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FORMATION OF NEW COPPER ANTIMONY OXIDES BY SOLID STATE REACTION BETWEEN $CuSb_2O_6$ AND CuO UNDER ATMOSPHERIC AND HIGH PRESSURE

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ABSTRACT

Two kinds of new copper antimony oxides, $Cu(I)_4SbO_{4.5}$ and $Cu(II)_9Sb_4O_{19}$, were produced by solid state reaction between $CuSb_2O_6$ and CuO at 1120 - 1150 °C in atmosphere and at 1000 - 1100 °C under a solid pressure of 10 kbar or an oxygen pressure of 10 bar, respectively. This $Cu_4SbO_{4.5}$ was in a different form, called form II, from form I of $Cu_4SbO_{4.5}$ resulting from thermal decomposition of $CuSb_2O_6$ in an oxygen-free atmosphere. X-ray powder diffraction pattern of $Cu_9Sb_4O_{19}$ was indexed on the basis of body-centered cubic unit cell with a_o=9.620 A. This oxide 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.

INTRODUCTION

The only copper antimony oxide hitherto known is the compound, $CuSb_2O_6$, which has a deformed trirutile structure.1) One of the authors has reported the synthesis of a new copper antimony oxide, $Cu(I)_4SbO_{4.5}$, by thermal decomposition of $CuSb_2O_6$ in an oxygen-free atmosphere.2) Since this new compound is formed by removing Sb_2O_3 and O_2 from $CuSb_2O_6$, an attempt was made to produce the new oxide by reacting $CuSb_2O_6$ with CuO in air by adding CuO to $CuSb_2O_6$ instead of substracting Sb_2O_5 from $CuSb_2O_6$. Subsequently, the high pressure reaction of $CuSb_2O_6$ with CuO at 10 kbar was attempted to produce the crystals of $Cu_4SbO_{4.5}$. This high pressure reaction fortuitously leads to formation of another new copper antimony oxide of $Cu_9Sb_4O_{19}$.3,4) This new oxide was

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found to also form from reaction of $CuSb_2O_6$ and CuO under an oxygen pressure of 10 bar. This paper reports formation of new copper antimony oxide, $Cu(I)_4SbO_{4.5}$ and $Cu(II)_9Sb_4O_{19}$, by solid state reaction between $CuSb_2O_6$ and CuO under atmospheric and high pressure, respectively.

EXPERIMENTAL

The starting materials were cupric oxide (Kanto Chem Co.), sieved to $<$ 325 mesh, and antimony trioxdie (Wako Chem. Co.), heated in air to 400 °C. An equimolecular mixture of the oxides was heated at a rate of 5 °C/min to 1000 °C in air to prepare $CuSb_2O_6$. Powder mixtures of $CuSb_2O_6$ and CuO with mole ratios ranging from 2 to 9 were heated at 950 - 1150 °C in air to produce $Cu_4SbO_{4.5}$. Then, mixtures of $CuSb_2O_6$ and CuO in mole ratios (n) of 2 - 7 were pressed into pellets which were placed into a platinum capsule. The pellets were heated for 2 - 24 hr in a piston cylinder-type high pressure apparatus at 900 - 1250 °C and 10 kbar. Both products obtained by the reactions under atmospheric and high pressure were identified by X-ray powder diffraction (XRD). The high pressure reaction of $CuSb_2O_6$ with CuO was also carried out at 950 - 1115 °C under an oxygen pressure of 10 bar in a quartz tube which had been evacuated and sealed off. This pressure was attained by decomposition at about 700 °C of $KClO_4$ which was separately placed in the quratz tube. The compositions of both the new oxides were determined by X-ray fluorescence analysis. The valence states of the copper and antimony in the new oxides were determined by X-ray photoelectron spectroscopy (XPS). The stability of $Cu_9Sb_4O_{19}$ in air was investigated with a simultaneous TG-DTA apparatus.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of products obtained by reaction between $CuSb_2O_6$ and 7CuO in air. By 950 °C, the presence of $Cu_4SbO_{4.5}$ was already evidence in the mixtures (Fig.1D). Pure $Cu_4SbO_{4.5}$ containing neither $CuSb_2O_6$ nor CuO was obtained only by heating the mixtures of mole ratio 7.0 or 9.0 at 1120 -1150 °C (Fig.1A and B). X-ray diffraction of the product obtained by heating at above 1100 °C shows a splitting of some of the $Cu_4SbO_{4.5}$ peaks into doublets, characteristic form II (Fig. 1 A, B and C), different from form I resulting from thermal decomposition of $CuSb_2O_6$ in an oxygen-free atmosphere. Further investigation of the differences between the two forms of $Cu_4SbO_{4.5}$ showed that while form I is stable in air at 600 °C, form II decomposes under these conditions to CuO and another unknown phase (Fig.1E). On heating the phase of Fig.1E in air to 1100 °C, this phase slowly reverted to $Cu_4SbO_{4.5}$ of form I. Thermogravimetry indicated that the various mixtures of $CuSb_2O_6$ and CuO lose oxygen at temperatures of 900 - 950 °C. It thus appears that the reaction between $CuSb_2O_6$ and CuO proceeds with evolution of oxygen, producing $Cu_4SbO_{4.5}$ in form II. X-ray fluorescence analysis showed the new oxide to have a Cu/Sb ratio of 4.0. Semiquantitative ESR of the new oxide suggested that the copper is almost entirely in the monovalent state. XPS suggested a predominantly pentavalent state of the antimony. These analytical data show the new oxide to have a composiiton of $Cu_4SbO_{4.5}$.

