錫摻雜鑭錳氧化物薄膜及其磁性傳輸性質、電子結構與微結構之研究

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中文摘要

本論文有系統地探討錫摻雜鑭錳氧化物 $Ls_{1-x}Sn_xMnO_3$ (x=0.1－0.5)製程、結構對其物性的影響。在鑭錳氧化合物中使用錫四價離子來取代鑭三價離子的課題，因製備不易而較少有系統性的研究成果報導，且發表的文獻亦存有許多尚待釐清的爭議，本論文詳細比較此材料的錫摻雜濃度、磁傳輸行為、電子結構與微結構間之相互影響，並提供明確的證據以釐清一些重要的議題。

首先，我們研究以脈衝雷射蒸鍍法在鈦酸鍶基板上製備晶軸取向優異的 $La_{0.7}Sn_{0.3}MnO_3$ 薄膜。雖然直接成長的樣品並未顯現出絕緣－金屬相轉變，在溫度約為 170K 時均顯現順磁－鐵磁相轉變。值得注意的是，經過熱處理之後的樣品，不但改善了晶格結構也同時趨使材料在 315K 時顯現龐磁阻材料典型之絕緣－金屬相轉變溫度並將順磁－鐵磁相轉變溫度提升至 320 K。我們認為在未經退火熱處理的樣品中，錫與鑭離子巨大的半徑差距以及薄膜與基板的磊晶關係所產生的應力，係促使其載子傳輸侷限化之重要原因，也因此壓抑了發生絕緣－金屬相變所需之長程鐵磁有序之轉變。從初步的 x 光吸收光譜 (XAS)量測結果可發現： $La_{0.7}Sn_{0.3}MnO_3$ 中的錳呈現了 Mn^{3+}/Mn^{2+}混合

價，顯示摻雜四價的錫離子的確造成了在錳的 e_g 能帶中電子摻雜的效應。

為深入研究此一現象，我們針對成長在鑭鋁氧基板之 $La_{0.7}Sn_{0.3}MnO_3$ 薄膜作更進一步的分析。從穿透電子顯微鏡分析，清楚顯示直接成長的 $La_{0.7}Sn_{0.3}MnO_3$ 薄膜與基板間有極佳磊晶關係，同時各種元素組成均勻分佈於樣品中。這證明我們已經可以在不破壞鈣鈦礦結構且沒有組成分佈不均勻的出現的情況下，成功地製備出 $La_{1-x}Sn_xMnO_3$ 系統中 $x=0.3$ 的樣品，並釐清文獻上所稱無法在鑭錳氧化物中摻雜錫之迷思。另一方面，在氧氣與氫氣中進行熱處理後，$La_{1-x}Sn_xMnO_3$ 薄膜呈現絕緣－金屬相轉變同時在相轉變溫度上也有顯著的提升，是否為應力釋放後的本質特性或有其他效應產生則仍待釐清。我們由穿透電子顯微鏡的元素組成分佈分析的結果發現熱處理後，樣品中有錫化合物出現，故熱處理可能同時導致所得到的薄膜樣品成為缺鑭的鑭錳氧化合物，而非原生成之摻錫鑭錳氧化物。

最後，我們有系統的研究了 $La_{1-x}Sn_xMnO_3$ ($x=0.1-0.5$) (LSnMO)的電子結構與磁性質。我們觀察到直接成長的 LSnMO 在摻雜範圍 $x=0.1-0.5$ 時皆屬於鐵磁絕緣體材料，和前述無秩序的結構妨礙長範圍的磁有序而導致這類樣品呈現鐵磁絕緣體的性質的機制吻合。我們亦發現隨著所摻雜錫量的增加，LSnMO 的結晶結構愈趨劣化，同時其飽和磁化亦隨之急遽減弱。另一有趣的發現是在 $x=0.5$ 時，在 44K 會有一額外的磁性相轉變的現象。磁性質與微結構分析顯示在該摻雜濃度時，有 Mn_3O_4 的第二相析出。總結這些結果後，我們建立了 LSnMO 的相圖。結果顯示，電子摻雜錳氧化物的相圖與眾所熟知的電洞摻雜的相圖是不對稱的。

