Phase Analysis Studies in the System Cu_2O – CuO – Ta_2O_5

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The ternary system Cu_2O – CuO – Ta_2O_5 has been studied by X-ray powder diffraction methods after heat treatment of the samples at 1120 and 1440 K. In addition to the phases $\text{Cu}_3\text{Ta}_7\text{O}_{19}$ and $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ on the Cu_2O – Ta_2O_5 line, two ternary phases exist: $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$ ($0 \leq x \leq 0.12$) has a cubic perovskite-type structure with $a \approx 7.5$ Å, and $\text{Cu}_x\text{Ta}_3\text{O}_8$ ($0.77 \leq x \leq 0.85$) is orthorhombic with a structure of $\text{LiNb}_6\text{O}_{15}\text{F}$ -type. The variation of the unit cell parameters with composition has been studied for these two phases. Magnetic measurements between 70 and 350 K showed Curie-Weiss behaviour.

Although there have been several studies over the past 20 years on the phases occurring in the Cu–Ta–O and Cu–Nb–O systems, some of the results have been contradictory, and our knowledge is still rather incomplete.

A series of investigations of complex systems involving Ta_2O_5 or Nb_2O_5 in combination with Cu_2O , CuO and/or NbO_2F has therefore been undertaken at this laboratory to provide more information on these systems.

In the earlier publications on the Cu–Ta–O system, a perovskite-type phase of the composition CuTaO_3 was reported as a valence isomer.^{1,2} A high pressure non-perovskite modification of that stoichiometry has also been reported.³ No further communication confirming the existence of an ABO_3 -type compound has appeared since.

Two independent groups reported^{4,5} the preparation of a compound with divalent copper, CuTa_2O_6 , having cubic symmetry with the perovskite unit cell parameter doubled ($a = 7.52$ Å). This compound could be obtained at 1200 °C. In a subsequent report on CuTa_2O_6 the space group $Pm\bar{3}$ was suggested on the basis of spectral data and X-ray powder diffraction results. The

crystal structure of CuTa_2O_6 was first refined by Hong.⁷ This perovskite-type structure was described as built of strongly distorted TaO_6 octahedra creating a square coplanar configuration at the A-sites, suitable for accommodation of Cu^{II} atoms. CuTa_2O_6 has also been reported to show a slight distortion from cubic to tetragonal symmetry in an olive green sample prepared at 1000 °C.⁸

In a recent study⁹ the structure of a crystal obtained from a 10 $\text{CuO}/\text{Ta}_2\text{O}_5$ flux was refined. The intensity distribution in the single crystal pattern indicated orthorhombic symmetry, but no deviation from cubic symmetry was observed in the powder patterns. A wide homogeneity range, $\text{Cu}_{1+x}\text{Ta}_2\text{O}_6$ with $0 \leq x \leq 0.30$, was suggested without further details. The refinement indicated a composition of $\text{Cu}_{1.03}\text{Ta}_2\text{O}_6$ of the single crystal studied.

In a previous study at this laboratory¹⁰ a compound $\text{Cu}_{0.80}\text{Ta}_3\text{O}_8$ was obtained at 1445 K with a structure representing a version of the $\text{LiNb}_6\text{O}_{15}\text{F}$ -type.¹¹ Two phases with monovalent copper have recently been reported by Jahnberg,¹² viz. $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and $\text{Cu}_3\text{Ta}_7\text{O}_{19}$, having structures based on stacking of $\alpha\text{-U}_3\text{O}_8$ -type layers.^{12,13} The first compound was obtained at both 800 °C and 1100 °C, while the second could be prepared only at the lower temperature.¹⁴

In this paper a phase analysis of the Cu_2O – CuO – Ta_2O_5 system is reported.

