Contents lists available at ScienceDirect

# Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# Thermodynamic investigations on the growth of CuAlO$_2$ delafossite crystals

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## ARTICLE INFO

## ABSTRACT

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) measurements with copper oxide/aluminum oxide mixtures were performed in atmospheres with varying oxygen partial pressures and with crucibles made of different materials. Only sapphire and platinum crucibles proved to be stable under conditions that are useful for the growth of CuAlO$_2$ delafossite single crystals. Then the ternary phase diagram Al$_2$O$_3$–CuO–Cu and its isopleth section Cu$_2$O–Al$_2$O$_3$ were redetermined. Millimeter sized crystals could be obtained from copper oxide melts with 1–2 mol% addition of aluminum oxide that are stable in platinum crucibles held in oxidizing atmosphere containing 15–21% oxygen.

## 1. Introduction

The technological interest in developing transparent conducting oxide (TCO) or transparent semiconducting oxide (TSO) materials has seen a dramatic increase in recent years. Established TCO's, such as CdO, $\beta$-Ga$_2$O$_3$, In$_2$O$_3$, SnO$_2$ and ZnO [1,2] are n-type semiconductors in which electrons act as main charge carriers. However, in semiconductor electronics, p-n-junctions are of major importance where hole conduction is required in the p-type parts [3]. P-type TCO's could find their applications in functional p-n heterojunctions for transparent solar cells, ultraviolet-emitting diodes (LED) [4,5], touch screens, thermoelectric converters and other transparent optoelectronic devices [6]. Unfortunately the valence bands of most oxides are very flat. This impedes high hole mobility which would be important for commercial devices. Some copper(I) compounds, including the delafossite type CuAlO$_2$ were identified belonging to the small group of prospective p-type TCO's [7].

In the ternary delafossite oxide structure of CuAlO$_2$ {O − Cu − O} dumbbell layers are stacked with AlO$_6$ octahedra and hexagonal Cu layers perpendicular to the c axis [8]. CuAlO$_2$ delafossite has trigonal symmetry (space group $R\bar{3}m$), with $a = b = 2.857$ Å, $c = 16.939$ Å, an indirect bandgap of 2.22 eV and a direct gap of 3.4 eV [9].

So far, CuAlO$_2$ has mainly been prepared as nanocrystalline films by chemical-vapor deposition (CVD) [10], polycrystalline thin layers by pulsed laser deposition [4,11] or by radio frequency (RF) reactive magnetron sputtering [12] and powder synthesis by sol gel method [13]. There was also a general hydrothermal synthesis method described whereby polycrystalline delafossite materials can be synthesized [14]. Only scarce reports on the growth of small single crystal can

be found in the literature [8,9,15,16] and all of them rely on crystallization from melt solutions (self flux) based on excess copper oxides (Cu$_2$O, CuO) and Al$_2$O$_3$. This results in millimeter-sized (0001) platelets with several 100 μm thickness. It is surprising that on the one hand recent authors used often both Cu$_2$O and CuO as components of the flux, but on the other hand not much attention was given to the growth atmosphere. Via the reaction

$$Cu_2O + \frac{1}{2}O_2 \rightleftarrows 2\,CuO + \Delta H \tag{1}$$

both copper oxides are in equilibrium. The enthalpy of the exothermal oxidation (1) as calculated with the FactSage integrated thermodynamic databank system [17] changes almost linearly from −142 kJ/mol at 0 °C to −129 kJ/mol at 1200 °C. This means that the lower $\Delta H$ at higher temperature $T$ and low oxygen fugacity (expressed as partial pressure $p_{O_2}$) shift (1) to the educt side with copper(I) oxide (details were explained elsewhere [18])

Over the whole experimental temperature and oxygen partial pressure range ($RT \leq T \leq 1300$ °C) and $0.1 \leq p_{O_2} \leq 1$ bar) aluminum occurs exclusively as Al$^{3+}$, and hence Al$_2$O$_3$ can be considered as a component of the system. 2 CuAlO$_2$ = Cu$_2$O·Al$_2$O$_3$ is the 1:1 intermediate compound in the pseudobinary system Cu$_2$O–Al$_2$O$_3$. However, via (1) CuO will be present in the system, and can form with Al$_2$O$_3$ the spinel phase CuAl$_2$O$_4$ [19–22]. It will be shown later that under certain experimental conditions also metallic copper can be formed, and consequently the concentration triangle Al$_2$O$_3$–CuO–Cu in Fig. 6a) will be used in this paper to discuss growth conditions for CuAlO$_2$ delafossite crystals.

