Effect of Cu-Excess on the Electrical Properties of $Cu_x AlO_2(1 \le x \le 1.06)^*$

Deng Zanhong^{1,†}, Fang Xiaodong¹, Tao Ruhua¹, Dong Weiwei¹, Li Da¹, and Zhu Xuebin²

(1 Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China)

(2 Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China)

Abstract: Cu-excess Cu_x AlO₂ ceramics with delafossite phases were synthesized using sol-gel. In the composition range of $1 \le x \le 1.04$, there are no detectable non-delafossite phases. Weak diffraction peaks of CuO are observed when $x \ge 1.04$. The room temperature conductivity of the Cu_{1.04} AlO₂ sample is improved by nearly an order of magnitude over that of the CuAlO₂ sample. The major defect mechanism responsible for the conductivity enhancement is proposed to be substitution defects of CuAl (Cu²⁺ ions substitute Al³⁺ ions). The composition formula unit for Cu-excess Cu_x AlO₂ may be expressed as Cu(Al_{1-y}Cu_y)O₂.

Key words: sol-gel processes; p-type transparent conducting oxide; CuAlO₂ PACC: 8270G; 6780M; 7360P CLC number: O472⁺. 4 Document code: A Article ID: 0253-4177(2008)06-1052-05

1 Introduction

Delafossite oxides ABO_2 (A is Cu and Ag, B is trivalent cation, such as Al, Cr, In, Ga, Sc, La) have gained intense interest in optoelectronic fields since CuAlO₂ was found to be a p-type transparent conducting oxide (p-TCOs)^[1]. As the key components of alloxide transparent devices, the p-TCOs have potential applications in "invisible circuits"^[2]. However, the conductivities of these p-TCOs are much lower than those of n-TCOs, such as tin-doped indium oxide (ITO) and ZnO^[3,4]. To enhance p-type conductivities, acceptor-doping on the B-site as well as nonstoichiometric (excess oxygen and/or excess metal cations) in these delafossite oxides are of interest for study^[5~7].

The delafossite structure can be described as sheets of edge-shared BO₆ octahedra alternating stacked with close-packed A-ions layers. Delafossites ABO₂ can form either rhombohedral 3R (R $\overline{3}$ m) or hexagonal 2H (P6₃/mmc) structures, depending on the stacking of the layers^[8]. Previous studies suggest that the delafossites with small B-cation radii (including CuAlO₂) are composed primarily of the 3R structure. However, the CuAlO₂ powders synthesized by Ingram *et al*.^[9] showed a 3R major phase with a small amount of 2H structure.

CuAlO₂ is a p-TCO with typical delafossite structure. Previous studies have shown that it has a nonstoichiometric nature of Cu-deficient that is responsible for its p-type conductivity. However, the defect mechanism is still not completely understood. Previous studies have shown that CuAlO₂ prepared by solid state reaction does not allow significant cation offstoichiometry. On the other hand, low-temperature hydrothermal synthesized nominal CuAlO₂ powders show an average atomic ratio of Cu/Al of 0.86 and a defect complex of Al on a Cu-site stabilized by two bound oxygen interstitials, $(Al_{Cu} 2O_i)$ is proposed, which serves as an acceptor dopant to set the hole concentration^[9]. However, there are no reports of the effect of Cu-excess on the transport properties of pure bulk CuAlO₂ ceramics as far as we know. In this paper, a series of nominal Cu-excess copper aluminum oxides were synthesized by sol-gel, which has been reported to useful for preparing nonstoichiometric oxide ceramics^[10]</sup> and films^{<math>[11,12]}</sup>. The dependence of struc-</sup> tural and electrical properties on Cu/Al atomic ratio is also investigated. Previous researchers have shown that a considerable amount of O-excess can exist in some delafossites, e. g., $CuScO_{2+\delta}$ ^[13] and Cu- $LaO_{2+\delta}$ ^[14]. The oxygen content of the samples in this work is not quantified. For convenience, the compositions will be identified simply by the formula unit $Cu_x AlO_2$.

