
- Mira, J., Rivas, J., Hueso, L., Rivadulla, F., Quintela, M. A. L., Rodríguez, M. A. S and Ramos, C. (2001). Strong reduction of lattice effects in mixed-valence manganites related to crystal symmetry. *Physical Review B*, 65(2), 024418-024423.
- Mott, I. G. A. a. N. F. (1969). Polarons in crystalline and non-crystalline materials. *Advanced in Physics*, 18(71), 41-102.

Ohring, M. (2002). The materials science of thin films: Academic Press, San Francisco.

- Okuda, T., Tomioka, Y., Asamitsu, A and Tokura, Y. (2000). Low-temperature properties of La_{1-x} Ca_x MnO₃ single crystals: Comparison with La_{1-x} Sr_x MnO₃. *Physical Review B*, *61*(12), 8009-8015.
- Pankova´, M. S., and Chromik, S`., Sedla´c`kova´, I. V. v., K., Lobotka, P., Lucas, S., and Stanc`ek, S. (2007). Epitaxial LSMO films grown on MgO single crystalline substrates. *Applied Surface Science*, 253, 7599-7603.
- Panwar, N., Sen, V., D.K. Pandya and Agarwal, S. K. (2007). Grain boundary effects on the electrical and magnetic properties of Pr_{2/3}Ba_{1/3}MnO₃ and La_{2/3}Ca_{1/3}MnO₃ manganites. *Materials Letters*, 61, 4879-4883.
- Pi, L., Zheng, L and Zhang, Y. (2000). Transport mechanism in polycrystalline La _{0.825} Sr_{0.175} Mn_{1-x} Cu_x O₃. *Physical Review B*, 61(13), 8917-8921.
- Qin, H., Hu, J., Chen, J., Zhu, L and Niu, H. (2004). The Nd Doping Effect on the Room Temperature Magnetoresistancein Manganites (La_{1-x}Nd_x)_{0.67}Sr_{0.33}MnO₃ (x= 0.3). *Materials Transactions*, 45(4), 1251-1254.
- Qin, H., Hu, J., Chen, J., Zhu, L and Niu, H. (2010). Advances in the growth and characterization of magnetic, ferroelectric, and multiferroic oxide thin films. *Materials Science and Engineering: R: Reports, 68*(4), 89-133.
- Ramirez, A. (1997). Colossal magnetoresistance. *Journal of Physics: Condensed Matter*, 9, 8171-8199.
- Ramirez, A., Schiffer, P., Cheong, S., Chen, C., Bao, W., Palstra, T., Gammel, P., Bishop, D and Zegarski, B. (1996). Thermodynamic and Electron Diffraction Signatures of Charge and Spin Ordering in La_{1-x}Ca_xMnO₃. *Physical Review Letters*, 76(17), 3188-3191.
- Rijnders, G., and Blank, D. H. A. (2006). Growth Kinetics During Pulsed Laser Deposition. *Pulsed Laser Deposition of thin films*, 177-190.
- Rivadulla, F., Rivas, J and Goodenough, J. (2004). Suppression of the magnetic phase transition in manganites close to the metal-insulator crossover. *Physical Review B*, 70(17), 172410-172413.
- Roy, S., Dubenko, I., Edorh, D. D and Ali, N. (2004). Size induced variations in structural and magnetic properties of double exchange LaSrMnO nanoferromagnet. *Journal of Applied physics*, 96, 1202.
- Ruotolo, A., Miletto Granozio, F., Oropallo, A., Pepe, G., Perna, P., Scotti di Uccio, U., Pullini, D., Innocenti, G and Perlo, P. (2007). Novel low-field magnetoresistive devices based on manganites. *Journal of Magnetism and Magnetic Materials*, 310(2), e684-e686.

