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SOLID-STATE REACTIONS IN THE SYSTEM Cu–Sb–O; FORMATION OF A NEW COPPER(I) ANTIMONY OXIDE

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ABSTRACT

The solid-state reactions in the system Cu–Sb–O were investigated by thermogravimetry and X-ray diffraction. Equimolar mixtures of CuO and Sb_2O_3 form Cu(II)Sb_2O_6 when slowly heated in air up to 1000°C. The first step in this reaction is the oxidation of Sb_2O_3 to Sb_2O_4 at 380–500°C, followed by further oxidation of Sb_2O_4 and the formation of $CuSb_2O_6$ at 500–1000°C. Thermal decomposition of $CuSb_2O_6$ in a flowing nitrogen atmosphere occurs in three stages; the first, with an activation energy of 356 kJ mole^{-1}, results in the formation of a new copper(I) antimony oxide, with a composition of $Cu_4SbO_{4.5}$, as determined by atomic absorption analysis and X-ray fluoresecence. Confirmation of predominantly monovalent copper and pentavalent antimony in the new compound was by ESR and ESCA, respectively. Two forms of $Cu_4SbO_{4.5}$ have been distinguished; one of these (form II) has a structure of lower symmetry, and decomposes when heated in air at 600°C to a mixture of CuO and another new copper antimony oxide, as yet uncharacterized. On further heating to 1100°C in air, $Cu_4SbO_{4.5}$ (form I) gradually reforms. Details of these reactions are summarized and X-ray powder data presented for $Cu_4SbO_{4.5}$.

INTRODUCTION

Considerable interest exists in interoxide compounds because of their potential uses in energy conversion and storage applications. A recent study of the formation and electrical properties of $Ag_2Sb_2O_6$ [1] has shown this defect pyrochlore to have interesting electrical conductance properties at higher temperatures. Since Cu^+ is in some ways similar to Ag^+, it was suspected that the Cu(I) analogue, if formed, might have useful photoelectrochemical properties, particularly in view of the semiconducting behaviour of Cu_2O itself.

Syntheses of various compounds of pentavalent antimony with monovalent oxides have been reported [2–4], but the only copper antimony oxide to have been prepared is the Cu(II) compound, $CuSb_2O_6$, which has a deformed

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trirutile structure and was synthesized by Byström et al. [5] by solid-state reaction between CuO and Sb_2O_3.

The initial aim of the present work was to synthesize the monovalent copper compound $Cu_2Sb_2O_6$ by reaction between copper(I) and antimony oxides. Although the compound could not be prepared in this way, another Cu(I) compound, $Cu_4SbO_{4.5}$, was prepared by thermal decomposition of $CuSb_2O_6$ in a flowing atmosphere of oxygen-free nitrogen. The new compound could also be prepared by reaction between $CuSb_2O_6$ and CuO. This paper reports on some aspects of the sold-state chemistry of the system Cu–Sb–O, including the formation of $CuSb_2O_6$ and its decomposition to $Cu_4SbO_{4.5}$.

EXPERIMENTAL

The starting materials were cupric oxide (99.4% purity, BDH Ltd.) sieved to < 300 mesh, and antimony trioxide (chemical reagent grade, Hopkin and Williams Ltd.). The antimony trioxide was found to be senarmonite (α-Sb_2O_3) by X-ray analysis. $CuSb_2O_6$ was prepared from an equimolecular mixture of the oxides, well blended in an agate mortar and heated in ~ 50 mg cm^{-2} aliquots in 20 mm × 16 mm alumina crucibles. The heating was carried out in air in a Mettler model 21 thermobalance at a rate of 6–10°C min^{-1} up to 1000°C, complete reaction being confirmed by X-ray diffraction. The $CuSb_2O_6$ was finely ground, $\sim$ 10 mg cm^{-2} charges were thinly spread on an alumina plate and isothermally decomposed in the thermobalance at 980–1020°C for 0–240 min under a flowing atmosphere of oxygen-free nitrogen (90 ml min^{-1}). When a degree of decomposition of about 72% was reached, the reaction was quickly stopped by purging the thermobalance with air. The X-ray diffraction pattern of the resulting brown material showed it to be a compound not listed in the JCPDS files. The composition of the new compound was determined by X-ray fluorescence and atomic absorption spectroscopy, for which a solution was prepared by $KHSO_4$ fusion. The presence of Cu(I) and the valence state of the antimony in the new compound was investigated by ESR and ESCA, respectively. An alternative synthesis of the new compound was attempted by heating a mixture of $CuSb_2O_6$ and CuO at 950–1150°C for 24 h in air, the presence of the new compound being confirmed by X-ray diffraction.

