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A High-Yield Hydrothermal Preparation of $CuAlO_2$

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Delafossite-like (ABO_2) compounds are known to have interesting luminescence properties[1,2] and applications in catalysis,[3−6] and they have received renewed interest with the discovery that $CuAlO_2$ thin films exhibit both p-type conductivity (1 S/cm) and transparency (∼70% over the visible spectrum).[7,8] The delafossite structure type is constructed from alternate layers of two-coordinate A-site cations and edge-shared BO_6 octahedra. This structure type can accommodate several monovalent A cations (Pd^I, Pt^I, Cu^I, and Ag^I) and a variety of trivalent B-site cations ($0.53\ \text{Å} < r(B^{3+}_{VI}) < 1.09\ \text{Å}$).[9] Most delafossite-like compounds are synthesized by direct or cation-exchange reactions in the solid state.[10−15] Oxides with noble metals are difficult to prepare by high-temperature solid state techniques because of their tendency to decompose before reaction occurs. Early hydrothermal work by W. J. Croft *et al.* employed thin-walled platinum tubes at 400 °C under 2700 atm to synthesize $AgFeO_2$ from Ag_2O and Fe_2O_3.[16] Phase-pure $AgFeO_2$ could only be isolated from unreacted Ag_2O through treatment of the two-phase product with dilute nitric acid. Later, R. D. Shannon *et al.*[17−19] reported the hydrothermal synthesis of $CuMO_2$ (M = Co, Fe, Al, Ga, In, and Rh) and $AgMO_2$ (M = Co, Cr, Fe, Ga, In, and Tl), at higher temperatures (500−700 °C) and higher pressure (3000 atm). With a few exceptions ($CuAlO_2$, $CuGaO_2$, and $CuRhO_2$) the products were isolated as single crystals. Polycrystalline samples of $CuAlO_2$, $CuGaO_2$, and $CuRhO_2$ could not be isolated phase-pure.

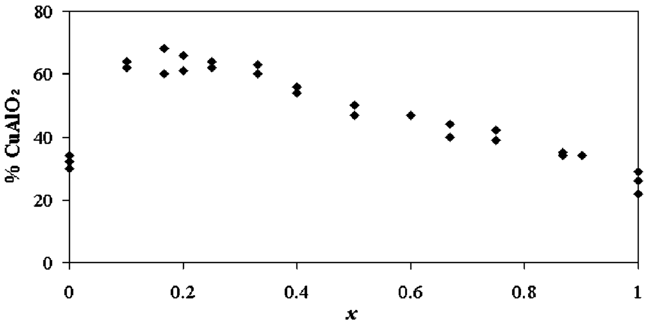

Figure 1. Phase percentages, as obtained from a peak intensity comparison of each Rietveld refined mixture of Cu_2O, CuO, and $CuAlO_2$ vs *x* in Scheme 1.

Scheme 1

$$x\,CuO + \frac{1-x}{2}\,Cu_2O + \frac{x}{3}\,Al + \frac{3-x}{6}\,Al_2O_3 \xrightarrow[H_2O]{NaOH} CuAlO_2$$

Here we describe a general hydrothermal synthesis method whereby polycrystalline delafossite materials can be synthesized under more desirable and practical conditions. The Teflon (fluoro(ethylene-propylene)) pouch technique[20] was employed to synthesize $CuAlO_2$ at low temperature (<215 °C) and low pressure (<10 atm).[21] Molar ratios were varied based on *x* in accordance with Scheme 1. For $x = 0$, the reaction is simply a dissolution and subsequent reaction of the Cu^I and Al^{III} species, as attempted by Shannon *et al.*[20] For other *x* values, a redox reaction occurs involving the Cu^{II} and Al^0 redox couple. The coefficients in this reaction represent the reduction of Cu^{II} to Cu^I and the oxidation of Al^0 to Al^{III}. 3R-$CuAlO_2$, in mixture with Cu_2O and CuO, was observed in yields of up to 70%, by X-ray diffraction.[22] (Figure 1) The presence of CuO is first observed for $x = 0.4$ and increases along with *x*. While present for all *x*, Cu_2O decreases as *x* increases from 0 to 1. The balance of the aluminum species was found

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(21) $CuAlO_2$ was synthesized by placing 0.2 g of NaOH(s) along with stoichiometric amounts of CuO, Cu_2O, Al, and Al_2O_3 in an FEP (fluoro(ethylene-propylene)) Teflon pouch. The pouch was sealed and placed in a 125-mL Teflon-lined autoclave (Parr) filled with 80 mL of deionized water. The total contents of each pouch were held constant to 0.8 g. The autoclave was sealed and first heated to 150 °C for 5 h to allow H_2O to enter the permeable membrane of the pouch and dissolve the NaOH(s). This was followed by a 210 °C step for 48 h, with subsequent cooling to room temperature at 6 °C/h. Gray-black $CuAlO_2$ crystallites, ranging from 5 to 10 μm, were recovered by filtration.

(22) To confirm phase formation and purity, powder X-ray diffraction (XRD) data for each sample were collected every 0.05° for $10° < 2\theta < 70°$ on a Rigaku diffractometer with Ni-filtered Cu Kα radiation. For phase-pure samples, data were collected every 0.02° for $10° < 2\theta < 110°$. Rietveld refinements were performed using the FULLPROF software program. (Rodriguez-Carvajal, J. *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr*; Toulouse, France, 1990; p 127).