- Sahana, M., Hegde, M., Shivakumara, C., Prasad, V and Subramanyam, S. (1999). Colossal magnetoresistance in potassium doped lanthanum manganite: a comparative study of polycrystalline solid and thin film. *Journal of Solid State Chemistry*, 148(2), 342-346.
- Sahu, D., Mishra, D., Huang, J. L and Roul, B. (2007). Annealing effect on the properties of La_{0.7}Sr_{0.3}MnO₃ thin film grown on Si substrates by DC sputtering. *Physica B: Condensed Matter*, *396*(1-2), 75-80.
- Sahu, D., Mishra, D., Hung, S., Pramanik, P and Roul, B. (2007). La_{0.67} Ca_{0.33}MnO₃ thin films on Si (100) by DC magnetron sputtering technique using nanosized powder compacted target. *Materials Research Bulletin*, 42(6), 1119-1127.
- Sahu, D. R. (2012). La_{0.7}Sr_{0.3}MnO₃ film preparedbydcsputteringonsiliconsubstrate: Effect of workingpressure. *Journal of Physics and Chemistry of Solids*, 73, 622-625.
- Sahua, D. R. (2010). Lateral parameter variations on the properties of La_{0.7}Sr_{0.3}MnO₃ films prepared on Si (1 0 0) substrates by dc magnetron sputtering. *Journal of Alloys and Compounds*, 503, 163-169.
- Salamon, M. B., and Jaime, M. (2001). The physics of manganites: Structure and transport. *Reviews of Modern Physics*, 73(3), 583.
- Schramm, S., Hoffmann, J., and Jooss, C. (2008). Transport and ordering of polarons in CER manganites PrCaMnO. *Journal of Physics: Condensed Matter*, 20, 395231.
- Shinde, K., Pawar, S., Shirage, P and Paward, S. (2012). Studies on morphological and magnetic properties of La_{1-x}Sr_xMnO₃. *Applied Surface Science*, 258(19), 7417-7420.
- Sirenaa, M., N. Haberkorna, M. G., L.B. Steren, J. Guimpel (2004). Oxygen and disorder effect in the magnetic properties of manganite films. *Journal of Magnetism and Magnetic Materials*, 272-276, 1171-1173.
- Snyder, G. J., Hiskes, R., DiCarolis, S., Beasley, M. R and Geballe, T. H. (1996). Intrinsic electrical transport and magnetic properties of La_{0.67}Ca_{0.33}MnO₃ and La_{0.67}Sr_{0.33} MnO₃ MOCVD thin films and bulk material. *Physical Review B*, 53(21), 14434.
- Solanki, P., Doshi, R., Khachar, U., Choudhary, R., & Kuberkar, D. (2011). Thickness dependent transport and magnetotransport in CSD grown La0. 7Pb0. 3MnO3 manganite films. *Materials Research Bulletin*, 46(7), 1118-1123.
- Spankova, M., Chromik, S., Vavra, I., Sedlackova, K., Lobotka, P., Lucas, S and Stancek, S. (2007). Epitaxial LSMO films grown on MgO single crystalline substrates. *Applied Surface Science*, 253(18), 7599-7603.