RESULTS AND DISCUSSION

Formation of $CuSb_2O_6$

Byström et al. [5] obtained $CuSb_2O_6$ by heating a mixture of CuO and Sb_2O_3 in air at 1000°C for 20 h [5]. Our attempts to repeat this synthesis failed to produce single-phase $CuSb_2O_6$, since X-ray analysis of the product showed small unidentified peaks in addition to those of the desired phase. Further, the weight gain during the reaction was less than theoretically predicted for complete reaction, and the product consisted of yellowish $CuSb_2O_6$ mixed with a brown coloured phase. Failure to prepare single-phase $CuSb_2O_6$ by rapid heating to 1000°C may be due to the volatilization of Sb_2O_3 before it has had the chance to oxidize to Sb_2O_4. For this reason, dynamic heating of the mixture to 1000°C at a rate of 6–10°C min^{-1} in the thermobalance was used to synthesize $CuSb_2O_6$. It was found that a thick layer of reactant in the TG crucible produced a similar effect to that of rapid heating, due to insufficient oxygen being available at the bottom of the sample; thin sample layers of ~ 50 mg cm^{-2} were therefore used.

Figure 1 shows the weight-gain curves obtained by heating the CuO/Sb_2O_3 mixture at a rate of 6–10°C min^{-1} to 1000°C in air. Under the two reaction conditions illustrated by curves A and B, the formation of $CuSb_2O_6$ apparently consists of three steps. The first step (380–500°C) represents the oxidation of Sb_2O_3 to Sb_2O_4, confirmed both by X-ray analysis of the sample after heating to 500°C and by the observed weight gain, which is equal to the theoretical value for this oxidation (4.3%). The second and third steps (500–1000°C) on curve A correspond to further oxidation of Sb(IV) to Sb(V), followed by the formation of $CuSb_2O_6$, since X-ray analysis of the sample heated to 640°C showed the formation of a small amount of $CuSb_2O_6$, which is fully formed by 1000°C. The weight gain at 1000°C was in agreement with the theoretical gain for the formation of $CuSb_2O_6$. The

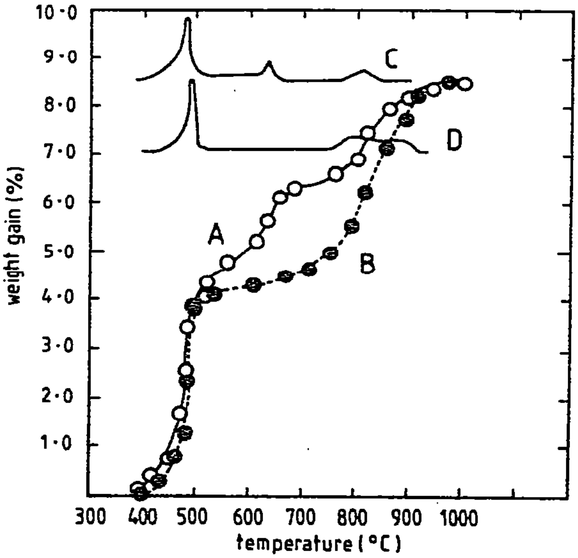


Fig. 1. TG and DTG curves for the formation of $CuSb_2O_6$ from equimolar CuO/Sb_2O_3 mixtures heated in air. (A) TG curve: 6°C min^{-1} and loosely packed sample. (B) TG curve: 10°C min^{-1} and tightly packed sample. (C) DTG curve of (A). (D) DTG curve of (B).

