

Crystal Structure of Cu_5SbO_6 – Synchrotron and Neutron Diffraction Studies

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One very interesting compound in the system Cu/Sb/O is the mixed-valence Cu_5SbO_6 which crystallizes in the high temperature modification as a modified Delafossite structure type. Single crystals of Cu_5SbO_6 has been synthesized by chemical vapour transport methods and characterised using single crystal X-ray diffraction and powder neutron and synchrotron diffraction.

1. Introduction

In the ternary copper-antimony-oxygen system four different compounds have been synthesised so far: CuSb_2O_6 , $\text{Cu}_9\text{Sb}_4\text{O}_{19}$, $\text{Cu}_4\text{SbO}_{4.5}$ and Cu_5SbO_6 , but only one crystal structure of CuSb_2O_6 has been resolved up to now [1-7]. CuSb_2O_6 has had its properties well studied, for its interesting structural and magnetic properties. At room temperature CuSb_2O_6 has a monoclinic distorted trirutile structure and a tetragonal trirutile structure at $T < 380$ K [8]. Because of the Jahn-Teller distortion of Cu^{2+} in an octahedral coordination sphere, the monoclinic structure is unusual compared to analogous antimonates such as ZnSb_2O_6 and FeSb_2O_6 which are tetragonal trirutile structures [4]. In this structure, antimony is +5 and copper is in the +2 oxidation state [7]. $\text{Cu}_9\text{Sb}_4\text{O}_{19}$ was synthesised by reacting CuO and CuSb_2O_6 under 10 kbar and 1000-1100 °C with a piston-in-cylinder apparatus [5], and 10 bar at 1100 °C and 10 kbar at 1000-1100 °C oxygen pressure. The high pressure was proposed to suppress the decomposition of Cu(I) to Cu(II) in the system [3]. The elemental composition of $\text{Cu}_9\text{Sb}_4\text{O}_{19}$ was confirmed with X-ray fluorescence, and in air it is stable to 945 °C after which it breaks down to CuSb_2O_6 and $\text{Cu}_4\text{SbO}_{4.5}$ [5]. The final known ternary copper antimonite is $\text{Cu}_4\text{SbO}_{4.5}$ / Cu_5SbO_6 . $\text{Cu}_4\text{SbO}_{4.5}$ was first reported in a series of papers describing its synthesis and powder X-ray characterisation [2, 4]. Kol'tsova and Chastukhin solved the phase diagram in the temperature range between 700°C and 1150°C and re-evaluated the composition of $\text{Cu}_4\text{SbO}_{4.5}$ to Cu_5SbO_6 while examining the Cu-Sb-O system in air [7].

The main perspective of this project is to describe the ternary phase Cu_5SbO_6 , obtain the crystal structures of Cu_5SbO_6 of all possible modifications. For the preparation a number of different methods will be applied, ranging from classical high-temperature sintering to chemical transport reactions for the preparation of single crystals. For the identification of the obtained compounds we used X-ray single crystal and powder diffraction, high resolution neutron and Synchrotron powder diffraction.

2. Experimental

Powder samples of Cu_5SbO_6 were prepared by mixing 10 CuO + Sb_2O_3 over the range 900 – 1120°C in 10 K steps, for 48 h with intermediate grinding and then air quenched. These samples were analysed by powder X-ray diffraction. Chemical vapour transport was used to synthesize single crystals of Cu_5SbO_6 . A mixture of 10 CuO + 1.7 Sb_2O_3 (excess of Sb_2O_3) were pre-heated in a sealed evacuated quartz tube, with PdCl_2 as transport agent. The mixture was placed in one end (source) and nothing in the other end (sink). The quartz tube was

placed in a two-zone furnace which heated the chemical side to 900°C and the sink side to 800°C.

Single crystal X-ray diffraction were collected on a Bruker SMART II diffractometer (MoK α , $\lambda = 0.71073 \text{ \AA}$). High resolution synchrotron X-ray diffraction pattern were collected on the powder diffraction beam-line at the Australian Synchrotron ($\lambda = 0.68950 \text{ \AA}$). Neutron diffraction patterns at room temperature and 4 K were measured using the high resolution powder diffraction diffractometer Echidna at ANSTO's OPAL facility as Lucas Heights.

