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SYNTHESIS OF A NEW COPPER ANTIMONY OXIDE, $Cu_9Sb_4O_{19}$, BY SOLID STATE REACTION BETWEEN CuO AND $CuSb_2O_6$ UNDER HIGH PRESSURE

Shiro SHIMADA,* Kohei KODAIRA, and Toru MATSUSHITA
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060

A new copper antimony oxide was synthesized by solid state reaction between CuO and $CuSb_2O_6$ in a 3.5:1 mole ratio at 1000 °C and 10 kbar and was found to have the composition $Cu_9Sb_4O_{19}$ by X-Ray fluorescence analysis. The new oxide could be indexed on the basis of a body-centred cubic unit cell with a_o=9.620 Å.

Compounds of pentavalent antimony oxide with copper oxide are rare. The only copper antimony oxide is the compound, $CuSb_2O_6$, which has a deformed trirutile structure.[1)] In a previous paper, it has been reported that a new copper(I) antimony oxide, $Cu_4SbO_{4.5}$, was prepared by a thermal decomposition of $CuSb_2O_6$ and also by a solid state reaction of CuO with $CuSb_2O_6$ in the mole ratio 7:1.[2)] Since the preparation of $Cu_4SbO_{4.5}$ by this reaction requires a long heat treatment of over 24 h at 1120-1150 °C, the high pressure reaction was thought to be facilitated. This high pressure reaction fortuitously leads to the formation of another new copper antimony oxide of $Cu_9Sb_4O_{19}$. This paper reports the synthesis of a new copper antimony oxide by the solid state reaction between CuO and $CuSb_2O_6$ under high pressure of 10 kbar.

The starting materials were copper(II) oxide (Kanto Chem.) and antimony(III) oxide (Wako Chem.), both of reagent grade. The CuO sample was fired at 500 °C for 2 h in air, then sieved to $<$325 mesh. The Sb_2O_3 sample which contained 1 wt% H_2O was dehydrated before reaction by heating in air to 380 °C. 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 of 2-7 were mixed and 40-50 mg charges were pressed into pellets, then placed into a platinum capsule. The pellets were reacted for 2 h 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 products obtained in the reaction were identified by X-Ray powder diffraction.

The existence of a new copper antimony oxide formed by the high pressure reaction of CuO with $CuSb_2O_6$ in the mole ratio 7:1 at 1120-1150 °C and 10 kbar was confirmed by X-Ray analysis. Since the phases CuO, $CuSb_2O_6$, and $Cu_4SbO_{4.5}$ were present in the reaction product, further high pressure reactions were carried out with various ratios of CuO/$CuSb_2O_6$=2-7 at 900-1250 °C to determine the conditions under which the new oxide can be produced in a pure state. The reaction of CuO with $CuSb_2O_6$ in the ratio 7:1 at 1150-1250 °C gave almost the same result as at 1120-1150 °C. The reaction with the ratio 7:1 at 1000 °C produced the new oxide together with residual CuO but containing neither $CuSb_2O_6$ nor $Cu_4SbO_{4.5}$. No reaction occurred at 900 °C. To eliminate the unreacted copper(II) oxide, high pressure reactions with mole ratios of less than 5.0 were conducted. Decreasing the mole ratio from 5.0 to 4.0 leaded to a decrease of unreacted CuO but a further decreased to 3.0 resulted in an appearance of $CuSb_2O_6$ instead of CuO. More $CuSb_2O_6$ was found with the ratio of 2.0. Thus, it is evident that the new oxide can be produce in a pure state by using a ratio between 4.0 and 3.0, and a complete absence of CuO and $CuSb_2O_6$ was found when the ratio of 3.5 was used.

Since the new oxide was found to be hardly attacked by hydrochloric acid solution, the new oxide obtained at a mole ratio of 4.0 was successfully purified by dissolving the unreacted CuO by HCl, giving pale greenish-yellow powders. X-Ray diffraction data for the new oxide are given in Table 1. The pattern could be indexed on the basis of a cubic unit cell with a_o=9.620 Å and the systematic absence (h+k+l=2n+1) shows this cell to have a body-centred symmetry. X-Ray fluorescence analysis showed that the mole ratio of Cu/Sb in the new oxide is about 2.25, corresponding to the composition, $Cu_9Sb_4O_{19}$, which is consistent with the result that the new oxide can be produced in a pure state with the ratio of 3.5 at 1000 °C.

Table 1. X-Ray diffraction data for the new copper antimony oxide, $Cu_9Sb_4O_{19}$. a_o =9.620 Å ($CuK\alpha_1$)

d_{obsd}	d_{calcd}	(hkl)	I/I_o	d_{obsd}	d_{calcd}	(hkl)	I/I_o
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	1.603	1.603	{442, 600	4
3.078	3.042	310	1	1.560	1.561	{532, 611	3
2.781	2.778	222	100	1.521	1.521	620	2
2.574	2.571	321	1	1.484	1.484	541	5
2.408	2.405	400	28	1.450	1.450	622	23
2.271	2.267	{330, 411	1	1.418	1.418	631	3
2.154	2.151	420	4	1.388	1.389	444	4
2.053	2.051	332	7	1.360	1.360	{543, 550, 710	4
1.966	1.964	422	6				
1.889	1.887	{431, 510	9				
1.757	1.756	521	2				

References

1) A. Bystrom, B. Hok, and B. Mason, Ark. Kemi. Mineral. Geol., 15B, 1 (1941).

2) S. Shimada and K.J.D. MacKenzie, Thermochim. Acta, 56, 73 (1982).

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