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Preparation and Characterization of a New Copper Antimony Oxide, $Cu_9Sb_4O_{19}$

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The new copper antimony oxide, $Cu_9Sb_4O_{19}$, was prepared by solid-state reaction between CuO and $CuSb_2O_6$ in a 3.5 : 1 mole ratio at 1000–1100°C and 10 kbar using a piston cylinder-type high-pressure apparatus. It is certain that the decomposition of Cu(II) to Cu(I) in mixtures of CuO and $CuSb_2O_6$ hinders the formation of $Cu_9Sb_4O_{19}$ at temperatures $\gtrsim$1200°C. The $Cu_9Sb_4O_{19}$ powder pattern could be indexed on the basis of a body-centered cubic unit cell with $a_0 = 9.620$ Å. The $Cu_9Sb_4O_{19}$ was found to decompose to $Cu_4SbO_{4.5}$ + $CuSb_2O_6$ with evolution of oxygen at 950–990°C in air by TG and DTA. The Cu $2p$ XPS showed the more ionic character of the copper ions in $Cu_9Sb_4O_{19}$ than in $CuSb_2O_6$. Furthermore, the asymmetric Sb $3d_{3/2}$ spectrum for $Cu_9Sb_4O_{19}$ suggested two types of Sb(V) with different chemical environments.

Introduction

Recently, new binary compounds of pentavalent (V,Nb,Ta) oxide with mono-divalent copper oxide have been synthesized and their structures determined (*1–4*). However, compounds of pentavalent antimony oxide with copper oxide are rare. The only copper antimony oxide hitherto known is the compound, $CuSb_2O_6$, which has a deformed trirutile structure (*5*). We have reported the formation of a new copper(I) antimony oxide, $Cu_4SbO_{4.5}$, which is obtained by thermal decomposition of $CuSb_2O_6$ in oxygen-free atmosphere and also by solid-state reaction of CuO and $CuSb_2O_6$ in air (*6*). In a previous short paper, it has been reported that another new copper antimony oxide, $Cu_9Sb_4O_{19}$, can be produced by solid-state reaction of CuO and $CuSb_2O_6$ under a high pressure of 10 kbar (*7*), but the reactions have been carried out only at 1000°C and no measurement of the properties concerning the new oxide has been made. This paper describes the detailed preparation of the new oxide of $Cu_9Sb_4O_{19}$ under 10 kbar, and its characterization, including the stability of the new oxide in air and the determination of the valence of the copper and antimony using X-ray photoelectron spectroscopy.

Experimental

The starting oxides of CuO and Sb_2O_3 were prepared according to the previous paper (*7*). An equimolecular mixture of the oxides was heated at a rate of 5°C/min up to 1000°C to prepare $CuSb_2O_6$. Powders of CuO and $CuSb_2O_6$ in mole ratios (n) of 2–7 were well mixed and charges (50–70 mg) were pressed into pellets, then placed into a platinum capsule with both ends tightly

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closed. The pellets were reacted for 2–24 hr in a piston cylinder-type high-pressure apparatus at 900–1250°C and 10 kbar. The sample was subsequently quenched to room temperature before the pressure was released. The temperature was measured within ±15°C with an Alumel–Chromel thermocouple in contact with the closed end of the Pt capsule. The reaction product was ground and identified by X-ray powder diffraction (Geigerflex RAD type, Rigaku Denki Co.). The powders obtained at n = 4.0 and 1000–1100°C were treated in hydrochloric solution to remove residual CuO, the purified new oxide thus obtained being used for the characterization studies. The stability of the new oxide in air was investigated with a simultaneous TG–DTA apparatus (Thermoflex 8085 Type, Rigaku Denki Co.). The heating was carried out at a rate of 10°C/min to 1100°C in air and the sample weight was about 20 mg. The composition of the new oxide was determined by X-ray fluorescence analysis (Rigaku Denki Co.). CuO and Sb_2O_3 powders were used as standards of known Cu and Sb concentration. The valence states of the copper and antimony in the new oxide were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed with Vacuum Generators ESCA 3 (VG Scientific Ltd.) using Al$K\alpha$ electron radiation. The 1s binding energy of contamination of carbon, 284.8 eV, was used for calibration. The errors in determining binding energies were within ±0.1 eV.

