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計畫主持人：楊尚霖教授
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中　華　民　國　97　年　10　月　25　日

行政院國家科學委員會專題研究計畫成果報告

鈣鈦礦結構超巨磁阻材料磁傳輸特性與電阻交換效應之諸元機制的綜合研究

Synthesis study on the mechanisms of magnetotransport characteristics and resistive switching effects in the perovskite CMR materials

計畫編號：NSC 96-2112-M-164-004
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主持人：楊尚霖教授　　修平技術學院電機工程系
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中英文摘要

探討鈣鈦礦結構超巨磁阻材料磁電傳輸特性及電阻交換機制是相當新穎的研究。本計畫主要的研究目的是應用計畫申請人多年來在磁性物理、氧化物製作及薄膜濺鍍的經驗，深入探討二元磁性奈米複合物中奈米等級晶粒內與晶界之載子傳輸特性，及金屬/鈣鈦礦結構超巨磁阻材料/金屬多層結構中之載子傳輸機制。本研究主要研究在低溫和低維度物體中， 電子的傳導行為深受到量子干涉(quantum interference)與表面效應的影響，因而當晶粒尺寸縮小至近奈米等級時，其微觀物理的諸元特性包含庫倫力作用(Columb interaction)、雙重交換作用(Double exchange)、穿隧效應(Tunneling effect)、及載子躍遷(Carrier hopping)等介觀物理(Mesoscopic physics)的性質與機制可預見的將極為不同。本計畫嘗試製做出不同組成之奈米複合物以了解在奈米尺寸下晶粒內(intragrain)與邊界(intergrain)對磁傳輸行為及低場磁阻所扮演的角色，並做深入探討。計畫中將研製不同成份的A/B 二元磁性鑭錳氧化物奈米複合物結構，以變溫電阻率量測、低磁場場冷卻零場冷卻磁矩(LF FC-ZFC magnetization)、高場磁矩、磁滯曲線等的量測來研究與微米等級晶粒邊界的磁傳輸特性的差異。首先，以溶膠凝膠法(Sol-gel method)製作奈米等級之不同A（磁性鑭錳氧化物）與B（金屬或氧化物）成份來調變晶粒邊界的自旋極化耦合條件，以觀察傳輸載子在晶粒邊界的傳導電子溫度倚變躍遷情形。再者，以控制製程參數方式製作奈米等級不同尺寸晶粒以觀察晶粒核心與邊界不同比例時對傳導電磁特性的影響，探討對磁阻特性影響的機制。最後，對照計畫申請人目前實驗結果，微米級晶粒低溫時發現的Kondo 效應在奈米尺寸以下時是否仍然存在。本計畫另一主要的研究目的是深入探討二元磁性奈米複合物中奈米等級晶粒內與晶界之載子傳輸特性。使用化學及固態燒結法製作$(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$陶瓷複合物。計畫中針對樣品的結構及磁傳輸將作詳細的研究。在系統中磁化率皆隨SiO_2含量的增加而降低，而電阻係數在

$(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$中會急劇增加。主要乃是$SiO_2$進入晶界區域形成導電網路的絕緣阻隔，以提升其磁阻變化率。本計畫相關研究結果已發表於SCI 期刊 ***Physica Status Solidi (b), Vol. 244, No. 12 (2007) 4415***與***Physica Status Solidi (c), Vol. 4, No. 12 (2007) 4556***。另外對於晶界及其複合物的磁電特性已接受將於ACM2008亞洲磁性研討會(2008.12.10韓國釜山)發表論文。
關鍵字：鈣鈦礦；磁阻；複合材料；電阻係數；磁性材料；電性；磁滯。

The diluted magnetic properties of $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ ceramic composites, are prepared by using chemical and solid-sate sintering route. Magnetic and transport properties of $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites are explored in this study. Ferromagnetism is gradually attenuated due to the magnetic dilution induced by the increase of SiO_2 content. Clearly irreversible behavior is observed in the zero-field cooling and field cooling curves at a low field of 100 Oe. Saturation magnetization decreases as x increases, while ferromagnetic transition temperature remains around 346K for all composites. All of the composites exhibited ferromagnetic hysteresis behavior which can be modeled by the law of approach to saturation in the form $M = M_S(1-a/H^n)$ where $0 \leqq n \leqq 1$ [3]. The term a/H^n expresses the deviation of magnetization from saturation. The larger factor *n* and smaller factor *a* for $La_{0.7}Pb_{0.3}MnO_3$-rich samples resulting in sharper square curves which should be associated with the long-range spin order of ferromagnetic coupling.