3. Results

3.1. Crystal Structure of Cu₅SbO₆

Single crystal XRD on crystals of Cu₅SbO₆ formed by the chemical transport revealed the structure of the high temperature form of Cu₅SbO₆. The new structure type is a modified and distorted Delafossite structure, which contains a mixture of Cu⁺ and Cu²⁺ in the same compound. It contains layers of Cu²⁺O₆ and Sb⁵⁺O₆ octahedra with Cu¹⁺ between them, this is shown in Figure 1 below. The Cu₂SbO₆ - layers can be described as (Cu²⁺_{2/3}Sb⁵⁺_{1/3})O₂ in accordance to the pure Delafossite structure type (CuFeO₂), which contains FeO₂ layers. In Cu₅SbO₆ the magnetically active CuO₂ layer is diluted in an ordered fashion with non-magnetic Sb⁵⁺ forming Cu²⁺-Cu²⁺ pairs. This layer could also be observed in the Na containing compound Na₃Cu₂SbO₆ [8]. The Cu⁺ cations which are 'sandwiched' between them show the typical 2-fold dumbbell coordination sphere.

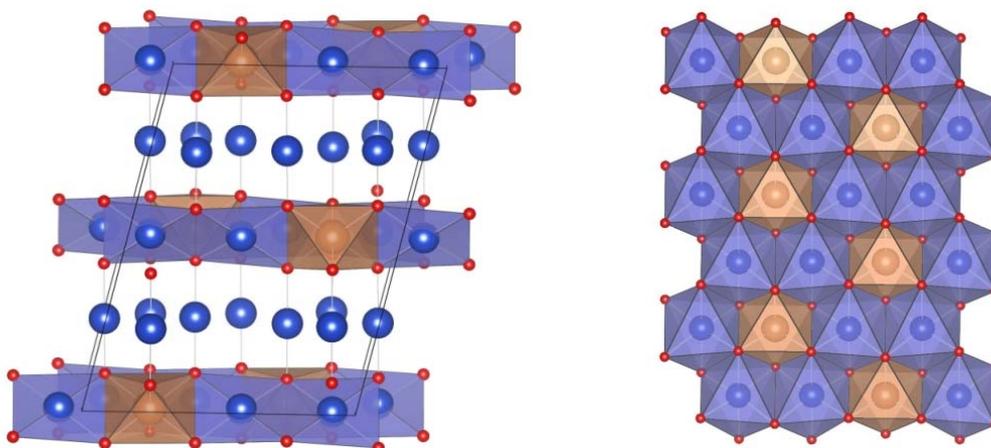


Fig 1. Left: Side view of the crystal structure of Cu₅SbO₆; Right: View of the Cu₂SbO₆ layer with likely Cu-O bonds including longer distances

The SbO₆ octahedra is regular with 1.958(9) to 2.034(7) Å bond distances, while the CuO₆ octahedra have four short bonds of 1.982(9) to 2.028(8) Å, and two longer bonds of 2.327(8) and 2.368 Å. A comparison of the crystal structure with just the four Cu-O bonds, and one including the longer ones are shown in Figure 2 below, which shows just the Cu₂SbO₆ layer. The crystallographic data are summarised in Table 1.

3.2 X-ray powder diffraction

X-ray powder diffraction for phase analysis of Cu₅SbO₆ was performed at various temperatures in air. This revealed the existence of at least two definite modifications of Cu₅SbO₆, one at temperatures below about 1000°C, and another at temperatures higher than about 1100°C, as well as an intermediate region between. It turned out, that the oxygen partial pressure used during the preparations seems to have an influence on the formation of a certain modification at a certain temperature. To examine the influence of the oxygen in the system a

mixture of CuO and Sb₂O₃ (10:1) and the previously prepared low temperature modification were sealed in an evacuated quartz tube and reheated at 950°C. Heating the CuO and Sb₂O₃ powders in a sealed evacuated quartz vessel at 950 °C produced a XRD pattern similar to the high temperature form. This suggests that the O₂ pressure generated by the reaction $10 \text{ CuO}_{(s)} + \text{Sb}_2\text{O}_{3(s)} \rightarrow 2 \text{ Cu}_5\text{SbO}_{6(s)} + \frac{1}{2} \text{ O}_{2(g)}$ prevented the formation of the low temperature version. The XRD of the low temperature Cu₅SbO₆ powder which was heated again at its formation temperature in a vacuum showed a change towards the high temperature phase. The process of the formation of the high-temperature modification in a closed system is not reversible at low temperatures in air.

Table 1. Fractional coordinates for Cu₅SbO₆; Space group *C2/c* (*No. 15*), *a* = 8.9372(11) Å, *β* = 5.5967(6) Å, *c* = 11.8667(14) Å and *β* = 103.697(9)°; R₁(obs) = 4.84 %, wR₂(all) = 13.77%

Atom	Wyckoff position	x	Y	z	U _{ani}
Sb	4c	1/4	¼	0	0.0076(4)
Cu(1)	8f	0.08325(9)	0.24851(11)	0.49810(7)	0.0098(4)
Cu(2)	8f	0.17134(10)	0.0973(2)	0.25700(7)	0.0146(4)
Cu(3)	4e	0	0.6271(3)	1/4	0.0150(4)
O(1)	8f	0.1176(7)	0.1224(9)	0.0967(5)	0.0122(11)
O(2)	8f	0.4452(7)	0.1218(8)	0.0911(5)	0.0113(11)
O(3)	8f	0.2243(7)	0.0732(8)	0.4189(5)	0.0098(10)