2 Experiment

Polycrystalline $Cu_x AlO_2$ ceramic pellets were synthesized by sol-gel, and the reaction mechanism is

^{*} Project supported by the National Natural Science Foundation of China (No. 50672097), the Director's Fund of Hefei Institutes of Physical Science, the Hundred Talents Program, and the Innovation Fund of Department of Applied Laser Techniques, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences

[†] Corresponding author. Email: address: zhdeng@aiofm.ac.cn Received 9 November 2007, revised manuscript received 8 January 2008



Fig. 1 XRD patterns of the $Cu_x AlO_2$ ceramic pellets The nominal molar ratio of Cu/Al is shown in the bottom left corner of each pattern.

discussed in detail in Ref. [10]. A batch of $Cu_x AlO_2$ (x = 1, 1.02, 1.04, 1.06) precursor solutions with desired compositions of Cu-acetate, $Cu(CH_3COO)_2 \cdot$ H_2O (Alfa Aesar, 99.9%) and Al-sec-butoxide, $Al[OCH(CH_3)CH_2CH_3]_3$ (Alfa Aesar, 97%) were dried respectively at 375 and 573K for several hours to expel the organics. The dried powders were ground and annealed at 1375K for 8h under air atmosphere, and then the annealed powders were reground, pressed into pellets, and annealed at 1373K for 3h. All the pellets were pressed under the same pressure and annealed in a batch in order to exclude the influence of experimental factors on the electrical properties.

A Philips X' pert PRO X-ray diffractometer (XRD) with Cu-K α source and an FEI designed Sirion 200 field-emission scanning electron microscope (FE-SEM) were used to check crystallization and microstructure. The electron dispersion spectrum (EDS) was used to determine the chemical composition of the prepared samples. The average crystal size of the samples was estimated from the XRD results using the Scherrer formula. The temperature dependence of the conductivity was measured by the standard four-probe method by means of the cryogenic refrigeration equipment.

3 Results and discussion

XRD analysis was performed on $Cu_x AlO_2 (x = 1, 1.02, 1.04, 1.06)$ ceramic pellets (Fig. 1). The full width at half maximum (FWHM) of CuAlO₂ (012) peaks are 0.102°, 0.122°, 0.102°, 0.102° with x = 1, 1.02, 1.04, 1.06, respectively, and the crystallite sizes estimated from the Scherrer formula are about 93 nm. For all the samples, the 3R delafossite phase is the dominant phase, and a small amount of 2H delafossite phase is also detected. In the composition range of x < 1.04, there are no detectable non-delafossite phases. With a further increase of x, a second-



Fig. 2 a lattice parameter of the Cu_x AlO₂ ceramic pellets



Fig. 3 c lattice parameter of the Cu_x AlO₂ ceramic pellets

ary phase CuO with weak diffraction peaks is observed.

The delafossite unit cell dimensions were calculated with the least mean squares determination and the results are shown in the Figs. 2 and 3. The a and clattice parameters have similar tendencies and the sample with x = 1.04 has minimum a and c lattice parameters. EDS analysis was carried out using the same measurement parameters and the results are shown in Table 1. All the pellets were polished to avoid the possibility that during the annealing process, copper oxide diffused to the surface of the pellets and helped account for the excess copper. Because EDS only detects the atoms at the surface and does not provide the actual stoichiometry of the bulk, the high porosities of all the samples whose calculated porosities are between $37\% \sim 39\%$ may still result in some deviation of the results from the actual stoichiometry of the samples. So the contents of Cu, Al, and O may not to be quantified, but a comparison of the Cu/Al ratio of each sample can give some information. With an

Table 1 EDS results, conductivities and activation energies of the $Cu_x AlO_2$ ceramic pellets