- Steren, L., Sirena, M and Guimpel, J. (2000). Substrate influence on the magnetoresistance and magnetic order in La_{0.6}Sr_{0.4}MnO₃ films. *Journal of Magnetism and Magnetic Materials*, 211(1), 28-34.
- Tang, G., Yu, Y., Chen, W and Cao, Y. (2008). The electrical resistivity and thermal infrared properties of $La_{1-x}Sr_xMnO_3$ compounds. *Journal of Alloys and Compounds*, 461(1), 486-489.
- Tao, R., Fang, X., Dong, W., Deng, Z., Pu, T and Zhu, X. (2007). Processing effects on the chemical solution deposition-derived La_{2/3}Ca_{1/3}MnO₃ films on SrTiO₃ (0 0 1) substrates. *Journal of Crystal Growth*, 306(2), 356-360.
- Tao Wang , X. F., Weiwei Dong, Ruhua Tao , Zanhong Deng, Da Li , Yiping Zhao, Gang Meng, Shu Zhou, Xuebin Zhu (2008). Mechanochemical effects on microstructure and transport properties of nanocrystalline La_{0.8}Na_{0.2}MnO₃ ceramics. *Journal of Alloys and Compounds*, 428, 248-252.
- Teplykh, A., Bogdanov, S., Valiev, E., Pirogov, A., Dorofeev, Y. A., Ostroushko, A., Udilov, A and Kazantzev, V. (2004). Size effect in nanocrystalline manganites La _{1-x} A _x MnO ₃ with A= Ag, Sr. *Physica B: Condensed Matter*, 350(1), 55-58.
- Tokura, Y. (2006). Critical features of colossal magnetoresistive manganites. *Reports on Progress in Physics*, 69, 797.
- Tomioka, Y., Koshimizu, M and Asai, K. (2009). Positron lifetime study of $Pr_{1-x}Ca_xMnO_3$ (x = 0.5, 0.3) during magnetic transition. *Radiation Physics and Chemistry*, 78, 1092-1095.
- Tripathi, R., Awana, V., Panwar, N., Bhalla, G., Habermier, H., Agarwal, S and Kishan, H. (2009). Enhanced room temperature coefficient of resistance and magnetoresistance of Ag-added La_{0.7}Ca_{0.3-x}Ba_xMnO₃ composites. *Journal of Physics D: Applied Physics*, 42, 175002.
- Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G andTokura, Y. (1995). Insulator-metal transition and giant magnetoresistance in La_{1-x}Sr_xMnO₃. *Physical Review B*, *51*(20), 14103-14109.
- Van Santen, J., and Jonker, G. (1950). Electrical conductivity of ferromagnetic compounds of manganese with perovskite structure. *Physica*, *16*, 599-600.
- Varshney, D., Dodiya, N and Shaikh, M. W. (2011). Structural properties and electrical resistivity of Na-substituted lanthanum manganites: $La_{1-x} Na_x MnO_{3+y}$ (x= 0.1, 0.125 and 0.15). *Journal of Alloys and Compounds*, 509(27), 7447-7457.

- Venimadhav, A., Hegde, M., Prasad, V., and Subramanyam, S. (2000). Enhancement of magnetoresistance in manganite multilayers. *Journal of Physics D: Applied Physics*, 33, 2921.
- Venimadhav, A., Hegde, M., Rawat, R., Das, I and El Marssi, M. (2001). Enhancement of magnetoresistance in La_{0.67}Ca _{0.33}MnO₃/Pr_{0.7}Ca_{0.3} Mn₃epitaxial multilayers. *Journal of Alloys and Compounds*, *326*(1), 270-274.
- Venkataiah, G., Krishna, D., Vithal, M., Rao, S., Bhat, S., Prasad, V., Subramanyam, S and Reddy, P. V. (2005). Effect of sintering temperature on electrical transport properties of La _{0.67} Ca _{0.33} MnO₃. *Physica B: Condensed Matter*, 357(3), 370-379.
- Venkataiah, G., Prasad, V., and Venugopal Reddy, P. (2007). Influence of A-site cation mismatch on structural, magnetic and electrical properties of lanthanum manganites. *Journal of Alloys and Compounds*, 429(1), 1-9.
- Vertruyen, B., Dusoulier, L., Fagnard, J. F., Vanderbemden, P., Vanhoyland, G., Ausloos, M., Delwiche, J., Rulmont, A and Cloots, R. (2004). Anisotropic behaviour in the magnetic field dependence of the low temperature electrical resistance of calcium-doped lanthanum manganate thin films grown by RF magnetron sputtering. *Journal of Magnetism and Magnetic Materials*, 280(2), 264-272.
- Vincent, H., Audier, M., Pignard, S andDezanneau, G. (2002). Crystal Structure Transformations of a Magnetoresistive La_{0.8}MnO_{3-d} Thin Film. *Journal of Solid State Chemistry*, *164*(2), 177-187.
- Viret, M., Ranno, L., and Coey, J. (1997). Magnetic localization in mixed-valence manganites. *Physical Review B*, 55(13), 8067.
- Vlakhov, E., Nenkov, K., Donchev, T., Mateev, E., and Chakalov, R. (2004). Ferromagnetic and charge ordering competition in strained thin films of La₁₋ _xCa_xMnO₃ system. *Vacuum*, 76(2-3), 249-252.
- Von Helmolt, R., Wecker, J., Holzapfel, B., Schultz, L., and Samwer, K. (1993). Giant negative magnetoresistance in perovskitelike La_{2/3}Ba_{1/3}MnO_x ferromagnetic films. *Physical Review Letters*, 71(14), 2331-2333.
- Williamson, G., and Hall, W. (1953). X-ray line broadening from filed aluminium and wolfram. *Acta Metallurgica*, 1(1), 22-31.
- Wolf, S., Awschalom, D., Buhrman, R., Daughton, J., Von Molnar, S., Roukes, M., Chtchelkanova, A and Treger, D. (2001). Spintronics: A spin-based electronics vision for the future. *Science*, 294(5546), 1488-1495.