In a report on the separate systems CuO–Al$_2$O$_3$ and Cu$_2$O–Al$_2$O$_3$ it was found that the spinel CuAl$_2$O$_4$ is stable in air only up to 1000 °C

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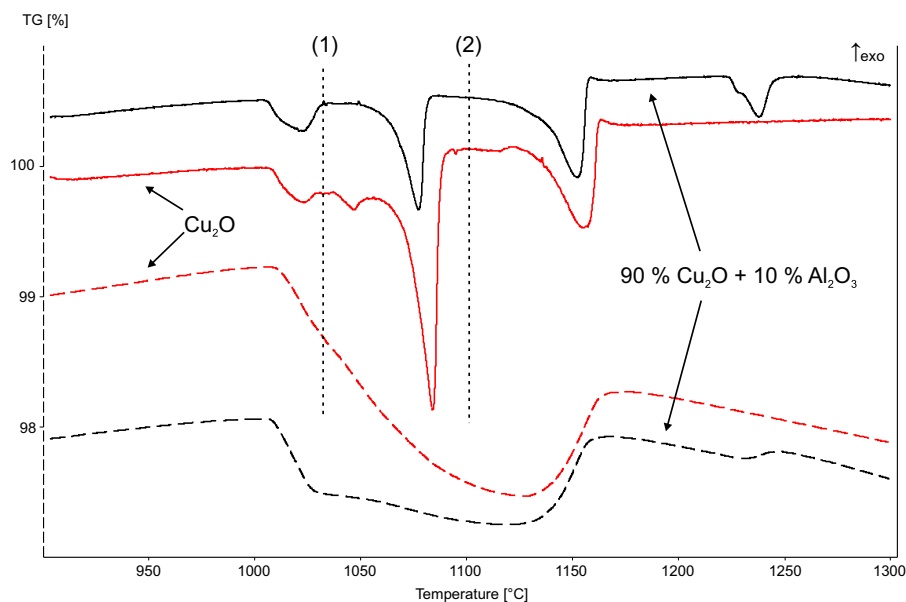
**Fig. 1.** DTA (solid) and TG curves (dashed) between 900 °C and 1300 °C (measured in air) for pure $Cu_2O$ and a 90/10 mixture with $Al_2O_3$. The DTA peaks between 1000 °C and 1150 °C are overlapped by redox processes (1) (mass change in TG curve).

and is then converted to $CuAlO_2$, which was stable to about 1260 °C [19]. Gadalla and White [20] reported the ternary $Al_2O_3$–$CuO$–$Cu_2O$ for oxygen fugacities $0.21 \leq p_{O_2}/\text{bar} \leq 1.0$. According to their data, single crystals of $CuAlO_2$ should crystallize from melts containing 10–20 mol% $Al_2O_3$ in $Cu_2O$, which is in slight contrast with the results that will be presented in this study. Nevertheless, their study proposes peritectic melting of $CuAlO_2$ at 1238 °C for $p_{O_2} = 0.21$ bar to $\alpha$-$Al_2O_3$ and a melt consisting mainly of $CuO$ and $Cu_2O$, which is in fairly good agreement with the results that will be presented here. For large $p_{O_2} \approx 0.4$ bar, the stability range for the $CuAl_2O_4$ spinel was found elsewhere [21] to be wider, compared to Gadalla and White [20], but this difference is not relevant for the growth of the copper(I) compound $CuAlO_2$.