	EDS results		Conductivity	
х	Cu/Al atomic	O/(Cu + Al)	- Conductivity	$E_{\rm a}/{\rm eV}$
	ratio	atomic ratio	/(0/ 011)	
1.00	1.148	1.1523	5.47×10^{-5}	0.20
1.02	1.168	1.1886	6.37×10^{-5}	0.20
1.04	1.178	1.0665	4.55×10^{-4}	0.22
1.06	1.191	1.1375	1.35×10^{-4}	0.24



Fig. 4 SEM images of the $Cu_x AlO_2$ ceramic pellets, where x is 1.00 (a), 1.02 (b), 1.04 (c), and 1.06 (d)



Fig. 5 Temperature dependence of conductivity for $Cu_x AlO_2$ samples The nominal molar ratio of Cu/Al is shown in the top right corner of the pattern.

increase of x, the measured Cu/Al ratio also increases, suggesting that some of the Cu was doped into the lattice. As oxygen interstitials O_i was reported in the triangles formed by Cu ions in the Cu sheet and have the lowest formation energy among the point defects of CuAlO₂^[15], O-excess is observed in all the samples, as shown in Table 1. Figure 2, Figure 3, and Table 1 show that *a* and *c* lattice parameters increase with the increase of oxygen content in the samples. Because the *a* and *c* lattice parameters are elongated by both O_i and Cu_{Al}, the large amount of O_i in all these samples may have a more dominant effect than Cu_{Al}.

The SEM images of the pellets are shown in Fig. 4. There is no obvious dependence of the particle size on the value of x. A large amount of pores can be seen in all the samples, which is consistent with the calculated porosities.

The temperature dependences of conductivities are shown in Fig. 5. The high porosities and small crystalline sizes (~93nm) of all the samples are responsible for the lower electrical conductivities than the CuAlO₂ sample prepared in Ref. [16], which has a porosity of 25. 1%. In the measured temperature ranges, all the samples show thermal activated conductivities. The conductivities shown in Table 1 increase as x increases when $x \le 1.04$, but further increasing x reduces the conductivity. Moreover, the room temperature conductivity of the sample with x = 1.04 (4. 55 $\times 10^{-4}$ S/cm) is enhanced about an order of magnitude more than that of the sample with x = 1 (5. 47× 10^{-5} S/cm). The activation energy (E_a) of each sample is obtained using the Arrhenius equation:

$$\ln\sigma = \ln\sigma_0 + \frac{-E_a}{k_B T}$$
(1)

and the results are shown in Table 1. The activation energies increase monotonously from 0. 20 to 0. 24eV as x increases, suggesting that there are transitions in the major defect mechanism.

Previous reports have suggested that in unintentional doped p-type $CuAlO_2$ there exist variations of acceptor defects, and have proposed the Cu vacancy "V_{Cu}", O_i , and defect complex of $(Al_{Cu}"2O_i")^{[15,17]}$. Since the results of the EDS analysis in our experiment suggest a Cu excess, the most preferable explanation is the substitutional acceptor defect of Cu_{Al}. The composition formula unit of $Cu_x AlO_2$ may be expressed as $Cu(Al_{1-y}Cu_y)O_2$. Since the radius of Cu^{2+} ions (about 0.072nm) is much smaller than that of Cu^{1+} ions (about 0.096nm), the substitution of Cu^{2+} ions on the Al^{3+} ion (about 0.051nm) sites is more favorable considering less structural disorders are introduced. Large amount of acceptor defect O_i plays an important role in the p-type conductivities in all the samples, but may not responsible for the conductivity enhancement in this experiment since O_i is reported to induce relatively deep levels in the band $gap^{[15]}$. In the range $1 \le x \le 1.04$, the hole carriers generated by the acceptor defect of Cu_{Al}^{2+} may have a dominant effect and are responsible for the conductivity enhancement. As the Cu/Al atomic ratio increases further, the secondary phase of CuO becomes un-neglectable. CuO is a metal deficient p-type semiconductor with copper vacancies generated at sinter temperatures lower than 1000°C. At higher sinter temperatures, the material is, with a good approximation, stoichiometric and has room temperature conductivity lower than 1×10^{-5} S/ cm^[18,19]. In our experiment, the sinter temperature of 1100°C is not favorable for the formation of copper vacancies in CuO, so the conductivity of CuO may be lower than that of CuAlO₂. This may be one reason why the conductivity decreases at x > 1.04. On the other hand, in n-type semiconductor materials, electrical properties are also sensitive to the structural defects such as structural disorders and stacking faults^[20,21]. In this experiment, as x increases, the carrier diffractions effects of structural disorders introduced by Cu_{Al}^{2+} defects and the secondary phase of CuO become un-neglectable and also contribute to the conductivity decrease at x > 1.04.

