Phase Analysis Studies in the System Cu_2O–Ta_2O_5*

Lena Jahnberg

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-10691 Stockholm, Sweden

Jahnberg, L., 1987. Phase Analysis Studies in the System Cu_2O–Ta_2O_5. – Acta Chem. Scand., Ser. A 41: 527–532.

By heating mixtures of Cu_2O and Ta_2O_5 *in vacuo* at 800–1100 °C, two different intermediate phases were prepared which are very close in composition: $Cu_5Ta_{11}O_{30}$ and $Cu_3Ta_7O_{19}$. They have similar structures, which are both built up of layers of α-U_3O_8 type (containing pentagonal bipyramids) and layers composed of octahedra. They differ only in the sequences of these layers. Other sequences occasionally occur and samples with disorder have also been prepared. Phases of low-Ta_2O_5 type are formed with small amounts of copper.

Several studies have been carried out on copper tantalum oxides. Most of this work has involved divalent copper. The phase $CuTa_2O_6$ has been reported by several authors as a cubic perovskite; it has also, more recently, been reported as tetragonal or orthorhombic and with a composition slightly deviating from the $CuTa_2O_6$ stoichiometry. These studies have been reviewed in Ref. 1, which also discusses phases with small amounts of CuO in low-Ta_2O_5 and a phase $Cu_xTa_3O_8$ ($0.77 \leq x \leq 0.85$) with mixed Cu(I) and Cu(II).

In earlier studies the phase $CuTaO_3$ has been reported to exist both as $Cu(I)Ta(V)O_3$ and $Cu(II)Ta(IV)O_3$.[2,3] According to Ref. 3 the former, with monovalent copper, was prepared at 1000 °C under vacuum or in an inert atmosphere, but had an unknown structure. The latter, prepared from Cu_2O and Ta_2O_5 in air, was a cubic perovskite. Since Ta(IV) is highly unlikely to be stable at high temperatures in air, this phase is very likely identical with the $CuTa_2O_6$ phase. Furthermore, a high-pressure modification of $CuTaO_3$ has been reported.[4]

In the course of studies of tantalum or niobium oxides containing α-U_3O_8-type layers of pentagonal bipyramids[5] the system Cu_2O–Ta_2O_5 has been studied, and the results are presented below.

Experimental

Mixtures of Cu_2O (Matheson, Coleman and Bell, min. 96 %) and Ta_2O_5 (Fluka AG, Buchs SG, min. 99.9 %) were heated in evacuated silica tubes in the temperature range 800–1100 °C. Some samples were prepared from Cu (Kebo, min. 99.9 %), CuO (Baker Analyzed, min. 99.9 %) and Ta_2O_5, with a slight excess of Cu to stabilize the monovalent state of copper. However the problem was rather the opposite: when tubes containing the Cu_2O–Ta_2O_5 samples were evacuated to 10^{-2} Torr, traces of copper metal appeared on the walls, indicating decomposition of the phases at low oxygen pressures. A thin Cu foil was used in some preparations to prevent the Cu_2O-rich samples from reacting with the silica tube. No significant differences were observed with these samples. At 1000–1100 °C the heating times were mostly 3–6 days and at lower temperatures 5 days to several weeks.

The samples were examined by means of Guinier powder diffraction using monochromated $CuK\alpha_1$ radiation [$\lambda = 1.54060$ Å (Ref. 6)]. For deriving unit cell parameters, the diffraction patterns were measured and evaluated with a film scanner system[7] using silicon as internal standard [$a = 5.43088$ Å (Ref. 8)]. The parameters were refined with the program PIRUM.[9]
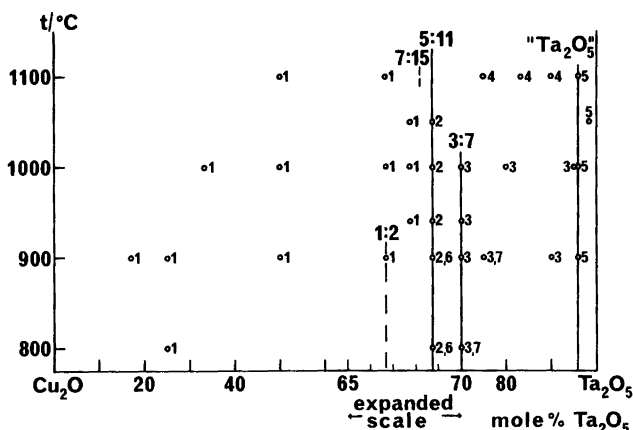
---

*Presented at the *XII Nordiska Strukturkemistmötet* in Sånga-Säby, Sweden, June 8–13, 1987.