The high resolution measurements using the powder diffraction beam-line at the AS could clearly distinguish between the high temperature modification and the low temperature modification. As it turns out at no temperature between 900°C and 1120°C neither the low nor the high temperature modification exists in pure form. The content of the LT-modification decreases with increasing temperature but it was not completely converted even if the temperature is very close to the melting temperature at 1150°C. Rietveld refinements on these Synchrotron data and powder neutron diffraction data on both, LT-Cu₅SbO₆ and HT-Cu₅SbO₆, confirm an ordering (high temp. modification) / disordering (low temp. modification) effect of the Sb⁵⁺ and Cu²⁺ ions in the brucite-like layers between the Cu¹⁺ atoms. It also shows that Cu₄SbO_{4.5} can now be identified as the low-temperature modification of Cu₅SbO₆. Neutron powder diffraction data seem to verify the incorporation of additional oxygen in the LT-modification, whereas no additional oxygen can be found in the HT-modification. The refinement results are summarised in Table 2.

Table 2. Fractional coordinates for low-temperature Cu₅SbO₆ at 900°C; Space group *C2/c* (*No. 15*), *a* = 2.97701(6) Å, *b* = 5.5952(1) Å, *c* = 11.5195(2) Å and *β* = 90.151(2)°; R_F = 3.64 %, R_{BRAGG} = 5.70%, R_P = 7.07 %

Atom	Wyckoff position	x	y	z	B _{ani}	SOF
Sb	4a	0	1/2	0	0.12(7)	1/3
Cu(1)		0	1/2	0		2/3
Cu(2)	4e	0	0.8568(6)	1/4	0.74(8)	1
O(1)	8f	0.503(3)	0.3581(6)	0.0903(2)	0.83(7)	1
O(2)	4e	0	0.534(8)	0.25	0.83(7)	0.038(4)

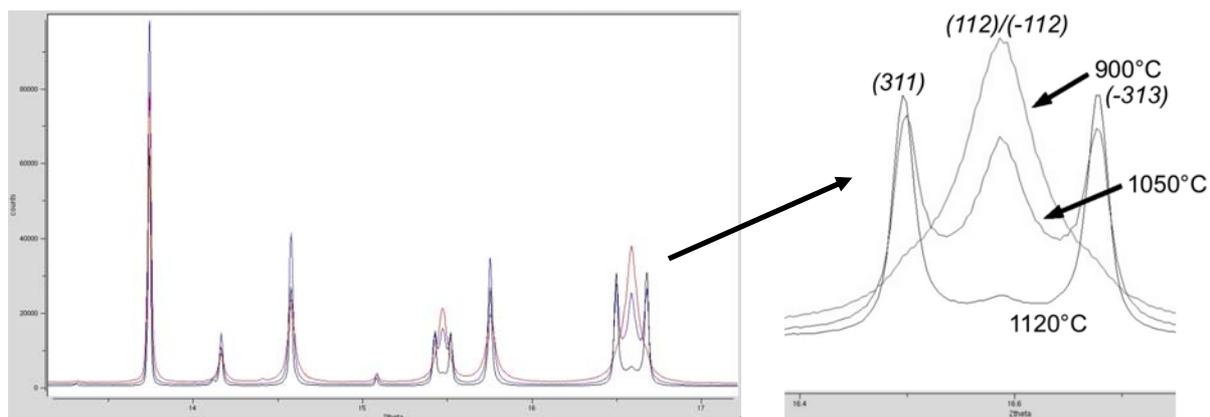


Fig 2. Left: Section of synchrotron high resolution powder patterns of 900°C, 1050°C and 1120°C samples; Right: (311)/(-313) reflexes (HT-Mod.) and (112)/(-112) reflexes (LT-Mod.) at about $2\theta = 16.6^\circ$.

4. Conclusions

Single crystals of the high temperature modification were prepared by chemical vapour transport of CuO and Sb₂O₃ oxides with PdCl₂ as transport agent and the crystals structure could be solved which can be described as a modified Delafossite structure. In this structure layers of ordered edge sharing Cu²⁺O₆ and Sb⁵⁺O₆ octahedra are formed. The Cu¹⁺ are incorporated between these planes. Powders of Cu₅SbO₆ at various temperatures were prepared and analyzed by x-ray, synchrotron and neutron powder diffraction. It can be found that two distinct modifications of Cu₅SbO₆ exist and both of which can be formed by the reaction of CuO and Sb₂O₃ in air. Both modifications are present in the whole temperature range between 900°C and 1150°C.

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