4 Conclusion

 $Cu_x AlO_2(x = 1, 1.02, 1.04, 1.06)$ ceramics were synthesized by sol-gel. In the composition range of x < 1.04, there are no detectable non-delafossite phases. Weak diffraction peaks of CuO are observed when $x \ge 1.04$. The conductivity of the sample with x = 1 is 5.47×10^{-5} S/cm at 300K. With an increase of x, the conductivity is improved and reaches a maximum of 4.55×10^{-4} S/cm when x = 1.04. This is nearly an order of magnitude larger than that of x = 1. The substitutional acceptor defect of CuAl²⁺ is believed to be the major defect mechanism responsible for the conductivity enhancement. These results suggest that the primary defect mechanism responsible for the conductivity in $CuAlO_2$ can be manipulated by varying the Cu/Al ratio in sol-gel synthesized ceramics.

References

- Kawazoe H, Yasukawa M, Hyodo H, et al. P-type electrical conduction in transparent thin films of CuAlO₂. Nature, 1997, 389 (6654):939
- [2] Thomas G. Materials science invisible circuits. Nature, 1997, 389 (6654):907
- [3] Chen Meng, Bai Xuedong, Huang Rongfang, et al. Structure and conductive mechanism of ITO and ZAO films. Chinese Journal of Semiconductors, 2000, 21(4):395 (in Chinese) [陈猛, 白雪冬,黄荣芳,等. In₂O₃: Sn 和 ZnO: Al 透明导电薄膜的结构及其导电机制.半导体学报, 2000, 21(4):395]
- [4] Yu Xuhu, Ma Jin, Ji Feng, et al. Properties of transparent conducting ZnO: Ga films prepared by RF magnetron sputtering. Chinese Journal of Semiconductors, 2005, 26(2): 314 (in Chinese) [余旭 浒, 马瑾, 计峰,等. 射频磁控溅射制备 ZnO: Ga 透明导电膜及特性. 半导体学报, 2005, 26(2): 314]
- $\begin{bmatrix} 5 \end{bmatrix}$ Banerjee A N, Ghosh C K, Chattopadhyay K K. Effect of excess oxygen on the electrical properties of transparent p-type conducting CuAlO_{2+x} thin films. Sol Energ Mat Sol C, 2005, 89(1):75
- [6] Kim H S, Lee B S, Ji S H, et al. Transport and magnetic properties of delafossite CuAl_{1-x} Mn_xO₂ ceramics. Phys Status Solidi B, 2004,241(7):1545
- [7] Park K, Ko K Y, Seo W S. Effect of partial substitution of Ca for Al on the microstructure and high-temperature thermoelectric properties of CuAlO₂. Mater Sci Eng B.2006,129(1~3):1
- [8] Jayalakshmi V, Murugan R, Palanivel B. Electronic and structural properties of CuMO₂ (M = Al, Ga, In). J Alloy Comp, 2005, 388 (1):19
- [9] Ingram B J, Mason T O, Asahi R, et al. Electronic structure and small polaron hole transport of copper aluminate. Phys Rev B, 2001,64(15):155114
- [10] Deng Z H, Zhu X B, Tao R H, et al. Synthesis of CuAlO₂ ceramics using sol-gel. Mater Lett, 2007, 61(3);686
- [11] Zhu X B, Dai J M, Li X H, et al. Chemical solution deposition preparation of double perovskite Sr₂FeMoO₆ film on LaAlO₃ (001) substrate. Mater Lett, 2005, 59(18):2366
- [12] Zhu X B, Yang J, Zhao B C, et al. Fabrication of $La_{0.8} Na_{0.2}$ -Mn_{1-x}Cu_xO₃ (x = 0, 0.05) thin films on YSZ substrates via chemical solution deposition.J Phys D,2004,37(17):2347
- [13] Kykyneshi R, Nielsen B C, Tate J, et al. Structural and transport properties of $CuSc_{1-x}Mg_xO_{2+y}$ delafossites. J Appl Phys, 2004, 96 (11):6188
- [14] Garlea O, Karie C, Bougerol C, et al. Structure of LaCuO_{2.66}; an oxidized delafossite compound containing hole-doped kagome planes of Cu²⁺ cations. Solid State Sci,2003,5(8);1095
- [15] Hamada I, Yoshida H K. Energetics of native defects in CuAlO₂. Physica B,2006,376/377:808
- Park K, Ko K Y, Seo W S. Thermoelectric properties of CuAlO₂.
 J Eur Ceram Soc, 2005, 25(12):2219
- [17] Ingram B J, Gonzalez G B, Mason T O, et al. Transport and defect mechanisms in cuprous delafossites. 1. comparison of hydrothermal and standard solid-state synthesis in CuAlO₂. Chem Mater, 2004,16:5616
- [18] Jeong Y K, Choi G M. Nonstoichiometry and electrical conduction of CuO.J Phys Chem Solids, 1996, 57(1):81
- [19] Lanke U D, Vedawyas M. Ion beam processing of oriented CuO