Results and Discussion

1. *Preparation of the New Oxide*

In the previous paper, solid-state reactions of CuO and $CuSb_2O_6$ were carried out at 1000°C and 10 kbar and the formation of a new copper antimony oxide was confirmed by X-ray analysis. Subsequently, the high-pressure reactions were performed at temperatures of 900–1250°C using various mole ratios of CuO and $CuSb_2O_6$ in order to find out the condition under which the new oxide can be formed in a pure state. Table I summarizes the experimental results for the high-pressure reactions of CuO and $CuSb_2O_6$ in mole ratios of 2–5 at 900–1200°C and 10 kbar. The relative amounts of detected phases were determined from the X-ray intensities, as shown in Fig. 1 in which X-ray diffraction patterns of the products obtained at n = 2.0–5.0 at 1100°C are illustrated. It is seen from Fig. 1 that the reaction at n = 5.0 produces the new oxide together with residual CuO. Decreasing the ratio from 5.0 to 4.0 leads to a decrease of residual CuO, but a further decrease to 3.0 results in the appearance of a very small

TABLE I

EXPERIMENTAL RESULTS FOR HIGH-PRESSURE REACTIONS OF CuO AND $CuSb_2O_6$ AT 10 kbar

$CuO/CuSb_2O_6$ mole ratio	Reaction temperature (°C)			
	900	1000	1100	1200
5		New oxide, $>$ CuO	New oxide, $>$ CuO	$Cu_4SbO_{4.5}$, $CuSb_2O_6 > CuO$
4	$CuSb_2O_6$, CuO	New oxide, $\gg$ CuO	New oxide, $\gg$ CuO	$CuSb_2O_6$, CuO, $Cu_4SbO_{4.5}$
3.5		New oxide	New oxide	
3	$CuSb_2O_6$, CuO	New oxide, $\gg CuSb_2O_6$	New oxide, $\gg CuSb_2O_6$	$CuSb_2O_6$, CuO, $Cu_4SbO_{4.5}$
2		New oxide, $CuSb_2O_6$	New oxide, $CuSb_2O_6$	

Note. The reactions of n = 7 at 1200°C produce the new oxide together with $CuSb_2O_6$, CuO, and $Cu_4SbO_{4.5}$.

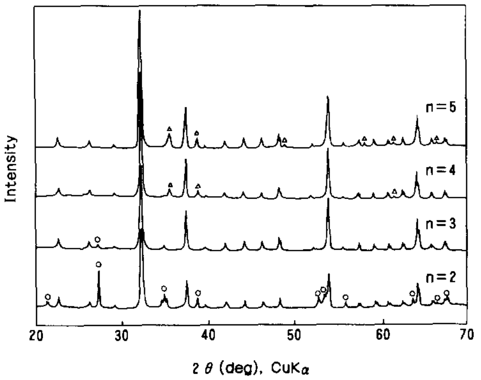

FIG. 1. X-Ray diffraction patterns of products obtained by reaction of $CuO/CuSb_2O_6$ mixtures with mole ratios (n) of 2–5 at 1100°C and 10 kbar. Unmarked peaks corresponds to the new oxide; (△) CuO; (○) $CuSb_2O_6$.

amount of $CuSb_2O_6$ instead of CuO. More $CuSb_2O_6$ is observed at $n = 2.0$. The reaction at these ratios extended to 24 hr gave the similar results as for 2 hr. Thus, it is evident that the single phase of the new oxide can be produced at ratios between 3.0 and 4.0. Actually, the complete formation of the new oxide is achieved when the ratio of 3.5 is used. The reactions at 1000°C give almost the same results as at 1100°C, as have been discussed in the previous paper (7). No formation of the new oxide occurs at $n = 3.0$ and 4.0 at 900°C. At 1200°C, the reactions at $n = 3.0$ and 4.0 produce $Cu_4SbO_{4.5}$ in addition to unreacted CuO and $CuSb_2O_6$. The reactions at 1250°C gave the similar results as at 1200°C. It is thus concluded from these results that the new oxide can be formed in a pure state at a ratio of 3.5 and 1000–1100°C. An unsuccessful attempt was made to obtain the new oxide directly by reaction of CuO with Sb_2O_3 at 1000–1100°C and 10 kbar.