Fig. 1. The system $Cu_2O-Ta_2O_5$. (5:11): $Cu_5Ta_{11}O_{30}$; (3:7): $Cu_3Ta_7O_{19}$; "Ta_2O_5": phase of low-Ta_2O_5 type; dashed lines indicate phases not formed in samples with corresponding compositions. Results of the analysis: 1: Cu_2O + (5:11); 2: (5:11), often with traces of (3:7) and/or "Ta_2O_5"; 3: (5:11) + more or less (3:7) + "Ta_2O_5", or (5:11) + "Ta_2O_5"; 4: (5:11) + "Ta_2O_5"; 5: "Ta_2O_5"; 6: (5:11) + (1:2); 7: (5:11) + (1:2) + "Ta_2O_5".

Results of the phase analysis

The results are summarized in Fig. 1. The region between 0 and 68 mole % Ta_2O_5 is a two-phase region involving Cu_2O and a phase which, according to a structure determination,[10] is expected to have the composition $Cu_5Ta_{11}O_{30}$ (68.75 mole % Ta_2O_5). This phase (which in the following will be called 5:11) is formed over the whole temperature range investigated. At the other end of the system a Ta_2O_5-like phase is formed, ap-

parently homogeneous from about 96 mole % Ta_2O_5.

From the stoichiometric composition of 5:11 to about 95 mole % Ta_2O_5 a third phase mostly appears together with 5:11 and "Ta_2O_5". Its composition is expected to correspond to 70 mole % Ta_2O_5, and in the following it will be called 3:7 (see below).

The samples formed in this region sometimes gave sharp diffraction lines for both 5:11 and 3:7 and sometimes diffuse lines for one or both

Table 1. Phases observed in the $Cu_2O-Ta_2O_5(-ZrO_2)$ systems.

Composition	Structure type[a]	Symmetry	Cell parameters/Å	Fig. of merit[b]
$Cu_5Ta_{11}O_{30}$	SD	hex.	a = 6.2297(2) c = 32.550(2)	M(20) = 34 F(86) = 51 (0.008, 200)
$Cu_3Ta_7O_{19}$	D	hex.	a = 6.2323(2) c = 20.156(1)	M(20) = 133 F(54) = 62 (0.007, 129)
$Cu_2O \cdot 25Ta_2O_5$	low-Ta_2O_5	orthorhomb.	a = 6.1940(5) b = 3.6607(4) (subcell) c = 3.8902(4)	
$Cu_{2.4}Ta_{3.6}Zr_{0.4}O_{11}$	S	trig. (rhomb.)	a = 6.2398(3) c = 37.342(3) (=3×12.447)	M(20) = 79 F(43) = 88 (0.008, 59)
"$Cu_7Ta_{15}O_{41}$"	SSD	hex.	a = 6.2262(2) c = 44.877(2)	M(20) = 40 F(74) = 96 (0.005, 143)
"$CuTa_3O_8$"	$NaNb_6O_{15}F$	orthorhomb.	a = 3.8843(4) b = 10.247(1) c = 14.880(1)	M(20) = 47 F(46) = 72 (0.008, 80)