EXPERIMENTAL

The starting materials were Cu_2O (Matheson, Coleman and Bell min 96.0 %), CuO (Baker Analysed, min 99.9 %) and Ta_2O_5 (Fuka, Buch

SG, min 99.9 %). To reduce weighing errors when the variation of properties within homogeneity ranges were to be studied, two stock mixtures having compositions near the extreme ends of the range were first prepared, and the intermediate samples were made by mixing appropriate amounts of these. Special precautions had to be taken to avoid unintentional oxidation of Cu_2O . Therefore, the silica tubes containing appropriate amounts of the compounds, thoroughly mixed, were dried, carefully evacuated to 0.1 Pa and sealed off. Samples representing compositions on the $\text{CuO}-\text{Ta}_2\text{O}_5$ line were also prepared in nonevacuated but sealed platinum tubes.

In general, samples were prepared by pre-heating, and then gradually increasing the temperature, keeping them for 3–5 days at the temperature of preparation and finally quenching the tubes in cold water. The low-temperature samples were pre-heated at about 870 K for a few days followed by annealing at 1120 K, while the high-temperature samples were pre-heated at about 1020 K and then held at 1440 K.

All samples were examined in an optical microscope and by X-ray diffraction using a Guinier-Hägg focusing camera with strictly monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda=1.540598 \text{ \AA}$).¹⁵ Potassium chloride ($a_{\text{KCl}}=6.2930 \text{ \AA}$)¹⁶ was used as an internal standard. The 2θ values were calculated from powder photographs followed by indexing and refinements of cell parameters by means of a least squares procedure.¹⁷ An automatic single beam microdensitometer designed for X-ray powder photographs was used.¹⁸ The magnetic susceptibility was measured using an automatized apparatus applying the Faraday method and using $\text{HgCo}(\text{SCN})_4$ as a standard.¹⁹ The measurement covered the temperature range 70 to 350 K. The density was determined from the apparent loss of weight in hexane, using an apparatus designed for density determination on small powder samples.²⁰

RESULTS AND DISCUSSION

The results of the phase analysis are summarized in Fig. 1, illustrating the isothermal diagram. For the sake of clarity only a representative selection of the compositions investigated have been indicated and listed in Table 1. The intermediate phases observed at 1120 K are marked A, C and D. A is a perovskite-type phase $\sim\text{CuTa}_2\text{O}_6$, C is $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and D is $\text{Cu}_3\text{Ta}_7\text{O}_{19}$.¹² Another phase B, $\text{Cu}_{-0.8}\text{Ta}_3\text{O}_8$,

reported previously,¹⁰ was observed only in the high-temperature experiments.

The perovskite-type and $\text{Cu}_{-0.8}\text{Ta}_3\text{O}_8$ phases have appreciable homogeneity ranges.

All samples with gross compositions $\text{CuO} \cdot n\text{TaO}_{2.5}$ ($n > 9$) gave complex X-ray powder patterns which were similar to that of Ta_2O_5 . These phases will be objects of further studies, which will include also high resolution electron microscopy.

A. The perovskite-type phase. A single phase was obtained at 1120 K for samples with compositions along the line $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$. The X-ray diffraction patterns indicated a cubic perovskite-type structure with $a \approx 7.5 \text{ \AA}$, as reported in Refs. 4 and 5 for CuTa_2O_6 . However, samples prepared at this composition (CuTa_2O_6), invariably showed weak extra lines of a Ta_2O_5 -like phase, and this composition thus does not seem to represent a single phase.

The unit cell parameter of the specimens on the line $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$ are observed to vary with composition within the range $0 \leq x \leq 0.12$, as seen from Fig. 2. The single phase sample with $x=0$ (on the line $\text{CuO}-\text{Ta}_2\text{O}_5$) has a unit cell parameter $a=7.516(1) \text{ \AA}$ (Table 2). The same parameter is obtained for this phase in two-phase samples obtained at the composition CuTa_2O_6 . It seems reasonable to assume that the composition

Fig. 1. Part of the phase diagram for the system $\text{Cu}_2\text{O}-\text{CuO}-\text{Ta}_2\text{O}_5$ at 1120 K and 1440 K. Broken lines refer to phase B, which could be prepared only at the higher temperature. The dashed area close to Ta_2O_5 is not yet explored and may contain several Ta_2O_5 -like phases.