The CuO used here was shown to decompose in air to Cu_2O at about 1000°C by TG and X-ray analysis. This decomposition temperature is close to the temperature (assumed to be at around 1000°C from Table I) at which the new oxide begins to form, leading us to postulate that at temperatures around 1000°C under 10 kbar, the CuO becomes sufficiently highly reactive without decomposition to combine with $CuSb_2O_6$, giving the new oxide. At about 1200°C, mole ratios of $n = 3$–5 give $Cu_4SbO_{4.5}$ as the product, while at $n = 7$ the products are the new oxide and $Cu_4SbO_{4.5}$. The presence of $Cu_4SbO_{4.5}$ containing Cu(I) indicates the decomposition of Cu(II) to Cu(I) at 1200°C even under a high pressure of 10 kbar, because it has been found (6) that $Cu^{I}_4SbO_{4.5}$ is formed with evolution of oxygen by reaction of CuO and $CuSb_2O_6$. Thus, it is certain that when the temperature is increased to ≥1200°C, the decomposition of Cu(II) to Cu(I) in mixtures of CuO and $CuSb_2O_6$ hinders the formation of the new oxides: it is not clear why the new oxide is still present at $n = 7.0$. It is assumed that the higher pressure of >10 kbar which suppresses the decomposition of Cu(II) permits the new oxide to be produced even at temperatures >1200°C.

Since the new oxide was found to be hardly attacked by hydrochloric acid solution, the product obtained at $n = 4.0$ was successfully purified by dissolving the residual CuO by HCl, giving pale greenish yellow powders. X-Ray diffraction data for the new oxide are given in Table II. The pattern could be indexed on the basis of a cubic unit cell with a lattice constant $a_0 = 9.620$ Å. The systematic absence ($h + k + l = 2n + 1$) shows this cell to have a body-centered symmetry. The (110) reflection was not observed. The weight percentages of copper and antimony in the new oxide were determined by X-ray fluorescence analysis as follows:

Anal. calcd for the new oxide: Cu, 42.0; Sb, 35.7. Found: Cu, 43.0; Sb, 36.0. This corresponds to the composition $Cu_9Sb_4O_{19}$ in which the ratio Cu/Sb = 2.25, agreeing with the result that the new oxide can be produced in a pure state with a $CuO/CuSb_2O_6$ ratio of 3.5 at 1000–1100°C, as

TABLE II

X-RAY DIFFRACTION DATA FOR THE NEW COPPER ANTIMONY OXIDE, $Cu_9Sb_4O_{19}$, $a_0 = 9.620$ Å ($CuK\alpha_1$)

d_{obs}	d_{calcd}	(*hkl*)	I/I_0	d_{obs}	d_{calcd}	(*hkl*)	I/I_0
4.824	4.810	200	13	1.702	1.701	440	31
3.936	3.927	211	11	1.650	1.650	433 530	1
3.408	3.401	220	6				
3.078	3.042	310	1	1.603	1.603	442 600	4
2.781	2.778	222	100				
2.574	2.571	321	1	1.560	1.561	532 611	3
2.408	2.405	400	28				
2.271	2.267	330 411	1	1.521 1.484	1.521 1.484	620 541	2 5
2.154	2.151	420	4	1.450	1.450	622	23
2.053	2.051	332	7	1.418	1.418	631	3
1.966	1.964	422	6	1.388	1.389	444	4
1.889	1.887	431 510	9	1.360	1.360	543 550 710	4
1.757	1.756	521	2				

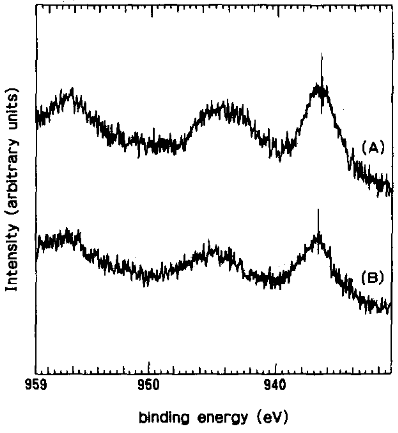

FIG. 3. Cu 2*p* XPS spectra. (A) $CuSb_2O_6$; (B) $Cu_9Sb_4O_{19}$. Spectrum recorded at 2.5×10^{-9} Torr; voltage, 12 kV; current, 20 mA.

shown in Table 1. As discussed below, the valence states of Cu and Sb were determined to be divalent and pentavalent, respectively, by XPS.