It is the aim of this work to define experimental conditions (melt composition, atmosphere, temperature regime, crucible material) where $CuAlO_2$ single crystals can be grown from self-flux. Self-fluxes are expected to result in crystals with less impurities, compared to growth from fluxes containing foreign components, such as hydro-thermal solutions, or by sol-gel processes [23,14,24].

## 2. Experimental

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) measurements were carried out with a Netzsch STA 409CD. A DTA/TG sample carrier with Pt/Pt90Rh10 thermocouples was used. Gas flow was set by a mass flow controller do deliver atmospheres ranging from 100% $O_2$ to 2% $O_2$ in Ar, and air. Measurements were conducted for 2%, 10%, 15%, 21%, 25%, 50% and 100% oxygen, but for clarity only results for $p_{O_2} = 0.1$, 0.21, 0.50 and 1 bar have been displayed. Samples were prepared by mixing powders of $Al_2O_3$ (Alfa Aesar, 99.997% purity) and $Cu_2O$ (Fox Chemicals, 99.99% purity) to concentrations between pure $Cu_2O$ and 15 mol% $Al_2O_3$ in $Cu_2O$, and homogenization was obtained by melting these powders together during DTA. For all measurements a temperature program was selected, which resembles the conditions during a real crystal growth run. With this program, it was possible to test potential crucible materials for their steadiness and to obtain some first information about redox processes of copper oxides. The powder mixtures were heated in crucibles (without lids) with a rate of 5 K/min to 1200 or 1300 °C (3 h dwell time) then slowly cooled down with 3 K/min to 900 °C and 1.5 K/min to 100 °C. The dwell time of 3 h was

chosen to test the stability of the respective crucible material and the upper temperature limit was defined by the melting temperature of the samples. Based on literature data (e.g. [20]), it was estimated that the liquidus temperature of the mixture is between 1200 and 1300 °C. In order to ensure that the $CuAlO_2$ phase was formed, the temperature program was run twice.

The phase compositions of all samples were characterized by X-ray powder diffraction with a GE Inspection Technologies XRD 3003 TT (Bragg Brentano geometry and Cu K$\alpha$ radiation).

The $CuAlO_2$ composition of the crystals was proven by X-ray fluorescence spectroscopy.

## 3. Results and discussion

First measurements gave information on the oxidation and reduction behavior of copper(I)oxide. If $Cu_2O$ (pure or mixed with $Al_2O_3$) was heated in an atmosphere containing $O_2$, oxidation to $CuO$ occurred around 350 °C, which is in agreement with Gadalla and White [20]. DTA-peaks between 1000 °C and 1150 °C result from endothermal melt processes and also from endo- or exothermal redox processes between $Cu^+$ and $Cu^{2+}$ (1). An oxidation process is connected with a mass increase in the associated TG curve, together with an exothermal DTA effect. A reduction is connected with a mass decrease because of oxygen release, and is endothermal. This is demonstrated by the red curves in Fig. 1 which were obtained with pure $Cu_2O$. The first three endothermal peaks are connected with a mass loss that is monotonous but changes in rate: E.g. at point (1) where the DTA curve is less endothermal, also the TG curve is flatter. Obviously the reaction rate is smaller at this point, and consequently mass loss is reduced, in agreement with a smaller endothermal effect. The reduction process $CuO \rightarrow Cu_2O$ is completed after the large sharp peak, at point (2) where the sample is still solid. A small exothermal effect after this point and a mass gain of almost 1% starting there indicates that $Cu_2O$ begins re-oxidizing partially back to $CuO$. This is surprising because according to Fig. 3 under constant $p_{O_2}$ a higher $T$ should result in lower rather than in higher valence. Obviously, the energy gain resulting from liquid mixture formation, in analogy to (2), is the driving force for the re-oxidation. With increasing $CuO$ content the sample can melt, giving rise to the following broad peak. Visual inspection of samples that were heated up to 1200 °C proved this.

An identical measurement with a $Cu_2O/Al_2O_3$ mixture (black curves