[a]Letter symbols indicate the sequence of single (S) and double (D) layers of pentagonal TaO_7 bipyramids along the c-axis. [b]Refs. 23 and 24.
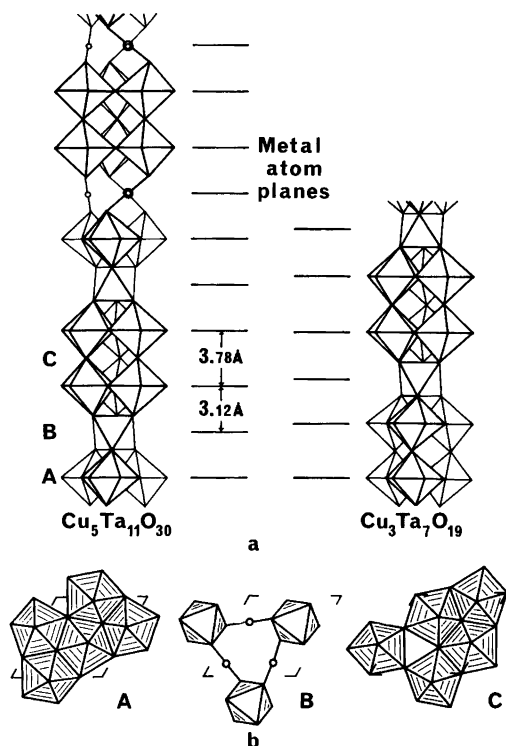
900 °C, a few samples with Ta_2O_5 content equal to or higher than that of 5:11, gave lines in the powder diffraction patterns similar to those of $Na_2Ta_4O_{11}$,[11] suggesting the presence of a $Cu_2Ta_4O_{11}$ phase. On further annealing at 900 °C this phase was transformed mainly into the 5:11 phase, but at 1100 °C additional new phases were formed. This is mentioned below in connection with discussion of the close structural relationships between most of the phases formed in this system.

In the two-phase region with Cu_2O and 5:11 some weak extra lines occur in the powder diffraction patterns (d-values/Å: 4.603, 4.208, 3.347 (strongest), 2.574, 2.367 and 1.674). Their existence has not been explained; only the strongest one is consistent with an SiO_2 line. These lines are most clearly seen in the most Cu_2O-rich samples, e.g. $5Cu_2O \cdot Ta_2O_5$ at 900 °C.

Description of the phases

The 5:11 phase is bright yellow, diamagnetic and has hexagonal symmetry (Table 1). From a structure determination[10] the composition is expected

Fig. 2. (a) Arrangement of polyhedra along the c-axis in $Cu_5Ta_{11}O_{30}$ and $Cu_3Ta_7O_{19}$. (b) The layers of polyhedra viewed along the c-axis. A and C: TaO_7 pentagonal bipyramids; B: TaO_6 octahedra and linear CuO_2.

phases. The 3:7 phase never occurred alone, although it was sometimes the dominant phase in samples of this composition at 900 °C. However, in some samples it was not formed at all. In this case the 5:11 phase gave very diffuse lines, indicating disorder. The 3:7 phase was not formed at 1100 °C, and it was slowly transformed to 5:11 when annealed at 900 °C for two months. Thus, 3:7 must be metastable, which explains why the results have not always been reproducible. The amount of 3:7 formed seems to be very much dependent on experimental conditions, such as oxygen pressure, homogeneity and rate of temperature change. The fact that traces of 3:7 and "Ta_2O_5" could be detected in samples with the stoichiometric composition of 5:11 is probably due to slight decomposition, giving copper metal as an additional phase.

When heated for about 10 days at 800 or

Table 2. Powder diffraction pattern for $Cu_3Ta_7O_{19}$. Reflections with asterisks overlap with those of other phases, and were not included in the refinement.

d_{obs}	I_{obs}	hkl	$2\theta_{obs}$	$2\theta_{calc}$
5.398	120	100	16.407*	16.410
5.212	44	101	16.997	16.993
5.040	138	004	17.583	17.587
4.759	35	102	18.630	18.634
3.683	11	104	24.147	24.143
3.360	562	006	26.507	26.512
3.115	168	110	28.631*	28.623
3.080	1000	111	28.969	28.971
2.9770	104	112	29.991	29.991
2.8522	24	106	31.337	31.339
2.8273	30	113	31.620	31.625
2.6991	54	200	33.165*	33.170
2.6746	25	201	33.478	33.475
2.6504	154	114	33.792	33.793
2.6068	146	202	34.375	34.374
2.5187	12	008	35.616	35.605
2.4660	544	115	36.403	36.413
2.3790	127	204	37.785	37.785
2.2844	61	116	39.412	39.410
		108		39.438
2.1147	112	117	42.723	42.722

