

Crookesite and sabatierite in a new light — A crystallographer's comment

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Abstract. Natural *crookesite* from Skrikerum, Sweden, is slightly copper-deficient ($\text{TlCu}_{6.8}\text{Se}_4$) as compared with the synthetic material TlCu_7Se_4 , which is isostructural with $\text{NH}_4\text{Cu}_7\text{S}_4$. The phase is tetragonal (space group $I\bar{4}$), the cell parameters of the mineral being $a = 10.4456(5)$ Å and $c = 3.9310(3)$ Å. For comparison, the parameters of the stoichiometric material are $a = 10.4524(2)$ Å and $c = 3.9736(1)$ Å. The chemical compositions were established by electron microprobe analyses on metallographically polished single crystals.

The diffraction data published for *sabatierite* correspond to a mineral of composition TlCu_4Se_3 , in contradiction to the microprobe data, TlCu_6Se_4 . Direct synthesis from the elements at 673 K did not yield any single phase at the latter composition. A new phase was found in the sulphur system with the probable composition TlCu_6S_4 . It is tetragonal ($I4/mmm$) with $a = 3.9465(1)$ Å and $c = 24.230(1)$ Å. The structure follows the same building principles as TlCu_2Se_2 and TlCu_4Se_3 .

Introduction

Mineralogical evidence exists for two thallium copper selenides, *crookesite* (Nordenskiöld, 1866) and *sabatierite* (Johan et al., 1978), but their crystallographic characterization is incomplete or contains contradictory elements. The former mineral was assigned the composition TlCu_7Se_4 (Johan et al., 1978) or TlCu_9Se_5 (Kvaček, 1979), possibly with small amounts of silver dissolved. A renewed microprobe analysis (Makovicky

et al., 1980) again suggested TlCu_7Se_4 , now on virtually silver-free material. Sabatierite was given the composition TlCu_6Se_4 (Johan et al., 1978; Makovicky et al., 1980).

In a recent study of the Tl-Cu-Se system, various ternary phases were characterized as regards both their composition and their crystallographic properties (Berger, 1987). At the composition " TlCu_7Se_4 " a single phase was obtained, while at " TlCu_6Se_4 " a three-phase mixture was established, that between TlCu_5Se_3 , TlCu_4Se_3 and Cu_{2-x}Se . The syntheses and annealings were performed at 673 K with TlSe, copper and selenium as starting materials. In view of these results, a few comments are needed on the current status of characterization of the two thallium minerals.

A crookesite sample was investigated by microprobe analysis and X-ray powder diffraction, while, unfortunately, no sample of sabatierite could be obtained. The equipment and procedures have already been described (Berger, 1987).

Results and discussion

A comparison between the d -values for crookesite and those of synthetic TlCu_7Se_4 (Table 1), clearly proves the phase identity. The microprobe data on the synthetic product (21.3% Tl, 46.1% Cu, 32.7% Se) are consistent with strict stoichiometry (Berger, 1987), while the author's mineral sample (Skrikerum, Sweden, 1866) must be assigned the formula $\text{TlCu}_{6.8}\text{Se}_4$ (21.8% Tl, 45.3% Cu, 32.9% Se). The relative standard deviations based on counting-statistics were of the order of 1%. No significant amounts of silver were detected, but there were inclusions of eucairite (AgCuSe). The presence of eucairite and berzelianite (Cu_7Se_4) might explain why the exact composition has been under dispute. Chemical analyses have been performed from time to time (Nordenskiöld, 1866; Johan et al., 1978; Kvaček, 1979; Makovicky et al., 1980), but only microanalysis on single crystals is reliable in a case where inclusions may occur.

Earley (1950) suggested an F-centred monoclinic cell for crookesite. This cannot, of course, be the true cell. However, Earley's tetragonal "subcell" is the correct one and was in fact used by Kvaček (1979) for indexing the powder diffraction data of the mineral to which the composition TlCu_9Se_5 was assigned. A synthesis at this composition (Berger, 1987) clearly gave a two-phase product, as evidenced by the diffraction lines of the main phase (TlCu_7Se_4) together with very weak ones due to Cu_2Se (Murray and Heyding, 1975). The latter phase also revealed its presence through a weak DTA peak at 408 K.