Keywords：Perovskite; Magnetoresistance; Composite materials; Magnetic materials; Electrical Properties; Hysteresis.

1. Introduction

Mixed-valence manganese oxides, $La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba, Pb, etc.), have been the materials under extensive studies because of the rich varieties of crystallographic, magnetic and electronic phases [1-5]. These materials exhibit a large magnetoresistance ratio (MRR, defined as $[\rho(H)-\rho(0)]/\rho(H)$), termed as colossal magnetoresistance (CMR), which is greatly useful for various industrial applications. However, due to the large magnetic field of the order of several teslas is required, this property is difficult to utilize for practical applications. For most room temperature applications one needs a large MRR under low field condition. Therefore, the important issues are to explore the principal factors, that determined the T_C and MRR, and to reduce the required field for these CMR compounds. Recently, researches indicate that grain boundaries and interfaces can be the major factors of magnetoresistance effects, which has attracted renewed interests on these materials. Several attempts [6-8] have been observed the enhancement of MRR through the composites of $La_{1-x}Sr_xMnO_3/CeO_2$ and $La_{1-x}Sr_xMnO_3$/silica [9-10]. These enhancements can be explained through the model of spin-polarized tunneling with insulator layer as a barrier. On the other hand, the enhancement of MRR has also been proved with the (CMR compound)/Ag composites [11] due to the formation of conduction

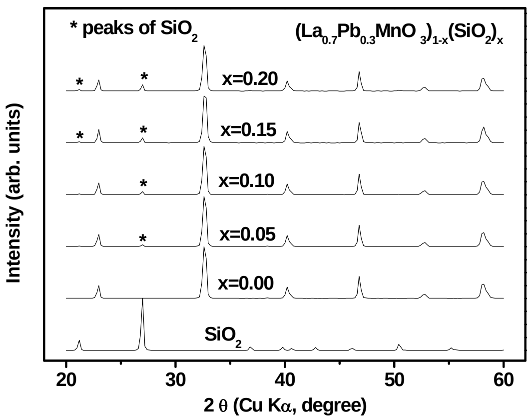

Fig. 1 X-ray diffractograms for the pure SiO_2 and $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites

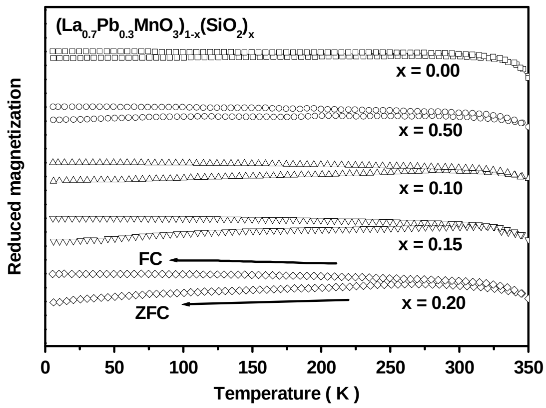

Fig. 2 Temperature dependence of ZFC and FC magnetization curves at an applied field of 100 Oe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites.

bridges by Ag particle among the grains of CMR compounds. In this article, we will demonstrate the synthesis of the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites. Variation of magnetic behaviors properties in these composites will also be discussed.