Table 3. Some selected lines from a powder diffraction pattern for a multi-phase sample with about equal amounts of phases 5:11 and 3:7.

d_{obs}	I_{obs}	Phase	hkl	$2\theta_{obs}$	$2\theta_{calc}$
8.15	44	5:11	004	10.852	10.863
6.578	14	sum	008	13.449	13.429
5.423	998	5:11	006	16.332	16.326
5.040	250	3:7	004	17.580	17.587
4.068	152	5:11	008	21.827	21.826
3.767	20	sum	0014	23.598	23.613
3.359	1448	3:7	006	26.510	26.512
3.296	634	sum	0016	27.034	27.047
3.253	1836	5:11	0010	27.393	27.378
3.032	20	sum	114	29.430	29.436
2.936	169	sum	116	30.420	30.418
2.879	44	sum	117	31.036	31.040
2.816	14	sum	118	31.754	31.745
2.750	14	sum	119	32.528	32.527
2.682	344	sum	1110	33.385	33.382

to be $Cu_5Ta_{11}O_{30}$. The product reported by Shick and Vorres[3] as $Cu(I)Ta(V)O_3$ seems, from its appearance and from X-ray diffraction data, to be identical with $Cu_5Ta_{11}O_{30}$. The structure contains single and double TaO_7 – pentagonal bipyramid layers of α-U_3O_8[12] type, three-dimensionally connected by TaO_6 octahedra and linearly coordinated Cu (Fig. 2).

The 3:7 phase has almost the same yellow colour as 5:11. It has not been possible to prepare this phase free from 5:11, and heating times of up to two months at 900 °C only increase the amount of 5:11. From the resemblance of the powder pattern to those of YTa_7O_{19}[13] and $CeTa_7O_{19}$[14] it could be indexed on the basis of a hexagonal cell with almost the same a-axis length as 5:11 (Table 1). The composition is therefore expected to be $Cu_3Ta_7O_{19}$ and the structure to contain double α-U_3O_8-type tantalum-oxygen layers (Fig. 2), as has been shown for $CeTa_7O_{19}$[15] and also $LaTa_7O_{19}$.[16] The Cu atom positions differ from those of Y, Ce and La, and are expected to be of the same type as in $Cu_5Ta_{11}O_{30}$. The indexed powder pattern is summarized in Table 2.

The fact that the compositions 5:11 and 3:7 are very close and that the structures differ only in the thickness of the α-U_3O_8-type layers introduces the possibility of intergrowth between the two structures. Many preparations have given powder diffraction patterns with diffuse lines, but indications of some ordered intergrowth have

also been obtained. In a powder diffraction pattern with sharp lines for both 5:11 and 3:7, several lines which belong to neither 5:11 nor 3:7 can be indexed with an axis $c = c(5:11) + c(3:7)$, as shown in Table 3. The strongest reflection (0016), between (006) of 3:7 and (0010) of

Table 4. Powder diffraction pattern for $Cu_{2.4}Ta_{3.6}Zr_{0.4}O_{11}$.

d_{obs}	I_{obs}	hkl	$2\theta_{obs}$	$2\theta_{calc}$
6.234	232	006	14.197	14.219
5.199	328	102	17.040	17.068
4.679	40	104	18.950	18.960
3.534	39	108	25.179	25.191
3.123	644	110	28.562	28.588
3.112		0012	28.663	28.664
3.073	95	1010	29.035	29.043
3.028	1000	113	29.474	29.492
2.7900	632	116	32.055	32.065
2.6747	110	202	33.476	33.484
2.5961	381	204	34.521	34.530
2.4941	494	119	35.980	35.987
2.3918	37	1014	37.575	37.575
2.3386	339	208	38.462	38.466
2.2035	46	1112	40.924	40.928
2.1890	164	2010	41.207	41.207
2.0748	110	0018	43.588	43.593
2.0395	131	211	44.381	44.384
2.0306	49	212	44.586	44.592
1.9701	139	215	46.032	46.033