2. *Characterization of* $Cu_9Sb_4O_{19}$

Figure 2 shows the TG and DTA curves of the purified new oxide powder heated at a rate of 10°C/min to 1100°C in air. It is seen that the 5.2% weight loss begins at 945°C and finishes at 990°C, corresponding to the endotherm at 950–990°C. The new oxide powder changes color from pale yellowish green to reddish brown on heating. X-Ray analysis shows that the reddish brown powder consists of $CuSb_2O_6$ and $Cu_4SbO_{4.5}$: the new oxide was found still to exist at 920°C. Thus, the thermal change is due to the decomposition of

$$Cu_9Sb_4O_{19} \rightarrow Cu_4SbO_{4.5} + \tfrac{1}{2}CuSb_2O_6 + \tfrac{3}{2}O_2 \quad (1)$$

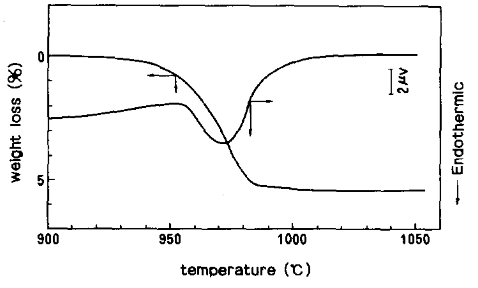

FIG. 2. TG–DTA curves of the new oxide powder. Heating rate: 10°C/min; in air; sample weight: 20 mg.

The weight loss of 5.2% observed at 945–990°C is approximately equal to the calculated loss of 4.7% based on the above equation. Accordingly, the new oxide of $Cu_9Sb_4O_{19}$ cannot persist at temperatures higher than 945°C in air.

Figures 3 and 4 show the Cu 2*p* and Sb 3*d* X-ray photoelectron spectra, respectively, of $CuSb_2O_6$ and $Cu_9Sb_4O_{19}$. The Cu 2*p* spectrum of $CuSb_2O_6$ shows that characteristic broad level $2p_{3/2}$ at 936.4 eV together with the specific shakeup satellite structure for Cu^{2+} $2p_{3/2}$ at a binding energy about 9 eV higher. The spectrum of $Cu_9Sb_4O_{19}$ is almost the same as for $CuSb_2O_6$, but with a higher $2p_{3/2}$ energy level (936.7 eV). Thus, the copper ions in both $CuSb_2O_6$ and $Cu_9Sb_4O_{19}$ can be assigned to Cu^{2+}. A slightly different energy level of $2p_{3/2}$ in $CuSb_2O_6$ and $Cu_9Sb_4O_{19}$ could result from slightly different environments of Cu^{2+} ions in both oxides. The Sb 3*d* spectra in both

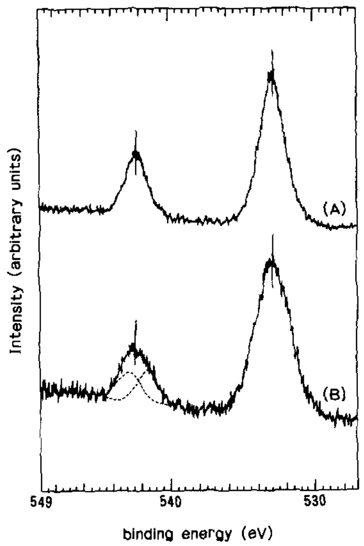

FIG. 4. Sb 3*d* XPS spectra. (A) $CuSb_2O_6$; (B) $Cu_9Sb_4O_{19}$. The measuring condition is the same as for Fig. 3. Peak stripping procedures resulted in the Gaussian components are indicated by the broken curves.

$CuSb_2O_6$ and $Cu_9Sb_4O_{19}$ have the $3d_{5/2}$ and $3d_{3/2}$ energy levels at 532.8 and 542.2 eV, respectively, as shown in Fig. 4. These energy levels are almost the same, suggesting that the ionic character of the antimony ions may be very similar in both oxides. Comparison of the $3d_{5/2}$ energy levels in both oxides with published data (*8*) indicates that the Sb 3*d* spectra can be attributed to Sb(V): it should be noted, however, that the $3d_{5/2}$ energy levels are much higher than those in other Sb(V) compounds ($\Delta E_B = 4.3$ eV, where ΔE_B is the chemical shift between the free Sb atoms and a Sb(V) ion). This assignment of Sb(V) agrees with a previous paper stating that Sb(III) is oxidized to Sb(V) when $CuSb_2O_6$ is formed by reaction of CuO with Sb_2O_3 (*6*). Furthermore, the Sb $3d_{3/2}$ spectrum for $Cu_9Sb_4O_{19}$ is asymmetric, apparently composed of two overlapping spectra, suggesting the presence in $Cu_9Sb_4O_{19}$ of two Sb(V) species, that is, two types of Sb(V) with different chemical environments.

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