The d -values obtained from the crookesite sample — interfering calcite was removed by hydrochloric acid — lie between those found by Kvaček (1979) for a Bukov sample and those by Earley (1950) for a Skri-

kerum sample. The mineral gave (cf. Table 1) $a = 10.4456(5)$ Å and $c = 3.9310(3)$ Å, while Kvaček (1979) reported $a = 10.449(4)$ Å and $c = 3.956(8)$ Å. The synthetic product (Berger, 1987) has a significantly larger cell, $a = 10.4525(2)$ Å and $c = 3.9736(1)$ Å. This variance is entirely due to a different copper content, as indicated by the chemical analyses. Moreover, treatment of TlCu_7Se_4 with ammonia solution leaches copper from the material, which affects the c -axis the most, making it decrease (Berger, 1987).

The axial a/c -ratio of $\text{TlCu}_{7-x}\text{Se}_4$ lies very close to $\sqrt{7}$, the more so for the mineral ($x = 0.2$) than for the stoichiometric material. Consequently, natural crookesite yields a powder pattern with only partly resolved doublets (cf. Table 1). It is in fact possible – at least for data with poor resolution – to index a large portion of the low-angle lines on a primitive cubic (c) cell with $a_c = a_t/\sqrt{2} \approx 7.4$ Å. However, this model eventually gives mathematically impossible values for $h^2 + k^2 + l^2$ (such as 23, 28, 31 and 39) at higher angles. Hiller (1940) suggested $a_c = 14.69$ kX, implying body-centring with incredibly many extra extinctions. In the sulphur system, which shows large resemblances to the selenium system, Sobott (1984) indexed a compound TlCu_9S_5 on a cell with $a_c = 7.2$ Å from diffractometer data. A Guinier film taken of his specimen disclosed minute line splittings of the main phase and the very weak extra lines of accompanying Cu_2S (Berger and Sobott, 1987). Intensity calculations based on the coordinates of $\text{NH}_4\text{Cu}_7\text{S}_4$ (Gattow, 1957) showed very good agreement with the data observed for both TlCu_7Se_4 and TlCu_7S_4 . Accordingly, all these phases are isostructural.

The characterization of *sabatierite* presents a larger problem, partly because no specimen could be obtained for analysis. The mineral was assigned the composition TlCu_6Se_4 on the basis of microprobe analyses (Johan et al., 1978; Makovicky et al., 1980). However, this does not fit with the diffraction data. An orthorhombic (o) model was chosen where $b_o \approx a_o/\sqrt{2}$ (Johan et al., 1978). Another possibility discussed but discarded, was a tetragonal (t) I-centred lattice with $a_t = a_o$ and $c_t = 2c_o$. Of these two alternatives, the value of the density obtained for the orthorhombic cell, 6.8 g/cm^3 , was the more reasonable. Considering the well-characterized phases along the tie-line $\text{TlSe} - \text{Cu}_2\text{Se}$, this value appears far too low. A density of at least 7.2 g/cm^3 would be appropriate.

A study of the d -values found (Johan et al., 1978) shows that, in fact, they are the values expected for TlCu_4Se_3 (Klepp et al., 1980). The intensities also fit well this tetragonal model, where $a_t = a_o$ and $c_t = c_o$, taking possible texture effects into consideration. Moreover, the orthorhombic model gives far too many unobserved reflexions to be credible (Table 2). Thus, the X-ray data no doubt belong to TlCu_4Se_3 , which must occur as a mineral. Is this now the mineral to be called *sabatierite*, or does another occur with the composition TlCu_6Se_4 , as the microprobe data would suggest?