DTG curve (Fig. 1D) corresponding to the TG curve (Fig. 1B) indicates that under these conditions (tightly packed sample heated at 10°C min^{-1}), the second and third steps of the reaction overlap; in this case, oxidation to Sb(V) would be expected to be retarded by the diminished access of oxygen to the inner parts of the sample. However, these experiments show that under appropriate conditions such as illustrated by curve A of Fig. 1, stoichiometric $CuSb_2O_6$ can be prepared. These conditions were used to synthesize the starting material for the decomposition experiments described below.

Formation of a new copper antimony oxide by thermal decomposition of $CuSb_2O_6$

In the previous section it was noted that under some experimental conditions, loss of Sb_2O_3 by volatilization, or incomplete oxidation due to an insufficient oxygen supply resulted in the formation of a mixture of $CuSb_2O_6$ with a previously unreported brown-coloured phase which appeared worthy of further study. Attempts to prepare this compound by heating excess CuO with Sb_2O_3 at 950–1200°C in air or by heating an equimolar mixture of CuO with Sb_2O_3 in oxygen-free nitrogen were unsuccessful, $CuSb_2O_6$ being formed in every case. However, it was noted that in nitrogen, $CuSb_2O_6$ thermally decomposes to the brown compound; this decomposition reaction was therefore studied by thermogravimetry to determine the conditions under which the new brown compound can be produced in a pure state.

Figure 2 shows TG curves of the decomposition of $CuSb_2O_6$ at a heating rate of 1°C min^{-1} in flowing nitrogen (curve A) and in air (curve B). The weight-loss curve in nitrogen consists of three steps, designated I, II and III on curve A. The weight loss which begins at 950°C rapidly continues with increasing temperature up to about 70% loss at 1070°C (step I). Between 70–80% loss (1070–1120°C), the rate of decomposition slows down (step II), increasing again above 80% loss (step III). The reactions involved in these steps are discussed in detail below, in terms of the decomposition kinetics. By contrast, the weight loss in air begins 150°C higher than in nitrogen, apparently proceeding in two steps, with an inflexion at about 80% loss. The marked suppression of the decomposition in air suggests that oxygen is evolved in the course of the reaction.

Isothermal decomposition curves determined at 980–1020°C in nitrogen are shown in Figure 3. It is seen that the decomposition proceeds in two linear steps, the first step covering the range 0–70% loss and the second occurring at 70–80%; the inflexion between the two steps is less clear at higher temperatures. This isothermal decomposition behaviour appears similar to that observed under dynamic conditions (Fig. 2). A brown-coloured product was always produced when the yellowish $CuSb_2O_6$ was heated in oxygen-free nitrogen at 980°C to about 72% weight loss, determined by the

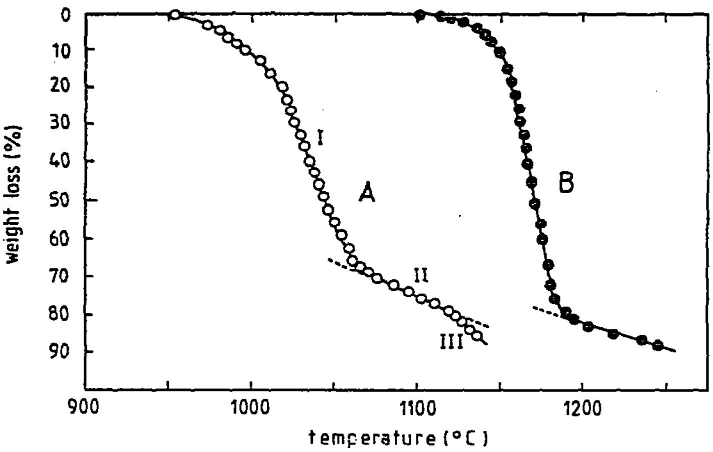


Fig. 2. TG curves for the decomposition of $CuSb_2O_6$. (A) In oxygen-free nitrogen (90 ml min^{-1}): (B) in air, Heating rate: 1°C min^{-1}.