Table 1. The results of the phase analysis for some representative samples with reference to Fig. 1.

A = perovskite-type phase $\sim\text{CuTa}_2\text{O}_6$ C = $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ B = $\text{Cu}_{0.8}\text{Ta}_3\text{O}_8$ D = $\text{Cu}_3\text{Ta}_7\text{O}_{19}$

No.	Gross composition			Observed X-ray powder patterns
	$p\text{CuO}_{0.5}$	$+q\text{CuO}$	$+r\text{TaO}_{2.5}$	
	p	q	r	
Temperature: 1120 K				
1	0	0.397	0.603	A+CuO
2	0.019	0.371	0.610	A+CuO
3	0	0.347	0.653	A
4	0.007	0.342	0.651	
5	0.026	0.329	0.645	
6	0.045	0.316	0.639	
7	0.064	0.304	0.632	
8	0.076	0.295	0.0629	A+Cu ₂ O+D
9	0.120	0.260	0.620	
10	0.050	0.300	0.650	
11	0	0.330	0.670	
12	0.300	0	0.700	
13	0	0.060	0.940	A+Ta ₂ O ₅ -type phase
14	0.030	0.125	0.845	"CuTa ₂ O ₆ "=A+Ta ₂ O ₅ -type phase
15	0.090	0	0.910	D+Ta ₂ O ₅ -type phase+C
				Ta ₂ O ₅ type phase
				Ta ₂ O ₅ type phase+A
				Ta ₂ O ₅ type phase+D
Temperature: 1440 K				
16	0.100	0.030	0.870	B+Ta ₂ O ₅ -type phase
17	0.108	0.081	0.811	B+A
18	0.133	0.067	0.800	B
19	0.158	0.053	0.789	
20	0.180	0.040	0.780	
21	0.210	0.021	0.769	
22	0.250	0.020	0.730	
23	0.310	0	0.630	B+C
				B+C
				C

$x=0$ is the lower bound of the homogeneity range. The upper limit of the homogeneity range is close to $x=0.12$, as is evident from Fig. 2 and Table 1. At this point 21 % of the Cu atoms are monovalent.

Specimens of $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$ ($0 \leq x \leq 0.12$) synthesized in the way mentioned above are brown. Fully oxidized samples with $x=0$ are green. The diffraction lines were sharp, and no splitting that would indicate a symmetry lower than cubic could be observed.

When specimens are prepared at high temperature (1440 K) their colour becomes black. Samples with starting composition corresponding to point 1 in Fig. 1, for example, were green when

prepared at low temperature and gave the value $a=7.516 \text{ \AA}$ for the cell parameter of the perovskite phase. Prepared at 1440 K they are black, and the a value is $7.527 \text{ \AA}$, which corresponds to $x \approx 0.10$ according to Fig. 2. There is thus strong evidence that there is a loss of oxygen and an increase in the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ ratio at the higher temperatures. Hong,⁷ Longo *et al.*⁸ and Vincent *et al.*⁹ also obtained a black phase using a flux method at high temperatures.

The density was measured for two single phase samples with $x=0$ and $x=0.10$ prepared at 1120 K. The calculated densities assuming four formula units of $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$ per unit cell, agree well with the observed values. The sample with

Fig. 2. Unit cell parameter a (in Å) and Curie constant C ($\text{m}^3 \text{K mol}^{-1}$) as functions of copper content x for the perovskite-type phase $\text{Cu}_{1.05+x}\text{Ta}_{1.98}\text{O}_6$. The numbers of the samples refer to Fig. 1 and Table 1.

$x=0$ gave the values $\rho_{\text{obs}}=8.14 \text{ g cm}^{-3}$ and $\rho_{\text{calc}}=8.15 \text{ g cm}^{-3}$, while the sample with $x=0.10$ gave $\rho_{\text{obs}}=8.20 \text{ g cm}^{-3}$ and $\rho_{\text{calc}}=8.21 \text{ g cm}^{-3}$.