2. Experimental

The samples of $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites were synthesized by two steps. First, the powder of pure $La_{0.7}Pb_{0.3}MnO_3$ was prepared by the conventional ceramic fabrication technique of solid-state reaction. After wet-milled by SPEX 8000M, well-dried hyperfine powders (La_2O_3, $PbCO_3$, and $MnCO_3$) were mixed by Retsch Mix Miller MM-2000 in a stoichiometric ratio. Samples were calcined in air at 850ºC for 24 hours with intermediate grindings for three times. After grinding, the combined powders of $La_{0.7}Pb_{0.3}MnO_3$ and SiO_2 with stoichiometric ratios were mixed and then pressed into disk-shape pellets with a diameter of 12 mm and a thickness of 2 mm. The disk samples were sintered in air at 750ºC. The structure and phase purity of the samples were examined by the diffraction patterns recorded with a powder diffractometer (Rigaku, MAX-2200PC, Cu-Kα radiation) at room temperature. The measurements of magnetization between 5K and 350K were performed by a Quantum Designed superconducting quantum interference device MPMS-5S SQUID magnetometer. The ZFC-FC curves were taken in an applied field of 100 Oe. The curves of temperature-dependence magnetization in an applied field of 50 kOe were also recorded at 5K and 50 kOe.

3. Results and Discussion

Figure 1 shows the XRD patterns of pure SiO_2 and $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites samples, which indicated that the pure samples have synthesized. The

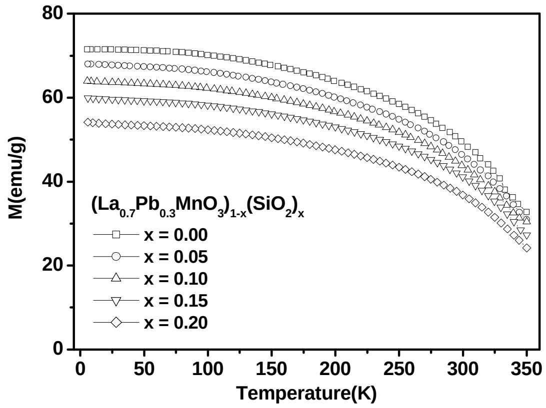

Fig. 3. Temperature dependence of magnetization curves in an applied field of 50 kOe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites.

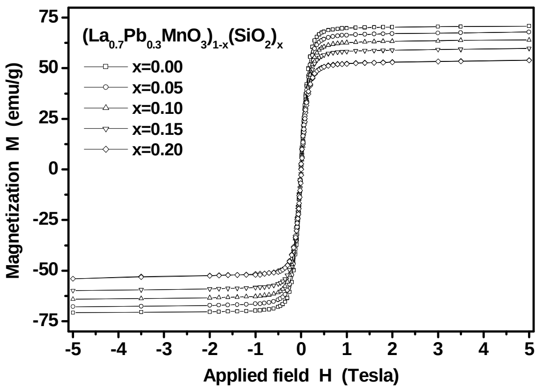

Fig. 4 Field dependence of magnetization curves recorded at 5 K from −50 to 50 kOe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites.

XRD spectra of the combined samples reveal two different sets of XRD peaks for $La_{0.7}Pb_{0.3}MnO_3$ and SiO_2. No extra phase is observed and one can conclude that the reactions between the $La_{0.7}Pb_{0.3}MnO_3$ and SiO_2 grain boundaries are negligible.

The ZFC-FC magnetization curves for all samples are measured as shown in Fig. 2 to exam the spin order and magnetic behaviors in a low field of 100 Oe. The ZFC-FC magnetization measurement is a common way to observe the spin order behaviors of magnetic materials. For x=0 compound, the ZFC-FC magnetization curves are almost overlap except at very low temperature, which exhibit a ferromagnetic spin order. Conversely, the irreversibility is found for SiO_2 combined composites. In these SiO_2 combined compounds, the ZFC curves coincide with the FC curves only near the high temperature region and indicate the suppression of ferromagnetism. Separations are observed as a λ-shape curve when the temperature are decreasing below the ferromagnetic-paramagnetic transition temperature T_C (defined as the temperature where the slop, $|dM/dT|$, reaches a maximum value in the ZFC curve). The unchanged T_C (around 350K) indicates no variation in the composition of $La_{0.7}Pb_{0.3}MnO_3$ due to low temperature sintering. Due to the $La_{0.7}Pb_{0.3}MnO_3$ grains are partly separated by SiO_2, it is reasonable that the Mn-Mn ferromagnetic exchange would be interrupted and the spin disorder of Mn would occur at the grain interfaces, as a consequence.

