

行政院國家科學委員會專題研究計畫 成果報告

研發具有離子導電性、超導電性、磁阻性或可以防止鐵腐蝕的金屬氧化物 研究成果報告(精簡版)

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中 華 民 國 98 年 05 月 05 日

行政院國家科學委員會補助專題研究計畫 ☒ 成果報告
☐ 期中進度報告

研發具有離子導電性、超導電性、磁阻性或可以防止鐵腐蝕
的金屬氧化物

**Development of metal oxides with ionic conductivity,
superconductivity, magnetoresistance or for the iron
corrosion inhibition**

計畫類別：☒個別型計畫

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成果報告類型（依經費核定清單規定繳交）：☒精簡報告

本成果報告包括以下應繳交之附件：

☒出席國際學術會議心得報告及發表之論文各一份

執行機構及單位名稱：淡江大學化學系

中 華 民 國 98 年 5 月 5 日

一、中文摘要

本計畫的執行成果包含以下幾篇已發表、將出版、送審中和研究生畢業論文，列舉於下。(1) 電聚合 PPDT 與聚苯胺雙層膜於鐵片上防止腐蝕，發表在 2008 年台灣鋼鐵技術國際研討會。(2) 以 XANES 光譜研究 $\text{Gd}_2\text{Zr}_2\text{O}_7$ 的相變化，即將發表在 SCI 收錄之 J. Chin. Chem. Soc. (3) $(\text{La}_{1-x}\text{Sr}_{1+x})(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_4$ 的製備和磁性，即將發表在 SCI 收錄之 J. Supercond. Novel Magnet. (4) 添加 Li_2O_3 對合成 $(\text{Y}_{2-y}\text{Li}_y)\text{Ti}_2\text{O}_7$ 的效應，送審中。(5) $\text{Gd}_2\text{Zr}_2\text{O}_7$ 的製備和 fluorite-pyrochlore 的相轉變，送審中。(6) $(\text{Bi}_{2-x}\text{Pb}_x)(\text{Sr}_{2-y}\text{R}_y)\text{CuO}_6$ ($\text{R} = \text{La}, \text{Pr}$) 之結構、氧計量與超導性研究是碩士班研究生洪勝男的畢業論文。

關鍵詞：氧化物、取代、固態電解質、晶體結構、離子導電性、超導性、鐵的腐蝕防治

Abstract

In this progress report, titles of 6 research papers were listed. They are (1) Corrosion protection of steel by the electropolymerization of PPDT and aniline bilayer films, published in the Taiwan 2008 International Steel Technologies Symposium Proceedings. (2) XANES spectroscopic studies of the phase transition in $\text{Gd}_2\text{Zr}_2\text{O}_7$, to be published in the J. Chin. Chem. Soc. (3) Preparation and magnetic properties of $(\text{La}_{1-x}\text{Sr}_{1+x})(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_4$ to be published in the J. Supercond. Novel Magnet. (4) Effect of Li_2O_3 addition on the preparation of $(\text{Y}_{2-y}\text{Li}_y)\text{Ti}_2\text{O}_7$ submitted for reviewing. (5) Preparation and fluorite-pyrochlore phase transformation in $\text{Gd}_2\text{Zr}_2\text{O}_7$, submitted for reviewing. (6) Structure, oxygen stoichiometry and superconductivity of $(\text{Bi}_{2-x}\text{Pb}_x)(\text{Sr}_{2-y}\text{R}_y)\text{CuO}_6$ ($\text{R} = \text{La}, \text{Pr}$), a Master thesis.

Keywords: oxides, substitution, solid electrolyte, crystal structure, ionic conductivity, superconductivity, iron corrosion resistance.

二、緣由與目的

In our laboratory, oxide materials are prepared. Their properties, including, ionic conductivity, superconductivity and corrosion resistance are studied. Energy problems become more and more important these days, we devote some of our research efforts into the development of the solid oxide fuel cell related materials. Two series of ionic conducting materials were prepared and studied, they are $(\text{Y}_{2-x}\text{M}_x)\text{Ti}_2\text{O}_7$ ($\text{M} = \text{Li}, \text{Na}, \text{Ca}, \text{Sr}$) and $\text{R}_2\text{Zr}_2\text{O}_7$ ($\text{R} = \text{rare earth and Y}$). Two series of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ compounds were prepared and a K_2NiF_4 structure with magnetic properties are studied. Due to the new environmental protection regulations, Cr^{6+} is prohibited; we prepared bilayer polymer films to protect the Fe plate, which has no Cr content. High temperature superconductors have been studied since 1987. We still remain interesting in this field.

三、結果與討論

The authors, titles, and abstracts of the 3 published and to be published papers are listed as follows.