The magnetic susceptibility measurements, covering the temperature range 70–350 K,

showed paramagnetic behaviour of all samples investigated. The thermal variation of the magnetic susceptibility obeyed the Curie-Weiss law. The variation of C (the Curie constant) with x , shown in Fig. 2, is in concord with a decrease in

Table 2. X-Ray powder diffraction pattern of $\text{Cu}_{1.03}(\text{Cu}_{0.02}\text{Ta}_{1.98})\text{O}_6$. Figures of merits (26,27) $M(20)=32$, $F(20)=15$. Symmetry: Cubic. $a=7.516(1) \text{ Å}$; $\rho_{\text{obs}}=8.14 \text{ g cm}^{-3}$; $\rho_{\text{calc}}=8.15 \text{ g cm}^{-3}$.

$2\theta_{\text{obs}} (^\circ)$	$2\theta_{\text{obs}}-2\theta_{\text{calc}} (^\circ)$	$d_{\text{obs}} (\text{Å})$	$I_{\text{obs}} \cdot 1000/I_{\text{max}}$	h	k	l
11.621	-0.144	7.609	3	1	0	0
16.657	-0.011	5.318	60	1	1	0
23.540	-0.116	3.776	907	2	0	0
26.566	0.070	3.353	4	2	1	0
29.087	0.009	3.068	36	2	1	1
33.594	-0.107	2.666	1000	2	2	0
37.835	0.014	2.376	45	3	1	0
41.593	0.003	2.170	338	2	2	2
45.103	0.005	2.009	29	3	2	1
48.390	-0.014	1.880	602	4	0	0
51.548	0.000	1.772	16	3	3	0
54.531	-0.029	1.682	760	4	2	0
57.456	-0.008	1.603	11	3	3	2
60.215	-0.061	1.536	975	4	2	2
63.014	0.002	1.474	8	5	1	0
68.303	0.005	1.372	9	5	2	1
70.855	-0.012	1.329	538	4	4	0
73.392	-0.005	1.289	16	5	3	0
75.881	-0.002	1.253	547	6	0	0
78.381	0.018	1.219	8	6	1	1

the amount of Cu^{II} when x is increased. The observed $\mu_{\text{eff}}/\text{Cu}^{\text{II}}$ in this compound ranges from 1.84–2.02 B.M., which is in agreement with previously observed values for Cu^{II} compounds. For example, a value of 2.04 B.M. has been reported for CuNbO_3F ,²¹ while 1.91 and 2.06 B.M. are the values previously obtained for ' CuTa_2O_6 '.^{8,22}

The copper atom distribution in this phase is not obvious, especially as copper exists in two valence states for $x > 0$. The following points can be made, however:

(a) The copper atoms should mainly occupy the A-site of the ideal perovskite structure, as is also suggested by Hong⁷ and by Vincent *et al.*⁹

(b) It seems reasonable to assume that there is a substitution of divalent copper for a small amount of tantalum, since vacancies at the B-sites are not likely. The radius of Cu^{II} in 6-coordination is 0.73 Å compared to 0.64 Å for Ta^{V} .²² The most probable cation distribution for $x=0$ can then be written as $\text{Cu}^{\text{II}}_{1.03}(\text{Cu}^{\text{II}}_{0.02}\text{Ta}^{\text{V}}_{1.98})\text{O}_6$. At the upper composition limit, $x=0.12$, the corresponding formula is $\text{Cu}^{\text{I}}_{0.24}\text{Cu}^{\text{II}}_{0.91}(\text{Cu}^{\text{II}}_{0.02}\text{Ta}^{\text{V}}_{1.98})\text{O}_6$. The magnetic measurements and densities are in reasonable agreement with this model.

(c) The observed expansion of the lattice when the value of x is increased may be caused mainly by two things: (i) the increased number of metal atoms in the unit cell and (ii) the replacement of divalent copper atoms by larger monovalent atoms at the same crystallographic site.