inflexion point on the TG curve. This inflexion point varied slightly from 70 to 73% weight loss, depending on sample thickness and nitrogen flow rate (or oxygen content), but provided the heating was carried out at 980°C up to this inflexion point, the product always possessed a virtually identical X-ray pattern, which corresponded with the pattern of the unknown phase obtained by rapidly heating a CuO/Sb_2O_3 mixture in air at 1000°C. The X-ray powder data for this phase do not occur in the JCPDS files, and are shown in Table 1. X-Ray diffraction further shows that step II of the reaction in nitrogen corresponds to further decomposition of the new brown phase to a mixture of CuO and Cu_2O. Thus, step I represents the formation of the new brown compound by the decomposition of $CuSb_2O_6$, and step II represents its further decomposition to copper oxides, which should eventually decompose to copper metal (step III, Fig. 2).

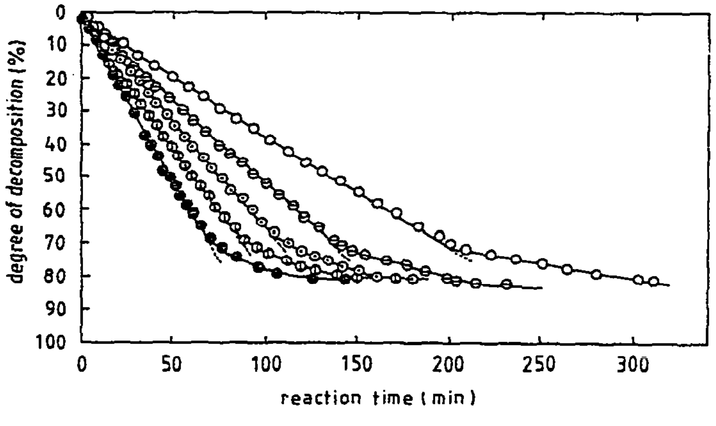


Fig. 3. Isothermal kinetic curves for the decomposition of $CuSb_2O_6$ in oxygen-free nitrogen. O, 980°C; ⊖, 990°C; ⊙, 1000°C; ⦶, 1010°C; ●, 1020°C. Flow rate of nitrogen: 90 ml min^{-1}.

TABLE 1

X-Ray powder pattern data for the new copper antimonate $Cu_4SbO_{4.5}$

d_{obs}	I/I_0	d_{obs}	I/I_0
5.72	34	2.002	26
4.51	6	1.933	10
2.876	100	1.774	10
2.788	21	1.728	5
2.706	57	1.578	49
2.614	5	1.546	16
2.550	49	1.485	21
2.508	66	1.438	18
2.380	90	1.415	5
2.254	5	1.382	13
2.166	5	1.357	11

X-Ray fluorescence analysis shows the new brown compound to have a Cu/Sb ratio of 4.0, in reasonable agreement with the results obtained by atomic absorption analysis (3.95 and 3.93 for samples prepared at 71.6 and 70.6% decomposition, respectively). Semiquantitative ESR of the new compound suggested that the copper is almost entirely in the monovalent state, the CuO content being certainly less than a few percent by weight. ESCA indicated that the antimony in the new compound has a binding energy E_B $(3d_{3/2})$ of 531.0 eV which, by comparison with published data [6], suggests a predominantly pentavalent state (although the interpretation of the ESCA data is complicated by variations in the position and shape of the peaks due to variations in the binding mode of the oxides and the relatively small differences in the binding energies of the 3 + and 5 + states of antimony). If the compound is assumed to contain only Cu(I) and Sb(V), its formula would be $Cu_4SbO_{4.5}$; taking account of the possibility of the Cu and Sb being in more than one valence state, a more strictly correct formulation would be $\mathrm{Cu(I)}_{4-x}\mathrm{Cu(II)}_x\mathrm{Sb(V)}_{1-x/2}\mathrm{Sb(III)}_{x/2}\mathrm{O}_{4.5}$, where $x << 1$ in the material synthesized under the most favourable conditions.