- Wu, B. (2008). High-intensity nanosecond-pulsed laser-induced plasma in air, water, and vacuum: A comparative study of the early-stage evolution using a physicsbased predictive model. *Applied physics letters*, 93, 101104.
- Wu, C., Qiu, J., Wang, J., Xu, M and Wang, L. (2010). Thermochromic property of La_{0.} ₈Sr_{0. 2}MnO₃ thin-film material sputtered on quartz glass. *Journal of Alloys and Compounds*, 506(2), L22-L24.
- Xiong, C., Xiong, Y., Meng, G., Jian, Z., Mai, Y., Xu, W., Xiong, J., Zhang, L., Ren, Z and Zhang, J. (2007). Structural study and magnetoresistance effect of epitaxial La 0.67 Sr 0.33MnO 3–δand Pr_{0.7} Ca _{0.3} MnO_{3–δ}multilayer films. *Physica B: Condensed Matter*, 390(1), 28-33.
- Xiong, Y., Xu, W., Mai, Y., Pi, H., Sun, C., Bao, X., Huang, W., & Xiong, C. (2008). The microstructure and electronic transport properties of mechanical milled La_{2/3}Ca_{1/3}MnO₃ perovskites. *Journal of Magnetism and Magnetic Materials*, 320(3-4), 257-262.
- Yang, S., Kuang, W., Liou, Y., Tse, W., Lee, S and Yao, Y. (2004a). Growth and characterization of La _{0.7} Sr_{0.3} MnO₃ films on various substrates. *Journal of Magnetism and Magnetic Materials*, 268(3), 326-331.
- Zainullina, R., Bebenin, N., Ustinov, V., Mukovskii, Y. M andShulyatev, D. (2007). Phase transitions in La_{1-x} Ca x MnO₃ single crystals. *Physical Review B*, 76(1), 014408-014411.
- Zener, C.(1951). Interaction between the d-sells in the transition metals.II.Ferromagnetic compounds of manganese with perovskite structure. Physical Review, 82(3), 403-405
- Zhang, Q., Nakagawa, T and Saito, F. (2000). Mechanochemical synthesis of La _{0.7} Sr _{0.3} MnO ₃ by grinding constituent oxides. *Journal of Alloys and Compounds*, 308(1), 121-125.
- Zhao, K., Feng, J., Huang, Y., Li, H and Wong, H. K. (2005). Magnetic coupling in La_{0.} ₆₇Ca_{0. 33}MnO₃/La_{0. 67}Sr_{0. 33}CoO₃/La_{0. 67}Ca_{0. 33}MnO₃ sandwiches. *Thin Solid Films*, 476(2), 326-330.
- Zheng, X., Wang, C and Zhu, J. (2003). Effect of columnar structure on magnetoresistivity properties of La _{0.8} MnO₃ thin films. *Journal of Magnetism and Magnetic Materials*, 267(2), 168-172.
- Zhou, Y., Wu, B andForsman, A. (2010). Time-resolved observation of the plasma induced by laser metal ablation in air at atmospheric pressure. *Journal of Applied physics*, *108*(9), 093504-093507.
- Zhu, X and Honglie Shen, K. T., Takeshi Yanagisawa, Mamoru Okutomi, Noboru Higuchi (2012). Characterization of La_{0.67}Sr_{0.33}MnO_z thin films synthesized by

metal-organic decomposition on different substrates. *Ceramics International* 94(9), 2783-2787.

Žutić, I., Fabian, J and Sarma, S. D. (2004). Spintronics: Fundamentals and applications. *Reviews of Modern Physics*, *76*(2), 323.