The Magnetotransport Properties, Electronic Structure, and Microstructure of Tin-Doped Manganite Films

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Abstract

In this dissertation, we have systematically studied the Sn-doped manganites $Ls_{1-x}Sn_xMnO_3$ (x=0.1 ─ 0.5) using various experimental probes. Due to the inherent difficulties of preparing pure phase samples, the issue of the substitution of tetravalent ion Sn^{4+} into $LaMnO_3$ manganite remains controversial and further studies are in order. We compared the detailed magneto-transport behaviors, electronic structure and microstructure analyses, and provided solid evidences that clarified some of the outstanding issues in this research field.

Firstly, we study the fabrication of single-phase $La_{0.7}Sn_{0.3}MnO_3$ thin films on $SrTiO_3$ substrates by pulsed laser deposition (PLD). The as-deposited films, though were insulating with no sign of insulator-metal transition (IMT), did display paramagnetic-ferromagnetic transition (PFT) around 170 K. *Ex-situ* annealing the films not only significantly improves the crystallographic quality but also raises IMT and PFT to 315 K and 320 K, respectively. The transport properties can be drastically changed by the strain originates from large ion-size

misfit between Sn and La and film/substrate epitaxial relation. The preliminary x-ray absorption spectroscopy (XAS) shows signature of Mn^{3+}/Mn^{2+} mixed-valence indicating that tetravalent Sn ions does result in electron-doping into the e_g band of Mn.

We also prepared the single-phase $La_{0.7}Sn_{0.3}MnO_3$ thin films on $LaAlO_3$ substrates by PLD. The as-deposited films, like those grown on STO substrates; all exhibit ferromagnetic insulator behaviors. The XAS of the as-deposited $La_{0.7}Sn_{0.3}MnO_3$ films also showed characteristics of Mn^{3+}/Mn^{2+} mixed-valence suggesting the realization of the electron-doping into the e_g band of Mn via the doping of tetravalent Sn ions. The transmission electron microscopy (TEM) analyses on the as-deposited $La_{0.7}Sn_{0.3}MnO_3$ films further confirmed that the films are epitaxial with uniform composition distributions. It is suggestive that the doping level of $x = 0.3$ in $La_{1-x}Sn_xMnO_3$ can be achieved without disrupting the perovskite structure or any composition inhomogeneity. On the other hand, *ex-situ* annealing in oxygen as well as in argon atmosphere, though both drive the films to display IMT and a marked enhancement in the transition temperature, the preservation of $La_{0.7}Sn_{0.3}MnO_3$ phase is somewhat doubtful. In the oxygen-annealing case, the evidence from the XAS measurements on Sn ions though showed the existence of tetravalent characteristics, the Hall measurements indicated that the obtained $La_{0.7}Sn_{0.3}MnO_3$ films are p-type in nature. Furthermore, the TEM analyses also revealed the emergence of the Sn-compounds, which may ultimately drive the obtained films into La-deficient $La_{1-x}MnO_3$ phases.

Finally, we investigated the magnetic properties and electronic structure as a function of doping concentration for $La_{1-x}Sn_xMnO_3$ with $x=0.1-0.5$. The as-deposited films were all ferromagnetic insulators with no sign of insulator-metal transition (IMT). It is believed that the structural disorder may have obstructed the long range magnetic ordering and resulted in ferromagnetic-insulator characteristics. Moreover, it is found that both the crystalline structure and saturated magnetization of the as-deposited films deteriorates with the increasing doping

level of Sn. The XAS of the as-deposited LSnMO films showed signatures of Mn^{3+}/Mn^{2+} mixed-valence indicating that tetravalent Sn ions indeed have resulted in electron-doping into the e_g band of Mn. The origin of the additional magnetic transition near 44K observed for $x > 0.3$ will be discussed base on the experimental results obtained from x-ray diffraction (XRD), and transmission electron microscopy (TEM). The phase diagram of the $La_{1-x}Sn_xMnO_3$ reveals that the properties of the electron-doped manganites are not symmetric to their hole-doped counterparts.