Table 5. Powder diffraction pattern for a phase with theoretical composition $Cu_7Ta_{15}O_{41}$.

d_{obs}	I_{obs}	hkl	$2\theta_{obs}$	$2\theta_{calc}$
7.492	38	006	11.802	11.823
5.615	184	008	15.770	15.785
5.358	125	101	16.532	16.546
5.247	198	102	16.883	16.898
5.075	98	103	17.461	17.469
4.860	78	104	18.239	18.240
4.622	36	105	19.185	19.187
4.489	38	0010	19.763	19.767
3.740	105	0012	23.769	23.774
3.661	34	109	24.295	24.293
		⎡0013		25.787
3.449	24	⎣1010	25.810	25.808
3.252	24	1011	27.404	27.392
3.206	549	0014	27.807	27.809
3.113	⎡371	110	28.655	28.652
3.104	⎣	111	28.741	28.722
3.083	74	112	28.938	28.932
3.071	86	1012	29.054	29.034
3.048	949	113	29.273	29.279
3.000	27	114	29.761	29.759
2.9412	216	115	30.365	30.366
2.9069	53	1013	30.733	30.729
⋮	⋮	⋮	⋮	⋮
2.4752	1000	1111	36.264	36.269

Table 6. Powder diffraction pattern for a phase of $NaNb_6O_{15}F$ type.

d_{obs}	I_{obs}	hkl	$2\theta_{obs}$	$2\theta_{calc}$
8.45	123	011	10.461	10.474
4.463	150	013	19.878	19.871
4.219	20	022	21.038	21.036
3.886	1000	100	22.868	22.876
3.719	358	004	23.908	23.901
3.527	82	111	25.233	25.219
3.328	919	031	26.765	26.758
3.009	657	024	29.669	29.653
2.9293	153	113	30.492	30.480
		⎡015		31.272
2.8565	312	⎣122	31.289	31.274
2.8122	269	033	31.795	31.784
2.6857	310	104	33.334	33.322
2.5606	33	040	35.015	34.999
2.5271	642	131	35.494	35.485
2.3789	490	124	37.786	37.779
2.3013	200	115	39.111	39.099
2.2774	143	133	39.538	39.521
2.2433	52	035	40.166	40.156
2.2316	48	026	40.386	40.373
2.1092	98	044	42.841	42.827

5:11, is in fact present, sometimes clear and sometimes very weak, in all sharp patterns yielded by samples in the composition region 5:11 to "Ta_2O_5", up to 1000 °C.

As shown in Fig. 2, the two structures contain six (3:7) and ten (5:11) metal atom planes perpendicular to the c-axis, making reflections $(006)_{3:7}$ and $(0010)_{5:11}$ strong. A combined unit cell would have 16 planes, corresponding to two single and four double layers, and thus a strong (0016) reflection. In the diffuse patterns the whole region between $(006)_{3:7}$ and $(0010)_{5:11}$ is diffuse.

In a structure with only single layers of pentagonal bipyramids the O:Ta ratio is 11:4. The possible phase $Cu_2Ta_4O_{11}$ would, however, have only 2/3 of the Cu positions occupied. This phase did not form in 1:2 composition samples, but for some samples richer in Ta_2O_5 lines indicating such a phase occurred in the powder pattern. This low occupancy of Cu positions seems to be possible only in combination with the other types of stacking, although always with a certain amount of disorder, leading to somewhat varying line positions. The Cu content can be increased to 2.4 by substitution of Zr for Ta. This results in about the same occupancy of the Cu positions as in $Cu_5Ta_{11}O_{30}$, and stabilizes the single-layer phase. The cell parameters and powder diffraction data for this phase are given in Tables 1 and 4.

One of the transformation products observed at 1100 °C may also be interpreted as an ordered combination containing four single and two double layers per unit cell (Table 1). This gives 14 tantalum planes and thus a strong (0014) reflection. The indexed powder pattern is summarized in Table 5. The theoretical composition would be 7:15. Electron microscopy studies are necessary for further elucidation of the intergrowth, and these are presently in progress.