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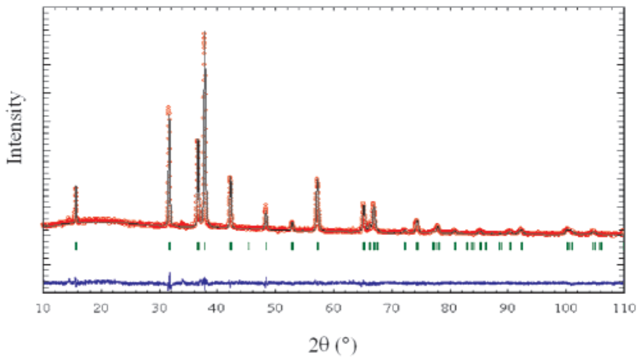

Figure 2. Observed (∘), calculated (line), and difference (bottom line) X-ray diffraction profiles for 3R-$CuAlO_2$. Calculated positions, those reflections that are marked with vertical bars, and intensities match those of JCPDS #77-2493; refined structural parameters ($a = 2.8617(2)$ Å, $c = 16.9407(8)$ Å, $z(O) = 0.1089(2)$) match single-crystal data.[10]

within the aqueous filtrate as determined by inductively coupled plasma (ICP) emission spectroscopy.

The limiting factor in the formation of $CuAlO_2$ is the reaction of the Cu^I species with the soluble aluminum. Cu^I species are unstable in basic media at standard pressure and temperatures up to 300 °C.[23,24] Although achieved in more extreme regions of temperature and pressure, the results of Shannon et al.[20] clearly illustrate that an aqueous Cu^I species can be evidenced at high pH. However, the exact process by which $CuAlO_2$ forms is not completely understood at this time. The heterogeneity of the system and the evolution of phases with time and temperature are currently under study. The synthetic scheme is a complex combination of solubility factors and redox reactions. In addition to the Cu^{II}/Cu^I and Al/Al^{III} couples, hydrogen gas is produced upon the dissolution and oxidation of Al in basic media. Owing to the permeability of the Teflon, some of the hydrogen gas crosses the pouch membrane and, consequently, is not available to reduce all of the Cu^{II} species. Therefore, some CuO would be expected in the final reaction mixture in cases where there is a high initial amount of CuO ($x > 0.4$). The presence of Cu_2O can be attributed to the inherent difficulty in producing a soluble Cu^I species.

To circumvent both the loss of reducing equivalents for copper and the solubility limitations that are encountered, reactions with copper deficiencies were attempted. Phase-pure 3R-$CuAlO_2$ (Figure 2) was obtained when the initial amount of both copper starting materials was decreased by an amount equal to that of the unreacted copper phase in the reaction product mixture.[25] For example, in the region, based on Scheme 1, where optimal results are achieved ($0.10 \leq x \leq 0.33$), 60−70% of the initial copper species reacted to produce $CuAlO_2$, while the other 30−40% remained as CuO and Cu_2O. Phase-pure $CuAlO_2$ was obtained by removing 30−40% on a proportional basis of both initial copper sources. ICP analysis of the filtrate revealed that the aluminum species remained, as before, in solution.

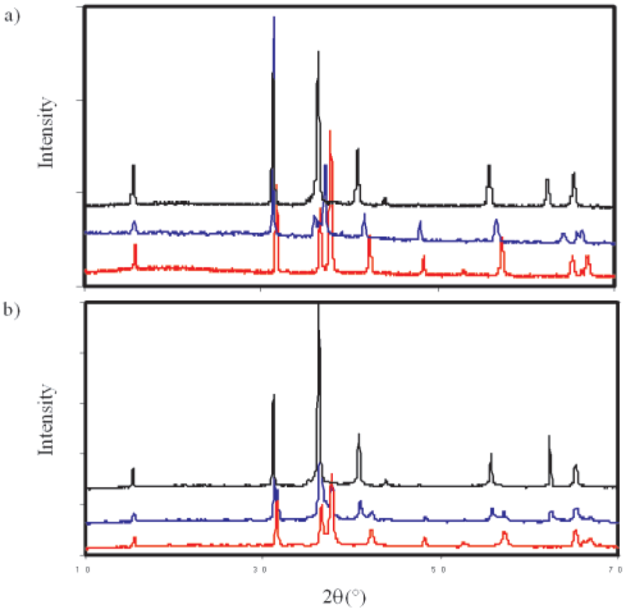

Figure 3. Powder X-ray diffraction patterns for (a) hydrothermal synthesis of $CuAl_{1-y}Ga_yO_2$ solid solution, where $y = 0$ (red), $y = 0.50$ (blue), and $y = 1.0$ (black); and (b) 1100 °C solid-state synthesis in air of $CuAlO_2$ (red), a two-phase product consisting of a 1:1 mixture of $CuAlO_2$ and $CuGaO_2$ (blue), and $CuGaO_2$ (black).

The universality of Scheme 1 can be demonstrated in that samples of $CuGaO_2$, $CuFeO_2$, and $CuLaO_2$ were also synthesized. Phase-pure polycrystalline samples of $CuGaO_2$ and the entire solid solution $CuAl_{1-y}Ga_yO_2$ ($0 \leq y \leq 1$) were also synthesized in a similar fashion as for $CuAlO_2$. This solid solution has, prior to this, not been reported for any other synthetic method (Figure 3).

Subtle composition and microstructure changes in the $CuAlO_2$ are under investigation. These structural details, as well as the electrical and optical properties for consideration as *p*-type transparent conductors, will appear in forthcoming contributions.

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