Taking account of all the known facts, the three stages in the decomposition of $CuSb_2O_6$ are summarized in Table 2. The suggested evolution of

TABLE 2

Decomposition of $CuSb_2O_6$ in nitrogen

Step I:	$4\,CuSb_2O_6 \rightarrow Cu_4SbO_{4.5} + 7/2\,Sb_2O_3^{\uparrow} + 9/2\,O_2^{\uparrow}$	950–1070°C
Step II:	$2\,Cu_4SbO_{4.5} \rightarrow 4\,Cu_2O + Sb_2O_3^{\uparrow} + O_2^{\uparrow}$	1070–1120°C
Step III:	$Cu_2O \rightarrow 2\,Cu + 1/2\,O_2^{\uparrow}$	1120°C~

Sb_2O_3 during stages I and II of the reaction is supported by the observation that α-Sb_2O_3 crystals were deposited in the cooler regions of the TG furnace, while the evolution of oxygen is suggested by the fact that both stages are slightly suppressed in air. The decomposition of $CuSb_2O_6$ in air differs slightly from the reaction in nitrogen in that the weight-loss curve does not show any inflexion at about 70% decomposition; under these conditions the reaction appears to proceed directly with evolution of Sb_2O_3 and O_2 to produce Cu_2O without the intermediate formation of $Cu_2SbO_{4.5}$ (Fig. 2B).

Although the linear portions of the TG curves corresponding to step II become curved at higher temperatures (Fig. 3), the decomposition rates of both steps I and II can be described reasonably well by the linear law

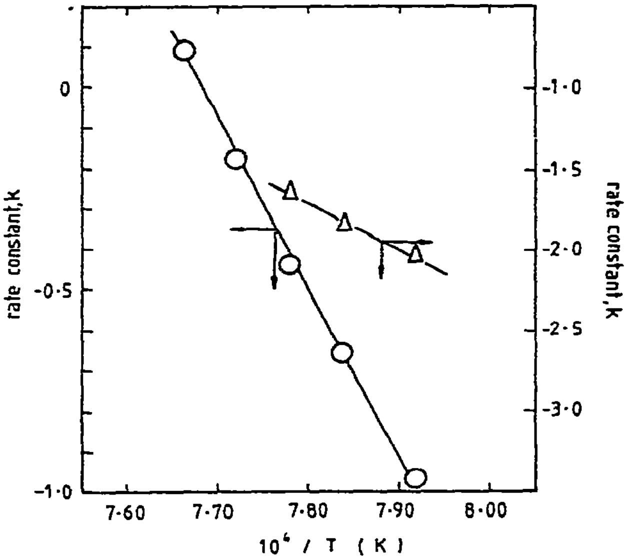
$$\alpha = kt \tag{1}$$

where α is the degree of decomposition, k is the rate constant, and t is the time. These linear rates may be identified with the vaporization rates of Sb_2O_3 and O_2 during steps I and II. Under dynamic gas flow conditions, equilibrium vapour pressures are not maintained above the sample and the vaporization rate may therefore be controlled by the interface reaction. The activation energies for steps I and II were determined to be 356 and 230 kJ mole^{-1}, respectively, from the temperature dependence of the rate constants (Fig. 4). These values reflect the energy required for the breakdown of the $CuSb_2O_6$ and $Cu_4SbO_{4.5}$ structures, respectively.

The $Cu_4SbO_{4.5}$ which occurs in step I of the decomposition reaction (hereafter called form I) was found to transform sluggishly into another slightly different form (form II) on heating in air at 1100°C for >24 h. The most obvious difference between the two forms is in their X-ray diffraction patterns, some of the peaks of form I being split into doublets in form II. This suggests that the structure of the latter is of lower symmetry. Other differences between the two forms are discussed in the next section. During the conversion of form I to form II by heating, the weight change is negligible, suggesting that form I is rather stable to oxidation at 1100°C. Form I does, however, react with Sb_2O_3 in air, taking up the oxygen necessary for its conversion back to $CuSb_2O_6$.