For another sample in which the single-layer phase was partially transformed at 1100 °C, the new phase could be indexed on the basis of an $NaNb_6O_{15}F$ cell[17] (see Tables 1 and 6). This is surprising, since $Cu_xTa_3O_8$ ($x = 0.80$) with mixed Cu(I) and Cu(II)[18] has the $LiNb_6O_{15}F$ structure.[19]

531

These two structures both contain pentagonal columns but have different types of tunnels between them.

The "Ta_2O_5" phase, occurring in the Ta-rich region of the system, is pale green with a powder pattern very similar to that of low-Ta_2O_5 (Table 1). The electron diffraction pattern of this Cu-containing phase shows, like that of Ta_2O_5 itself, spacing anomalies[20] indicating an incommensurable structure. Its formation is accompanied by formation of copper metal, mainly on the walls of the silica tube. This might indicate a disproportionation reaction of Cu(I) to a Cu(II) compound and Cu metal. Thus, "Ta_2O_5" should belong to the $CuO–Ta_2O_5$ system, in which Ta_2O_5-like phases occur over a range of compositions.[21,22] However, this is uncertain since metal-like traces on the tube walls have occurred with several other samples.

Disproportionation processes may be favoured when the preparations are carried out in platinum tubes. They give different results, and a trirutile phase occurs. The unexplained extra powder diffraction pattern lines mentioned above seem to have some connection with this phase. Further studies of this problem are in progress.

References

1. Wa Ilunga, P. N. *Chem. Commun. Univ. Stockholm* (1983) No. 7.
2. Krylov, E. I., Samarina, V. A. and Shtolts, A. K. *Dokl. Akad. Nauk SSSR 130* (1960) 556.
3. Shick, L. and Vorres, K. S. *AEC Accession No. 46244,* Rept. No. TID-22207, Paper D (1965).
4. Sleight, A. W. and Prewitt, C. T. *Mater. Res. Bull. 5* (1970) 207.
5. Jahnberg, L. *Mater. Res. Bull. 16* (1981) 513.
6. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett. 31* (1973) 972.
7. Johansson, K.-E., Palm, T. and Werner, P.-E. *J. Phys. E 13* (1980) 1289.
8. Hubbard, C. R., Swanson, H. E. and Mauer, F. A. *J. Appl. Crystallogr. 8* (1975) 45.
9. Werner, P.-E. *Ark. Kemi 31* (1969) 513.
10. Jahnberg, L. *J. Solid State Chem. 41* (1982) 286.
11. Jahnberg, L. *J. Solid State Chem. 1* (1970) 454.
12. Loopstra, B. O. *Acta Crystallogr. 17* (1964) 651.
13. Jahnberg, L. *Chem. Commun. Univ. Stockholm* (1971) No. XIII.
14. Rossell, H. J. and Scott, H. G. *Mater. Res. Bull. 11* (1976) 1231.
15. Gatehouse, B. M. *J. Solid State Chem. 27* (1979) 209.
16. Langenbach-Kuttert, B., Sturm, J. and Gruehn, R. *Z. Anorg. Allg. Chem. 543* (1986) 117.
17. Andersson, S. *Acta Chem. Scand. 19* (1965) 2285.
18. Wa Ilunga, P. N., Marinder, B.-O. and Lundberg, M. *Chem. Scr. 18* (1981) 217.
19. Lundberg, M. *Acta Chem. Scand. 19* (1965) 2274.
20. Spyridelis, J., Delavignette, P. and Amelinckx, S. *Phys. Status Solidi 19* (1967) 683.
21. Wa Ilunga, P. N. *Acta Chem. Scand., Ser. A 37* (1983) 117.
22. Wa Ilunga, P. N. and Sundberg, M. *Mater. Res. Bull. 19* (1984) 807.
23. De Wolff, P. M. *J. Appl. Crystallogr. 1* (1968) 108.
24. Smith, G. S. and Snyder, R. L. *J. Appl. Crystallogr. 12* (1979) 60.