1. Yi-Ming Huang, Cheng-Yuan Hsi, Bo-Jyun Chen, Huey-Chuen I. Kao, Chi-Feng Wu, 2008 "Corrosion Protection of Steel by the Electropolymerization of PPDT and Aniline Bilayer Films," Taiwan 2008 International Steel Technologies Symposium, Nov. 2-5, Conference Proceedings, D38, pp. 1-8.

Abstract Bilayer film prepared by electropolymerization of 2-N-phenylamino-4,6-dimercapto-S-triazine (PDT) on structural quality hot rolled SAE1018 steel surface first and then aniline on top at room temperature were studied to understand the anti-corrosion effect. The first layer, PPDT was grown in 0.20 M $\text{Na}_2\text{CO}_{3(\text{aq})}$ and the second layer, polyaniline (PANI) was grown in 0.20 M $\text{H}_3\text{PO}_{4(\text{aq})}$ solution. Concentration of the monomers and electrolytes and electropolymerization times were varied to

find a better condition for making protecting films. The bilayer film under the adhesion tape test (ASTM D3359-02) is 4B (< 5% area removed) and 1 kg pencil hardness test (ASTM D3363-05) is 6-7. Fibrous polymer and cracks are found in SEM image for single layer PANI. On the other hand, homogeneous evenly covered layer of PPDT is observed under SEM on the cutting edge of the bilayer film. ΔE_{corr} of the bilayer film with respect to the bare substrate, ($E_{\text{corr(bilayer)}} - E_{\text{corr(Fe)}}$), is +0.283 V. Anti-corrosion effect is greatly enhanced by adding a buffer layer of PPDT between PANI and steel substrate.

2. M. Y. Lin, Y. F. Wang, D. C. Ling, H. S. Sheu, H.-C. I. Kao, "Preparation and magnetic properties of $(\text{La}_{1-x}\text{Sr}_{1+x})\text{-(Mn}_{0.5}\text{Co}_{0.5})\text{O}_4$," in press, Journal of Superconductivity and Novel Magnetism

Abstract A series of single phase $(\text{La}_{1-x}\text{Sr}_{1+x})(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_4$ ($0 \leq x \leq 0.4$) materials with tetragonal K_2NiF_4 structure were prepared by a solid state reaction method. They were prepared at 1400 – 1450 °C. XRD and Rietveld refinement were employed for the structural analysis. Both a and c -axes decrease with increasing the amount of Sr substitution. All of them show ferromagnetic property below room temperature. For the sample with $x = 0.10$, it has the largest remanence (B_R) and coercivity (H_C). Spin glass transition is observed at temperature < 50 K, which is field dependent, T_{sg} decreases with increasing the amount of substitution and applied magnetic field.

3. Yu-Hsuen Lee, Jin-Ming Chen, Jyh-Fu Lee, Huey-Chuen I. Kao, "XANES spectroscopic studies of the phase transition in $\text{Gd}_2\text{Zr}_2\text{O}_7$," in press, J. Chin. Chem. Soc.

Abstract The structural phase transition from the fluorite to pyrochlore and the strength of the coordination bond of Zr-O in $\text{Gd}_2\text{Zr}_2\text{O}_7$ were investigated by XANES spectra of both O and Zr K -edge. Energy difference of the O K -edge absorption

spectra at 532 and 536 eV was assigned to the crystal field splitting energy of 4d orbital (ΔE_{4d} , t_{2g} and e_g) of Zr ion. Besides, the samples prepared at higher temperatures, the 536 eV peak moves slightly to higher energy, whereas the absorption energy of 532 eV peak does not shift. The correlation between ΔE_{4d} and the strength of interaction between Zr (4d) and O (2p) orbitals have been found. Furthermore, two Zr K -edge absorptions at 18020 and 18030 eV of $\text{Gd}_2\text{Zr}_2\text{O}_7$ have been observed, the splitting energy (ΔE), peak intensity ratio (I_{18030}/I_{18020}), and FWHM of the first derivative of the absorption curve depend on the preparation temperatures. The effect of crystal symmetry and Zr-O bonding character on the XANES spectral profile was discussed.