films deposited on (100) YSZ by laser ablation. Nucl Instr Meth in Phys Res B,1999,155(1/2),97

hanced room-temperature ferromagnetism in Co-doped ZnO. J

[20] Song C, Pan S N, Liu X J, et al. Evidence of structural defect en-

Phys:Condens Matter, 2007, 19(17): 176229

 Song C, Liu X J, Geng K W, et al. Transition from diluted magnetic insulator to semiconductor in Co-doped ZnO transparent oxide. J Appl Phys, 2007, 101(10): 103903

铜过量对 $Cu_x AlO_2(1 \le x \le 1.06)$ 电学性能的影响^{*}

邓赞红^{1,†} 方晓东¹ 陶汝华¹ 董伟伟¹ 李 达¹ 朱雪斌²

(1中国科学院安徽光学精密机械研究所,合肥 230031)(2中国科学院固体物理研究所,合肥 230031)

摘要:采用溶胶-凝胶法制备了铜铁矿结构 Cu_xAlO₂ 陶瓷体材.当1≤x<1.04 时,样品为纯铜铁矿相,当 x≥1.04 时,样品中出现了 微弱的 CuO 相.样品 Cu_{1.04}AlO₂ 的室温电导率比名义组分 CuAlO₂ 大了近一个数量级.研究表明,替位式缺陷 Cu_{Al}(Cu²⁺离子取代 Al³⁺离子)是导致电导增加的主要受主缺陷机制,Cu 过量 Cu_xAlO₂ 的分子式可更准确地表示为 Cu(Al_{1-y}Cu_y)O₂.

关键词:溶胶-凝胶法;p型透明导电氧化物;CuAlO2
PACC: 8270G;6780M;7360P
中图分类号:O472⁺.4 文献标识码:A 文章编号:0253-4177(2008)06-1052-05

^{*}国家自然科学基金(批准号:50672097),中科院合肥物质科学研究院院长基金,中科院百人计划,安徽光学精密机械研究所激光应用技术中心创新人 才基金资助项目

^{*} 通信作者.Email:address:zhdeng@aiofm.ac.cn 2007-11-09 收到,2008-01-08 定稿