Table 1. Comparison between X-ray diffraction data of crookesite and those of synthetic TlCu_7Se_4 . The figure within brackets refer to the sources: [1]: Berger, 1987; [2]: Kvaček et al., 1979; [3]: Earley, 1950; [4]: this work, mineral sample from 1866 (cf. Nordenskiöld, 1866). The intensities were calculated using slightly modified parameters from $\text{NH}_4\text{Cu}_7\text{S}_4$. The calculated d -values emanate from least-squares refinements of the tetragonal cells. The indices at the left apply to all material and follow the order dictated by the stoichiometric material.

I_{calc}	I_{obs}	hkl	TlCu_7Se_4 [1]		Crookesite			
			d_{calc}	d_{obs}	d_{obs} [2]	d_{obs} [3] ^a	d_{obs} [4]	d_{calc} [4]
6	3	110	7.391	7.392			7.400	7.386
29	19	200	5.226	5.226	5.211	5.21	5.228	5.223
8	9	101	3.7142	3.7143				3.679
4	6	220	3.6955	3.6960	3.682	3.72	3.684	3.693
106	76	310 ^b	3.3053	3.3053	3.294	3.30	3.3045	3.3032
126	116	211	3.0275	3.0271	3.015	3.01	3.0090	3.0078
83	122	301	2.6197	2.6205			2.6078	2.6065
28		400	2.6131	2.6133	2.612	2.60	2.6124	2.6114
13	27	330	2.4637	2.4637	2.456	2.44	2.4623	2.4621
62	83	321	2.3420	2.3424				2.3322
18		420	2.3372	2.3374	2.333	2.32	2.3330	2.3357
89	91	411	2.1372	2.1374	2.132	2.11	2.1299	2.1295
8	10	510	2.0499	2.0497	2.028 ^c		2.0487	2.0486
58	72	002	1.9868	1.9873	1.973	1.971	1.9656	1.9655
—	—	112	1.9178					1.8994
4	1	202	1.8571	1.8574			1.8404	1.8396
66	100	501						
35		431	1.8501	1.8503	1.845	1.837	1.8448	1.8448
2	—	440	1.8477					1.8466
70	69	530	1.7926	1.7925	1.791	1.783	1.7912	1.7914
1	1	222	1.7499					1.7351
26	28	521	1.7440	1.7441			1.7394	1.7395
2		600	1.7421		1.735 ^c	1.729		1.7409
32	38	312	1.7028	1.7030	1.694	1.685	1.6887	1.6891
4	9	620	1.6527	1.6526	1.650	1.640	1.6516	1.6516
13	22	402	1.5816	1.5816			1.5707	1.5704
19	38	611	1.5772	1.5771	1.574	1.566	1.5736	1.5737
7	12	332	1.5466	1.5465	1.541	1.533	1.5357	1.5361
12	13	422	1.5138	1.5137			1.5040	1.5039
10	12	541	1.5099	1.5098	1.508	1.498	1.5065	1.5067
5	6	550						
1		710	1.4782	1.4781	1.477		1.4775	1.4772
17	21	631	1.4506	1.4503		1.442	1.4480	1.4477
2		640	1.4495		1.449			1.4486
6	7	512	1.4267	1.4266	1.421		1.4186	1.4183
5	6	701	1.3978	1.3976	1.397		1.3956	1.3951
4	3	730	1.3725	1.3726	1.372		1.3715	1.3716
2	—	442	1.3530					1.3458
5	—	721	1.3503		1.349			1.3478
63	64	532	1.3309	1.3308	1.327	1.322	1.3237	1.3240
—	—	103	1.3140					1.3002

Table 1. (Continuation)