四、參考文獻 (以上 3 篇成果按照摘要所提順序排列, 其他年代的成果列於後, 此部分不含研究生畢業論文)

1. 高惠春 (Huey-Chuen Kao), 陳玉娟 (Yu-Chung Chen), 楊育峰 (Yu-Feng Yang), 吳奇峰 (Chi-Feng Wu), "高分子-氧化矽複合材料塗膜防止鐵片生鏽 (Polymer-silicon dioxide composite film for iron plate corrosion protection)," 中華民國專利申請, 2008 年 4 月。
2. H.-C. I. Kao, Y. H. Lee, W. P. Su, H. S. Sheu, J. F. Lee, **2007** "Crystal Structure and XAS of $(\text{M}_{2-x}\text{Li}_{3x})\text{Ti}_2\text{O}_7$ ($\text{M} = \text{Gd}, \text{Y}$)," IoM East Asia - 6th Materials Processing, Properties and Performance (MP3) conference 13-16 September, Beijing, China
3. C. H. Wu, Y. C. Chu, D. C. Ling, S. H. Liu, W. F. Pong, H. S. Hseu, J. M. Chen, J. F. Lee, and H.-C. I. Kao*, **2007**, "Superconductivity dependent on the amount of Bi and Sr in the $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ compounds," *Physica C*, 460-462: 422-423. (September 1), (SCI).
4. J. W. Chen, H.-C. I. Kao*, H. S. Sheu, Y. P. Chiang and L. Horng, **2007**, "Crystal structure and magnetic properties of $(\text{R}_{0.5}\text{A}_{0.5})\text{NiO}_3$, where $\text{R} = \text{Gd}, \text{Yb}$ and $\text{A} = \text{Ce}, \text{Th}$ perovskites," *Inter. J. Mod. Phys. B*, 21: 3443-3447 (July 30), (SCI).

5. Huey-Chuen I. Kao*, Yu-Fong Yang, Yu-Juan Chen, Chi-Fong Wu, Wen-Chang Liaw and Hsin-Wu Tsai, **2007** "Protection of Fe plate by organic-inorganic materials via sol-gel process," International Community for Composites Engineering (ICCE-16) Conference Proceedings. 15-20 July, Haikou, China.
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7. Y. H. Lee, Y. J. Chen, J. J. Pan, D. C. Ling, and H.-C. I. Kao, **2006** "Effect of Ca substitution at the Tm site in the $\text{TmBa}_2\text{Cu}_3\text{O}_y$ superconductor," AIP Conference Proceedings 850, 485-486. (September).
8. C. Y. Lien, H.-C. I. Kao*, D. C. Lin, H. H. Lu, J. M. Chen and J. M. Lee, **2005** "Structure and superconductivity of $\text{Bi}_2(\text{Sr}_{2-x}\text{M}_x)\text{CuO}_6$ ($\text{M} = \text{La, Gd, Y}$) compounds," *Chin. J. Phys.* 43: 629–637 (June).
9. M. S. Wu, H.-C. I. Kao*, H. S. Sheu, Y. P. Chiang, L. Horng, R. F. Hsueh, S. L. Young, W. F. Pong and J. H. Huang, **2005** "Structure and properties of $(\text{La}_{2-x}\text{Sr}_x)\text{MnO}_4$ compounds," *Inter. J. Mod. Phys. B* 19: 541–548 (Jan. 30).
10. S. L. Young*, H. Z. Chen, Lance Horng, Y. W. Ho and H.-C. I. Kao, **2005** "Comparison of the magnetization behaviors in perovskite compounds $\text{La}_{0.7-x}\text{Ln}_x\text{Pb}_{0.3}\text{MnO}_3$ ($\text{Ln} = \text{Pr and Sm}$)," *Inter. J. Mod. Phys. B* 19: 563–568 (Jan. 30).
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14. C. H. Lin, C. M. Wang and H.-C. I. Kao*, **2003**, "Kinetic and stability of $\text{R}(\text{Ba}_{1.5}\text{Sr}_{0.5})\text{Cu}_3\text{O}_y$ ($\text{R} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho}$) superconductors in water," *Mat. Chem. Phys.* 82: 435–439 (November).
15. C. H. Chin and H.-C. I. Kao*, **2003**, "Effect of substitution in the $(\text{Gd}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_y$ and $\text{Gd}(\text{Ba}_{2-x}\text{A}_x)\text{Cu}_3\text{O}_y$ ($\text{A} = \text{Ca, Sr}$) superconducting compounds," *Physica C* 388–389: 381–382 (May).
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行政院國家科學委員會補助專家學者出席國際會議報告

96 年 9 月 31 日

報 告 人 姓 名	高惠春	服務機關名稱 ※ 及 職 稱	淡江大學化學系教授
會議期間及地點	97 年 9 月 12-16 日 中國北京市	本 會 核 定 補 助 文 號	NSC96-2113-M-032-003
會 議 名 稱	(中文) 第六屆材料製程、特性和成效國際會議 (英文) Sixth International Conference on Materials Processing for Properties and Performance (MP3-2007), Beijing		
發 表 論 文 題 目	(中文) $(M_{2-x}Li_{3x})Ti_2O_7$ (M = Gd, Y) 的結晶構造和 X-光吸收光譜 (英文) Crystal structure and XAS of $(M_{2-x}Li_{3x})Ti_2O_7$ (M = Gd, Y)		
<p>報告內容應包括下列各項：</p> <p>一、參加會議經過</p> <p>二、與會心得</p> <p>三、建議</p> <p>四、攜回資料名稱及內容</p> <p>五、其他</p>			