B. $\text{Cu}_{x-0.8}\text{Ta}_3\text{O}_8$. The phase $\text{Cu}_x\text{Ta}_3\text{O}_8$ is orthorhombic.¹⁰ It was difficult to prepare as a single phase when using Cu_2O as one of the starting materials. However, by replacing copper(I) oxide by an equivalent amount of Cu metal powder and CuO, single phase samples could be obtained at 1440 K. Attempts to obtain this phase at about 1220 K failed, therefore it seems reasonable to assume that it is a high temperature phase.

A variation in the length of the axes with x was observed, as seen in Fig. 3. The data suggested a homogeneity range $0.77 \leq x \leq 0.85$. No extra lines that would indicate a second phase could be seen in the powder patterns of samples with $x=0.75$, 0.80 (Table 3) and 0.85. The point $x=0.75$ is probably outside the single phase range, but the amount of additional phase is then too small to be detected in the powder patterns. The colour of

the single phase samples is reddish-brown.

The copper distribution in this phase has been reported previously.¹⁰ When x goes from 0.77 to 0.85 it changes from $0.54 \text{ Cu}^{\text{I}} + 0.23 \text{ Cu}^{\text{II}}$ to $0.70 \text{ Cu}^{\text{I}} + 0.15 \text{ Cu}^{\text{II}}$. The unit cell parameters thereby decrease, as seen in Fig. 3. The total number of copper atoms increases, but there is also a replacement of Cu^{II} by Cu^{I} . These atoms occupy different crystallographic positions: Cu^{I} is located in interstitial holes which are considerably larger than the interstices where Cu^{II} is located. This replacement may therefore explain the shrinkage of the unit cell when x is increased. A comparison can be made with $\text{Li}_{1-x}\text{Ta}_3\text{O}_{8-x}\text{F}_x$,²⁴ which is isostructural with $\text{Cu}_x\text{Ta}_3\text{O}_8$.¹⁰ The Li^{I} atoms in the former structure are suggested to

Fig. 3. Unit cell parameters and Curie constant C ($\text{m}^3 \text{K mol}^{-1}$) as functions of copper content x for the phase $\text{Cu}_x\text{Ta}_3\text{O}_8$. The numbers of the samples refer to Fig. 1 and Table 1.

Table 3. X-Ray powder diffraction pattern of $\text{Cu}_{0.80}\text{Ta}_3\text{O}_8$. Figures of merits (26,27) $M(20)=20$, $F(20)=25$. Symmetry: orthorhombic. $a=16.80(1)$ Å, $b=3.889(1)$ Å, $c=8.988(1)$ Å.

$2\theta_{\text{obs}}$ (°)	$2\theta_{\text{obs}}-2\theta_{\text{calc}}$ (°)	d_{obs} (Å)	$I_{\text{obs}} \cdot 1000/I_{\text{max}}$	h	k	l
9.883	0.051	8.943	16	0	0	1
10.580	0.057	8.355	24	2	0	0
11.204	0.049	7.891	30	1	0	1
19.766	0.028	4.488	16	0	0	2
20.473	0.033	4.335	25	1	0	2
22.449	0.031	3.957	53	2	0	2
22.868	0.018	3.886	1000	0	1	0
23.382	0.024	3.802	318	4	0	1
25.402	0.012	3.504	886	3	0	2
30.290	0.013	2.948	385	1	0	3
30.856	0.012	2.896	26	0	1	2
31.690	0.009	2.821	228	2	0	3
31.949	0.014	2.799	79	6	0	0
32.236	0.010	2.775	106	2	1	2
32.917	-0.043	2.719	250	4	1	1
33.278	0.012	2.690	70	5	0	2
33.509	0.016	2.672	56	6	0	1
33.930	0.015	2.641	16	3	0	3
34.416	-0.003	2.604	556	3	1	2
36.705	0.000	2.445	417	5	1	1

occur at nearly the same crystallographic sites as the Cu^{I} atoms in $\text{Cu}_x\text{Ta}_3\text{O}_8$. With increasing lithium content in the structure the lattice contracts;²⁴ the two structures thus behave similarly in this respect.