Table 1 summarizes the experimental results for the high-pressure reactions of $CuSb_2O_6$ with CuO in mole ratios of 2 - 5 for 2 hr at 900 -1200 °C and 10 kbar. The relative amount of detected phases were determined from X-ray intensities. It is seen that at 1000 - 1100 °C, the reaction at n=5.0 produces the new oxide, $Cu_9Sb_4O_{19}$, 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 appearance of a very small amount of $CuSb_2O_6$ instead of CuO. More $CuSb_2O_6$ is observed at n=2.0. When the ratio of 3.5 is used, the complete formation of the new oxide is achieved. 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 - 5 produce $Cu_4SbO_{4.5}$ in addition to $CuSb_2O_6$ and CuO. The reactions of $CuSb_2O_6$ with CuO at 960 - 1115 °C under an oxygen pressure of 10 bar also gave the same results as the case of 10 kbar. The complete formation of the new oxide at 10 bar was achieved only at 1100 °C, in contrast to its formation at 1000 - 1100 °C at 10 kbar. 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_o=9.620 A. The systematic absence (h+k+l=2n+1) shows this cell to have a body-centered symmetry. X-ray fluorescence analysis showed the new oxide to have a composition of $Cu_9Sb_4O_{19}$: the valence states of Cu and Sb were determined to be divalent and pentavalent, respectively, by XPS. Figure 2 shows the TG and DTA curves of the new oxide heated to 1100 °C in air. It is seen that the 10.4% weight loss begins at 945 °C and finishes at 990 °C, corresponding to the endotherm at 950 - 990 °C. The new oxide powder changed color from pale yellowish green to reddish brown on heating. X-ray analysis showed the reddish brown powder to consist of $CuSb_2O_6$ and $Cu_4SbO_{4.5}$. Accordingly, the new oxide of $Cu_9Sb_4O_{19}$ cannot persist at temperatures higher than 945 °C in air.

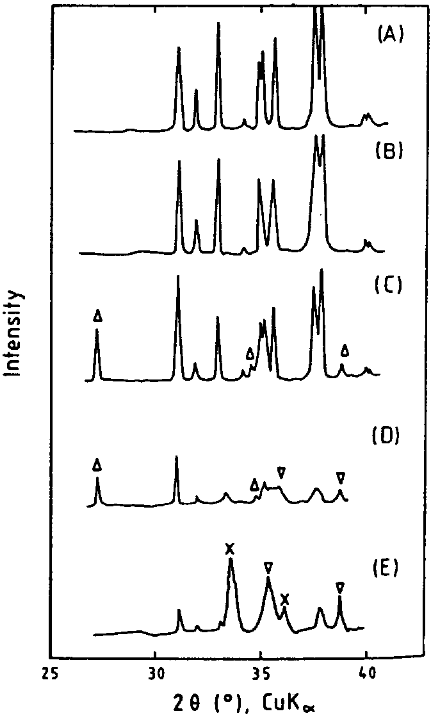

Figure 1 X-ray diffraction patterns of products obtained by reaction between 7CuO and $CuSb_2O_6$ in air.

(A) 1150°C, 24h; (B) 1120°C, 24h; (C) 1100°C, 24h; (D) 950°C, heating rate: 2°C/min; (E) product obtained by heating $Cu_4SbO_{4.5}$(II) at 600°C for 2h. Δ: $CuSb_2O_6$, X: unknown phase, ∇: CuO, unmarked peaks correspond to $Cu_4SbO_{4.5}$.

Table 1 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, ≫ CuO	New oxide, ≫ CuO	$CuSb_2O_6$, CuO, $Cu_4SbO_{4.5}$
3.5		New oxide	New oxide	
3	$CuSb_2O_6$, CuO	New oxide, ≫ $CuSb_2O_6$	New oxide, ≫ $CuSb_2O_6$	$CuSb_2O_6$, 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 $Cu_4SbO_{4.5}$.

Table 2. X-Ray diffraction data for the new copper antimony oxide, $Cu_9Sb_4O_{19}$. $a_0 = 9.620$ Å ($CuK\alpha_1$)

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

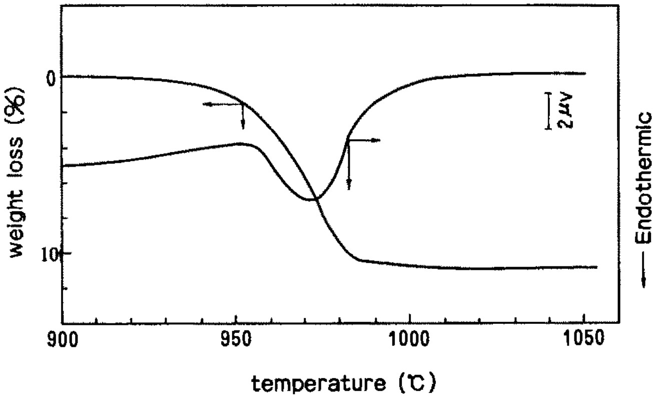

Figure 2 TG-DTA curves of the $Cu_9Sb_4O_{19}$ powder. Heating rate: 10°C/min, in air, sample weight: 20 mg.

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