※服務機關若係大專院校，請註明科系名稱。

※報告內容請另以稿紙書寫工整，俾本部輯印成冊送各相關單位參考應用

第六屆材料製程、特性和成效國際會議(MP3-2007)出席會議報告

一、參加會議經過、與會心得

第六屆材料製程、特性和成效國際會議 (MP3-2007) 選在北京舉行。9 月 12 日一大清早來到桃園國際機場與中原大學的陳玉惠教授一起搭機赴北京開會。抵達時，已是黃昏時分。我們住在會場隔鄰的五洲旅館，方便去開會。此旅館在奧運村旁，離市區有一段距離，附近仍有許多工程正在趕工中，到處圍籬，有些混亂。

9 月 13 日我們一起去北京大學，陳玉惠教授給了一個演講，聽眾發問踴躍，而且看得出來，學生們還滿有水準。演講完後，幾位學生帶我們參觀該校。看到了新、舊建築、湖泊及湖邊的楊柳，還滿漂亮的。淡江大學最早蓋的幾間教室被當作古蹟保存，聽說是仿北大校園建築。因此，特別留意該校建築物。果然，看到一些風味相同的建物。

下午，我們去清華大學，陳教授又給了一場演講，學生們還是一樣有水準，對學問有追求的熱情。接著，我們去參觀校園。校園分新、舊兩區，時間關係，我們選擇舊校區參觀。該區以西式建築為主，因為該校是庚子賠款所建，一切大概以洋人意見為主吧？感覺上好像置身美國很有歷史的大學中。我是台灣清華畢業校友，第一次參觀北京清大校園，沒想到，兩地建築迥異。

與北大、清大老師聊天中獲知他們近年來經費充裕，需要的設備都有，學生程度高又用功，他們的科研水平實在不容小覷。台灣學生真的得用功些才能跟別人拼。

當晚，MP3-2007 有個歡迎會，我們因為下午未報到，不清楚會議場所，就沒參加。其實，它就在我們住的旅館 2 樓舉行。當時，我們問過大廳的服務員，也未獲告知。顯然，飯店的管理還有待加強。

9 月 14 日早上會議正式開始，此會有 8 個議題，分別是 1. ultralight materials and structure, 2. fuel cell science and technology: bridging processing and performance, 3. materials in devices and systems, 4. computational methods in materials research and development, 5. nanomaterials and nanostructures, 6. superalloys, intermetallics and related materials, 7. synthesis and properties of surface coatings, 8. toughening and toughness measurement of films and coatings。主辦單位是 Institute of Materials (East Asia), Nanyang Technological

University, 北京航空航天大學、中國科學院固體物理研究所。本會共有 524 篇論文發表，規模還算大，議程排得很緊湊，除了 Plenary lectures 之外，分數組平行進行。我大部分的時間都去聽 Fuel cell science and technology: bridging processing and performance。內容非常精彩，收穫很多。也讓我得到一些心得，構思出未來要走的路。面對世界強敵，我們人單勢薄，設備不如人，最好不要去搶熱門的題目做。當下決定不再努力於電解質的製備或是離子導電度的研究。我們應該比較專注於學術探討。近幾年，我們做了一些具有 pyrochlore 結構的材料，它的結構與 fluorite 相似，不同溫度下會有相轉變，我們若朝此方向努力，可以不和別人硬碰硬，可以開展出一條獨特的路，也可以更加認識這些離子導電材料，算是此行最大的收穫。

9 月 15 日下午是壁報論文發表時間，我的論文以此方式發表。場地相當擁擠，大會提供的張貼文具很少，不是很理想。不知是否因為中國辦會議都「外包」給專業公司承接。他們不太會針對個別會議的需求提供所需的服務。講起來有些諷刺，「專家」來做反而做不好，不夠貼心。我的壁報吸引了一些對氧化物離子導電有興趣的人前來討論。此會中有許多做氧化物燃料電池的人參與，彼此切磋，收穫很多。

現在開會不提供厚厚一本議程，改成薄薄一張光碟，要統計與會人員來自何處，變成比較不便，所以，不知有多少國家的科學家參與此會。不過，新加坡好像來了不少人。新加坡的大學教授薪資相當高，又講英語，很容易吸引世界高手去任教，使得他們學校可在亞洲佔有領先地位。

二、攜回資料名稱及內容

光碟片一張。