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Manizheh Navasery was born on the 22th December 1971 in Ahvaz, IRAN. She received her primary school in Ahvaz from 1977 to 1982, her secondary school was continued in Hadaf high School from 1982 – 1990. She continued her university education in B. Sc. Degree in Applied Physics at Shahid Chamran University in Ahvaz and graduate in 1997. In 1997 she continued as a Master student in field of Superconductivity at Shahid Chamran University and graduate in 2000. She married on August 2006. Finally she entered University Putra Malaysia in July 2008 for PhD studying in field of Magnetic Materials.

LIST OF PUBLICATION

• JOURNAL PUBLICATION

- M. Navasery, S.A. Halim, S.K.Chen, K.P.Lim, R.A.Shukor, Structure, Electrical Transport and Magneto-Resistance properties of La_{5/8}Ca_{3/8}MnO₃ Synthesized with different manganese precursors, Modern Physics Letter B, Vol.26, No.6,2012.
- M. Navasery, S.A. Halim, S.K.Chen, K.P.Lim "High Curie temperature for La_{5/8}Sr_{3/8}MnO₃ thin films prepared by Pulsed Laser Deposition grown on glass substrate" Journal of Physics: International Journal of Electrochemical Science, 8, 2013(Accepted).
- M. Navasery, S.A. Halim, S.K.Chen, K.P.Lim "Characterization and mechanism of La_{5/8}Sr_{3/8}MnO₃ thin filmsPrepared by Pulsed Laser Deposition on different Substrates" International Journal of Electrochemical Science, 8, 2013 (Accepted).

CONFERENCE PRESENTATION

• INTERNATIONAL CONFERENCE

M. Navasery, S.A. Halim, S.K.Chen, K.P.Lim, R.A.Shukor, Growth and characterization of La_{5/8}Ca_{3/8}MnO₃ film prepared by pulsed laser deposition on silicon wafer substrate, presented in "The seven international of magnetic and superconducting materials (MSM11) at Avillion Resort Hotel, Port Dickson ,Negri Sembilan on 10th-13th October 2011.

• LOCAL CONFERENCE

- M. Navasery, S.A. Halim, K.P.Lim, S.K.Chen , Study of Structure and Electrical properties of La_{1-x}Ca_xMnO (x=1/8, 1/3 & 5/8) polycrystalline manganites, presented in "Fundemental Science Congress 2010, UPM on 18th-19th May 2010.
- M. Navasery, S.A. Halim, K.P.Lim, S.K.Chen, R.A.Shukor and N.Soltani, " Study of Structure and Electrical Transport properties of RE Ba₂Cu₃O_{7-x} (RE is Y, Gd and Nd) superconductors" presented in "Fundemental Science Congress 2011, UPM on 5th- 6th July 2011.
- M. Navasery, S.A. Halim, K.P.Lim, S.K.Chen and R.A.Shukor, "Growth and characterization of La_{2/3}Ca_{1/3}MnO₃ thin films by Pulsed laser deposition on Corning glass substrate" presented in 26th Regional Conference on Solid State Science and Technology 2011 (RCSSST 2011) at The Royal Bintang , Seremban,Negeri Sembilan on 22nd-24th Novomber2011.
- M. Navasery, S.A. Halim, K.P.Lim, S.K.Chen and R.A.Shukor, "Growth and characterization of La_{5/8}Ca_{3/8}MnO₃ thin films by Pulsed laser deposition on Fused silica substrate" presented in "Fundemental Science Congress 2012, UPM on 17th-18th July 2012.

• EXHIBITION AND AWARD

> Pameran Rekacipta Penyelidikan and Inovasi (PRPI 12) UPM 2012.

Abdul Halim Shaari, **Manizheh Navasery**, Chen Soo Kien and Lim Kean Pah " Enhancement of Magnetoresistance in LCMO/PCMO/LCMO Trilayers Grown on Si-Wafer by Pulsed Laser Deposition" **Silver Medal.**

> Pameran Rekacipta Penyelidikan and Inovasi (PRPI 12) UPM 2012.

Abdul Halim Shaari, Pan Kai Yap, **Manizheh Navasery**, Chen Soo Kien, Mohd Mustapha Awang Kechik, Lim Kean Pah and Wan Mohd Daud Wan Yusoff, "Room Temperature Ferromagnetic-Insulator Transition in LKMO prepared via Sol-Gel" **Silver Medal**.