Reaction between CuO and $CuSb_2O_6$

Since the new compound $Cu_4SbO_{4.5}$ is formed by decomposition of $CuSb_2O_6$ under conditions in which Sb_2O_3 and O_2 are removed in the vapour state, an attempt was made to obtain the new compound by reacting $CuSb_2O_6$ with CuO or Cu_2O, that is, by adding CuO to $CuSb_2O_6$ instead of subtracting Sb_2O_3 from $CuSb_2O_6$. Mixtures of CuO and $CuSb_2O_6$ with mole ratios ranging from 1.0 to 9.0 were heated at 950–1150°C in air, and in all cases $Cu_4SbO_{4.5}$ was produced. Thermogravimetry indicates that the onset of weight loss in the various mixtures occurs at 900°C and finishes at 950°C,



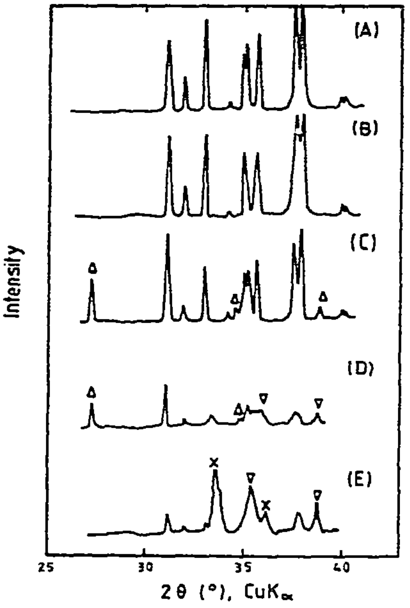
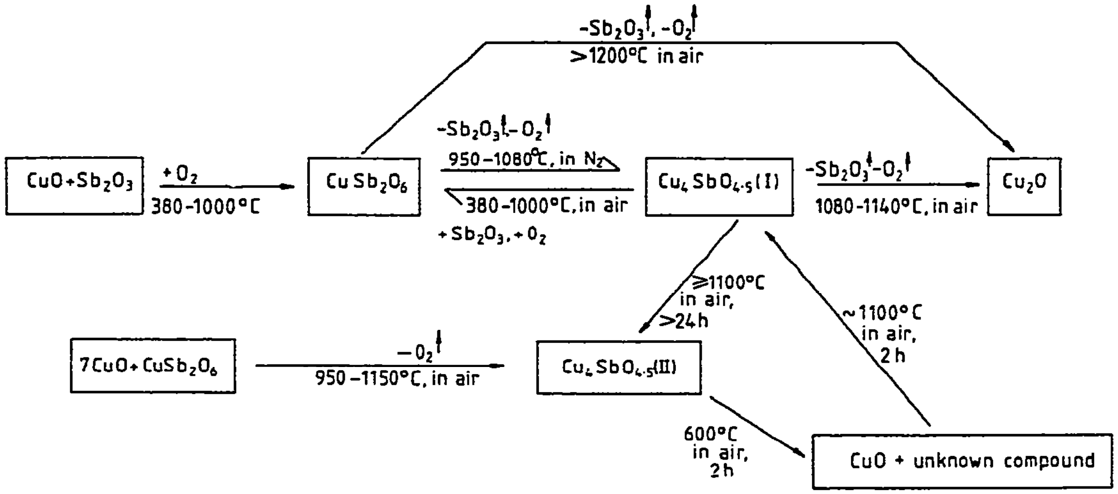


Fig. 4. Temperature dependence of rate constants for thermal decomposition of $CuSb_2O_6$. O, Step I; △, step II.

Fig. 5. X-Ray diffraction patterns of products obtained by reaction between 7 CuO and $CuSb_2O_6$ in air. (A) 1150°C, 24 h; (B) 1120°C, 24 h; (C) 1100°C, 24 h; (D) 950°C, heating rate: 2°C min^{-1}; (E) product obtained by heating $Cu_4SbO_{4.5}$(II) at 600°C for 2 h. △, $CuSb_2O_6$; X, unknown phase; ▽, CuO, unmarked peaks correspond to $Cu_4SbO_{4.5}$.

