



**UNIVERSITI PUTRA MALAYSIA**

**STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF La-  
AMn-O (A=Ca, Sr, Ba, Na AND K) IN BULK AND THIN FILM**

**NG SIAU WEI**

**FS 2011 88**

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**MASTER OF SCIENCE  
UNIVERSITI PUTRA MALAYSIA**

**2011**

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

**March 2011**

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

**STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF La-A-Mn-O (A=Ca, Sr, Ba, Na AND K) IN BULK AND THIN FILM**

By

**NG SIAU WEI**

**March 2011**

**Chairman:** Lim Kean Pah, PhD

**Faculty:** Science

Perovskite manganites oxide materials have attracted much attention due to their promising potential applications in the magnetic sensor or devices. In this research,  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $x = 0.33$  when A=Ca, Sr and Ba;  $x = 0.2$  when A=Na and K) in bulk form were prepared via solid state reaction method.  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) and  $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$  (LNMO) are then converted to thin film via pulse laser deposition method (PLD) on different substrates (corning glass, fused silica glass and  $\text{MgO}$  (100)) and deposition duration. Rietveld refinement of X-ray diffraction data showed that all samples are polycrystalline having trigonal crystal structure except for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (LCMO) and  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$  (LBMO) which are orthorhombic. From the Rietveld refinement, we observed that the lattice parameter, Mn-O bond length and bond angle changed in thin film which were influenced by the substrates type and deposition duration. The thickness of films was in the range of  $\sim 0.3\text{-}3.0 \mu\text{m}$ . The crystallite size for the thin film is between 15-22 nm. The grain size distribution for bulk samples are around  $1.0\text{-}2.0 \mu\text{m}$ . A huge change of surface microstructure can be observed for thin film samples, where the grain size is reduced to  $\sim 50\text{-}150 \text{ nm}$ .

Some nano-crack effects were observed in the thin film samples where this effect is due to the different coefficient of thermal expansion between the film and substrates during the annealing process. Thin film samples showed a much higher resistance (about 2-3 orders) due to the existence of disordered phase at the grain boundary and/or nano-crack barrier that causes higher scattering and/or tunneling effect when the electrons pass through them. The metal-insulator temperature ( $T_p$ ) for LSMO shifted to lower values in the thin films, probably due to the change of Mn-O bond length and bond angle. Conversely, LNMO system showed greater  $T_p$  value in thin film suggesting that the grain boundary effect might also contribute to the  $T_p$  changes. Nonetheless, the deposition duration and substrates used also influence the  $T_p$  value. Overall, negative magnetoresistance (MR) have been obtained for bulk and thin films. The MR value increases with decreasing temperature at low applied magnetic field which known as Low Field Magnetoresistance (LFMR). In thin film form the %MR value has been improved with -25% for LS\_M15 and -22% for LN\_M20 as compared to that of the bulk LSMO (-16%) and LNMO (-21%) when a magnetic field of 1 Tesla was applied at 90 K.

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

**SIFAT STRUKTUR, MAGNET DAN ELEKTIK BAGI PUKAL DAN FILEM  
NIPIS La-A-Mn-O (A=Ca, Sr, Ba, Na DAN K)**

oleh

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Bahan perovskit manganites oksida telah menarik perhatian ramai disebabkan oleh potensinya dalam aplikasi sensor magnetik atau peranti. Dalam kajian ini,  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $x = 0.33$  bila A=Ca, Sr dan Ba;  $x = 0.2$  bila A=Na dan K) disediakan melalui kaedah tindak balas keadaan pepejal dalam bentuk pukal. Kemudian,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) dan  $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$  (LNMO) telah ditukar menjadi filem nipis melalui keadah Mendapan Dedenut Laser (MDL) di atas substrat (kaca Corning 7059, kaca fused silica and MgO (100)) dan tempoh mendapan yang berbeza. Kaedah Rietveld menunjukkan bahawa semua sampel adalah polihablur dan membentuk struktur trigonal kecuali  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (LCMO) dan  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$  (LBMO) yang membentuk struktur ortorombus. Daripada kaedah Rietveld, kami mendapati bahawa kekisi, panjang ikatan Mn-O dan sudutnya berubah dalam bentuk filem nipis dimana perubahan ini adalah dipengaruhi oleh jenis substrat dan tempoh mendapan. Ketebalan filem nipis adalah dalam julat  $\sim 0.3$ - $3.0 \mu\text{m}$ . Saiz butiran bagi filem nipis adalah dalam julat 15-22 nm. Taburan saiz butiran bagi bentuk pukal adalah dalam julat 1.0-2.0  $\mu\text{m}$ . Perubahan yang besar di