Figure 3 shows the temperature dependence of magnetization curves in an applied field of 50 kOe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites. These samples undergo a paramagnetic to ferromagnetic transition with the decreasing of temperature. Saturation magnetization M_S (defined as the magnetization at 5K and an applied field of 50 kOe for comparison)

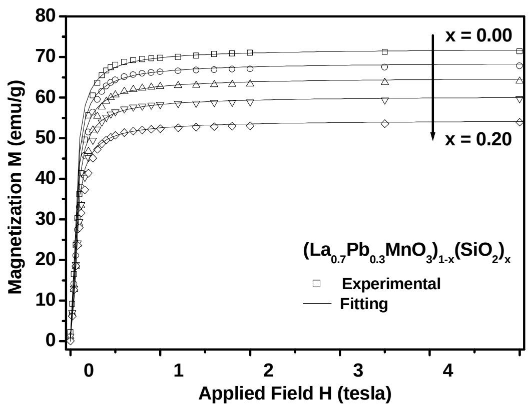

Fig. 6. Temperature dependence of magnetization curves in an applied field of 50 kOe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites.

decreases from 71.74 emu/g for x=0.0 to 54.21 emu/g for x=0.2 with the increase of SiO_2 content. Due to the magnetic dilution, the addition of SiO_2 does not change the T_C values (about 346K for all composites), but leads to a decrease in M_S. As would be expected, the decrease of content fractions of $La_{0.7}Pb_{0.3}MnO_3$ in these composites would results in the inverse proportion between M_S and x.

The field dependence of magnetization curves recorded at 5 K from −50 to 50 kOe for the $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ composites is shown as Fig. 4. All of the composites show relatively square loops indicating the similar magnetization process. The values of saturation magnetization M_S, obtained from the hysteresis curves at 5 K and 50 kOe, decrease with the increase of SiO_2 content. These results are consistent with the data of high-field magnetization in Fig. 3. The hysteresis fitting curves are given in Figs. 5. The hysteresis behavior

Table 1 Values of the fitting saturation magnetization M_{Sf} and factor a.

	M_{Sf}	a	n
x=0.00	71.9903	324.5867	1
x=0.05	68.5835	338.7230	1
x=0.10	64.8467	345.4385	1
x=0.15	60.2934	353.1646	1
x=0.20	54.3778	361.4719	1

can be modeled by the law of approach to saturation in the form $M = M_{Sf}(1 - a/H^n)$. The term a/H^n expresses the deviation of magnetization from saturation. The factor a is correlated with the ferromagnetic correlation length. The values of a and M_S are both listed in Table 1. Obviously, a increases as the increase of SiO_2 content. Therefore, the value of the factor a depends on the SiO_2 content of substitution and are associated with the stability of the magnetic phase. The smaller factor a for the $La_{0.7}Pb_{0.3}MnO_3$ rich samples resulting in sharper square curves should be associated with the long-range spin order of magnetic moment.

4. Conclusion

Ceramic composites of $(La_{0.7}Pb_{0.3}MnO_3)_{1-x}(SiO_2)_x$ are synthesized by using the chemical solid-state method. These composites were characterized for their structural and magnetic properties. Ferromagnetism is suppressed due to the magnetic dilution by the introduction of non-magnetic SiO_2. The appropriate fitting of hysteresis curves of the $La_{0.7}Pb_{0.3}MnO_3$ compounds to the law $M=M_S(1-a/H^n)$ is achieved. The smaller factor a for the $La_{0.7}Pb_{0.3}MnO_3$ rich samples resulting in sharper square curves should be associated with the long-range spin order of magnetic moment.

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