The magnetic susceptibility was found to be temperature dependent in the range investigated: 70–350 K, with the Curie–Weiss law nicely obeyed. The variation of the Curie constant C with x is indicated in Fig. 3. The values of $\mu_{\text{eff}}/\text{Cu}^{\text{II}}$ fall in the range 1.45–1.53 B.M. This is considerably lower than for the perovskite-type phase. An even lower value has, however, been reported for the corresponding niobium phase with LiNb_3O_8 -type structure.²⁵

Acknowledgements. I wish to express my gratitude to Professor Arne Magnéli who introduced me to the field, Professor Lars Kihlberg and Dr. Monica Lundberg for their constant interest in this investigation and for all their valuable comments and criticism. Thanks are also due to Mr. Bo Blom for his enthusiastic help with the magnetic measurements.

This project has been sponsored by the Swedish Natural Science Research Council.

REFERENCES

1. Krylov, E. I., Samarina, V. A. and Shtolts, A. K. *Dokl. Akad. Nauk SSSR* 130 (1960) 556.
2. Shick, L. and Vorres, K. S. *AEC Accession No. 4244*, Report TID-2220 D, 1965.
3. Sleight, A. W. and Prewitt, C. T. *Mater. Res. Bull.* 5 (1970) 207.
4. Felten, E. J. *J. Inorg. Nucl. Chem.* 29 (1967) 1168.
5. Kasper, H. *Rev. Chim. Miner.* 4 (1967) 759.
6. Reinen, D. and Propach, V. *Inorg. Nucl. Chem. Lett.* 7 (1971) 569.
7. Hong, H. Y. P. *Lincoln Laboratory, M. I. T., Solid State Research Report* 2 (1972) 33.
8. Longo, J. M. and Sleight, A. W. *Mater. Res. Bull.* 10 (1975) 1273.
9. Vincent, H., Bochu, B., Aubert, J. J., Jaubert, J. C. and Marezio, M. *J. Solid State Chem.* 24 (1978) 245.
10. Wa Ilunga, N. P., Marinder, B. O. and Lundberg, M. *Chem. Scr.* 18 (1981) 217.
11. Lundberg, M. *Acta Chem. Scand.* 19 (1965) 2274.
12. Jahnberg, L. *Mat. Res. Bull.* 16 (1981) 513.
13. Jahnberg, L. *J. Solid State Chem.* 41 (1982) 286.
14. Jahnberg, L. *Private communication*.

15. Deslattes, R. D. and Hening, A. *Phys. Rev. Lett.* 31 (1973) 972.
16. Hambling, P. G. *Acta Crystallogr.* 6 (1953) 98.
17. Werner, P.-E. *Ark. Kemi* 31 (1969) 513.
18. Johansson, K. E., Palm, T. and Werner, P. E. *J. Phys. E.* 13 (1980) 1289.
19. Blom, B. and Hörlin, T. *Chem. Commun. Univ. Stockholm* (1977) No. 5.
20. Niklewski, T., Nygren, M., Kihlborg, L. and Sävborg, Ö. *Chem. Commun. Univ. Stockholm* (1975) No. 12.
21. Lundberg, M. and Sävborg, Ö. *Chem. Scr.* 13 (1978-79) 197.
22. Krylov, E. I., Bazeuv, G. V. and Khan, V. P. *Izv. Akad. Nauk SSSR, Neorg. Mater* 5 (1969) 239.
23. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B* 25 (1969) 925.
24. Werner, P.-E., Marinder, B.-O. and Magnéli, A. *Mater Res. Bull.* 13 (1978) 1371.
25. Marinder, B.-O., Werner, P.-E., Wahlström, E. and Malmros, G. *Acta Chem. Scand. A* 34 (1980) 51.
26. De Wolff, P. M. *J. Appl. Crystallogr.* 1 (1968) 108.
27. Smith, G. S. and Snyder, R. L. *J. Appl. Crystallogr.* 12 (1979) 60.

Received June 4, 1982.