both temperatures being lower than that at which the thermal decomposition of pure CuO begins (1000°C). By 950°C, the presence of $Cu_4SbO_{4.5}$ was already evident in the mixtures (Fig. 5D). Pure $Cu_4SbO_{4.5}$ containing neither $CuSb_2O_6$ nor CuO was obtained only by heating mixtures of mole ratio 7.0 or 9.0 at 1120–1150°C (Fig. 5A and B), but it should be noted that there may be a tendency for unreacted $CuSb_2O_6$ to decompose to $Cu_4SbO_{4.5}$ in air at $>$ 1100°C, as shown in Fig. 2B. X-Ray diffraction of the material obtained by heating above 1100°C shows a splitting of some of the $Cu_4SbO_{4.5}$ peaks into doublets, characteristic of form II (Fig. 5A, B and C). During further investigation of the differences between the two forms of $Cu_4SbO_{4.5}$, it was found that while form I is stable in air at 600°C, form II decomposes under these conditions to CuO and another unknown phase (Fig. 5E). This reaction is reversible, the system slowly reverting to $Cu_4SbO_{4.5}$ (form I) on heating in air to 1100°C. It thus appears that the reaction between CuO and $CuSb_2O_6$ proceeds with evolution of oxygen, producing $Cu_4SbO_{4.5}$ in form I or II, depending on the temperature. These solid-state reactions are summarized in Scheme 1.



CONCLUSIONS

In the course of attempts to synthesize the Cu(I) analogue of $Ag_2Sb_2O_6$, a complex series of reactions has been identified in the system Cu–Sb–O. The starting material, Cu(II)Sb_2O_6, was synthesized from equimolar mixtures of CuO and Sb_2O_3 by slowly heating thinly-spread samples in air up to 1000°C. This preparation involves the oxidation of Sb_2O_3 to Sb_2O_4 at 380–500°C, followed by further oxidation of Sb_2O_4 and formation of $CuSb_2O_6$ at 500–1000°C. When $CuSb_2O_6$ is thermally decomposed at 980°C in a flowing atmosphere of oxygen-free nitrogen, it evolves Sb_2O_3 vapour and oxygen, forming a new copper(I) antimony oxide identified as $Cu_4SbO_{4.5}$ by analytical, ESR and ESCA evidence.

$$4\,CuSb_2O_6 \xrightarrow[N_2]{950-1070°C} Cu_4SbO_{4.5} + 7/2\,Sb_2O_3\uparrow + 9/2\,O_2\uparrow \qquad (2)$$

The kinetics of this reaction follow a linear rate law, with an activation energy of 356 kJ mole^{-1}. The new compound is further decomposed in nitrogen at higher temperatures, the kinetics again following a linear rate law with an activation energy of 230 kJ mole^{-1}

$$2\,Cu_4SbO_{4.5} \xrightarrow[N_2]{1070-1120°C} 4\,Cu_2O + Sb_2O_3\uparrow + O_2\uparrow \xrightarrow[N_2]{>1120^0} 8\,Cu + 2\,O_2\uparrow \qquad (3)$$

The new compound can also be prepared by reaction of CuO with $CuSb_2O_6$ in air at 1120–1150°C, but in a different form, called form II, to differentiate it from the form I compound resulting from thermal decomposition of $CuSb_2O_6$. Form II has a structure of lower symmetry than form I, as evidenced by a splitting of some of the X-ray diffraction peaks in the powder pattern of form II. The two forms are interconvertible; form I slowly converts to form II on heating in air at 1100°C for >24 h, whereas form II decomposes in air at 600°C to CuO and another new copper antimony oxide, at present uncharacterized, which then recombines to give form I of $Cu_4SbO_{4.5}$ at 1100°C.

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REFERENCES

1 K.J.D. MacKenzie and F. Golestani-Fard, J. Therm. Anal., 15 (1979) 333.
2 D.J. Stewart and O. Knop, Can. J. Chem., 48 (1970) 1323.
3 G. Duquenoy, Rev. Chim. Miner., 11 (1974) 474.
4 J.B. Goodenough and J.A. Kafalas, J. Solid State Chem., 6 (1973) 493.
5 A. Byström, B. Hök and B. Mason, Ark. Kemi, Mineral. Geol., 15B (1941) 1.
6 T.A. Carlson (Ed.), Photoelectron and Auger Spectroscopy, Plenum, New York and London, 1975, p. 366.