permukaan mikrostuktur dapat dikesan dimana saiz butiran berkurang menjadi ~50-150 nm bagi sampel filem nipis. Beberapa kesan nano-retakan dapat diperhatikan dalam filem nipis dan kesan ini adalah disebabkan oleh pekali pengembangan termal yang berbeza antara filem dan substrat semasa proses memijar. Sampel filem nipis menunjukkan kerintangan elektik yang jauh lebih tinggi (kira-kira 2-3 ganda) disebabkan oleh kewujudan fasa yang tidak tersusun di permukaan butiran dan/atau sekatan nano-retakan yang menyebabkan kesan serakkan spin dan/atau kesan penerowongan spin semasa elektron melaluinya. Suhu logam-penebat ( $T_p$ ) bagi LSMO menganjak ke nilai yang lebih rendah dalam filem nipis, ini mungkin disebabkan oleh perubahan yang berlaku di panjang ikatan Mn-O dan sudutnya semasa bertukar ke filem nipis. Sebaliknya, sistem LNMO menunjukkan nilai  $T_p$  yang lebih besar dalam filem nipis mencadangkan bahawa kesan sempadan butiran mungkin juga menyumbang bagi pertukaran  $T_p$ . Walau bagaimanapun, tempoh mendapan dan substrat yang digunakan juga mempengaruhi nilai  $T_p$ . Pada keseluruhannya, magnetorintangan (MR) negatif telah diperolehi bagi pukal dan filem nipis. Nilai MR bertambah dengan penyusutan suhu dalam keadaan medan magnet rendah yang dikenali sebagai kesan magnetorintangan medan rendah (LFMR). Sampel filem nipis telah meningkatkan nilai %MR dengan -25% bagi LS\_M15 dan -23% bagi LN\_M20 apabila berbanding dengan bahan pukal LSMO (-16%) dan LNMO (-20%) dalam medan magnet 1 Tesla pada suhu 90 K.

## **AKNOWLEDGEMENT**

First, I wish to express my deepest gratitude to my supervisory, Dr. Lim Kean Pah, who gave me lot of guide, comments, suggestions, constant encouragement and his time for helping me to understand and explore the colossal magnetoresistance and pulsed laser deposition technique during this research.

It is a pleasure to acknowledge my co-supervisor Prof. Dr. Abdul Halim Shaari for allowing me to use the facilities in the Magnetic and Superconductor Laboratory. This laboratory has given me a good learning environment to do my research work successfully. I would like to extend my sincere appreciation to my co-supervisor Dr. Chen Soo Kien for his willingness to help.

Many thanks to my lab colleagues, Mr. Wong Jen Ken, Mr. Tan Kwee Yong, Ms. Tan Kee Lee, Ms. Saeedah Ravandi, Mr. Albert Gan, Ms. Chin Hui Wei, Mr. Pan Kai Yap, Ms. Nurul Ain Shaaidi and Mr. Chang Seng Chong, who have always motivated, supported and encouraged me through out my work.

Further thanks to my friends, Ms. Wong Swee Yin, Ms. Josephine Liew, Dr. Lim Mei Yee, Ms. Caterine Ong, Ms. Chin Yee Siew, Ms Choo Weng Pei and Mr. Beh Hoe Guan, who have always share their experience and gave moral support for me during my study life. Not forget to thank all my high school friends who have always accompanied and encouraged me when I'm down.

My special thank to Ms. Kamsiah and Mr. Shaharuddin for their help in the XRD and Hall probe measurements. Appreciation is also given to Mr. Razak, for his technical help.

Last but not least, unlimited thanks to all my family members for their endless love, encouragement and support.



This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master. The members of the Supervisor Committee were as follows:

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## **DECLARATION**

I declare that the thesis is 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 institution.

**NG SIAU WEI**

Date: 21 Mac 2011



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