I_{calc}	I_{obs}	hkl	TiCu ₁ Se ₄ [1]		Crookesite			
			d_{calc}	d_{obs}	d_{obs} [2]	d_{obs} [3] ^a	d_{obs} [4]	d_{calc} [4]
1	7	602	1.3099					1.3032
5		800	1.3065	1.3064			1.3059	1.3057
8	20	213	1.2744	1.2743			1.2618	1.2616
4	17	622	1.2706	1.2706			1.2651	1.2645
12		651	1.2683					1.2662
35	43	820	1.2675	1.2676	1.267	1.259	1.2666	1.2667
11	9	303	1.2381	1.2379			1.2262	1.2264
7	25	741	1.2325				1.2303	1.2305
3		811		1.2321	1.231	1.225		
10		660	1.2318					1.2310
4	7	750	1.2151	1.2148	1.214		1.2141	1.2143
12	16	323	1.2047	1.2046	1.200		1.1933	1.1939
7	6	552	1.1860	1.1858	1.183		1.1808	1.1809
2		712						
19	23	413	1.1739	1.1738	1.171 ^c	1.160	1.1636	1.1639
3	4	642	1.1710	1.1712				1.1661
21	21	831	1.1692	1.1688			1.1672	1.1674
2		840	1.1686					1.1679
5	4	910	1.1543	1.1543	1.155		1.1540	1.1535
7	4	732	1.1292	1.1294				1.1248
25	38	503	1.1189	1.1190	1.116	1.108	1.1103	1.1101
14		433						
21	16	901	1.1147	1.1147			1.1134	1.1131
2	3	930	1.1018	1.1020				1.1011
12	15	523	1.0941	1.0940			1.0856	10.858
9	38	802	1.0917	1.0914				1.0876
9		761	1.0902	1.0902		1.083	1.0889	1.0887
9		921						

^a Transformed to Å units from kX by factor 1.002.

^b Rotation hkl includes hkl , the d -values being equal and their intensities being summed from powder diffraction.

^c Overlap by lines of berzelianite in the sample.

In the case of crookesite, different microprobe determinations yielded as different results as TiCu₇Se₄ and TiCu₉Se₅. The same systematic errors might be involved here too, since the suggested compositions are fairly similar. Especially fine-grained material can present large problems. Otherwise, *two* minerals must exist — probably with a similar crystal habit — one being responsible for the powder pattern (TiCu₄Se₃) and the other for the chemical analysis results (TiCu₆Se₄).

Synthesis of a possible product TiCu₆Se₄ at 673 K (Berger, 1987) yielded a three-phase mixture with TiCu₄Se₃ as the main constituent. Tédénac et al. (1981) cast some doubt on the existence of TiCu₆Se₄ and tried in vain

Table 2. Comparison between X-ray data of TiCu_4Se_3 and *sabatierite* (Johan et al., 1978). Orthorhombic indexing (see text) was used for the latter. The data for TiCu_4Se_3 were collected from a powder film on three-phase material obtained at the nominal composition TiCu_6Se_4 (claimed for *sabatierite*). Some reflexions were overlapped (given as *o* in the column of *d*-values) by the other phases, mainly by copper-deficient TiCu_5Se_3 having the cell parameters $a = 12.9034(4) \text{ \AA}$ and $c = 3.9776(2) \text{ \AA}$. The cell for TiCu_4Se_3 was $a = 3.9771(2) \text{ \AA}$ and $c = 9.8406(7) \text{ \AA}$. The observed intensities from overlapped reflexions were obtained from samples at other compositions containing this phase.

TiCu ₄ Se ₃ (tetragonal model)					Sabatierite (orthorhombic model)					
<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs}	<i>I</i> _{calc}	Observations related to model				Missing reflexions	
					<i>I</i> _{obs}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>	<i>d</i> _{calc} (Å)	<i>hkl</i>
001	9.847	9.841	0.1	0.1					9.778	001
002		4.920		0.05					5.624	010
100	3.980	3.977	0.6	0.8	5	3.987	3.986	100	4.889	002
101	3.689	3.687	0.4	0.4	2	3.705	3.691	101	4.875	011
003	3.281	3.280	0.9	1			3.690	012	3.259	003
102	3.094	3.093	10	10	10	3.089	3.089	102	3.252	110
110	2.813	2.812	1	0.7			3.086	111	2.302	113
111	2.706	2.704	6	4	2	2.818	2.820	013	2.298	120
103	2.5308	2.5305	2	2			2.812	020	2.241	014
004	<i>o</i>	2.4602		0.2	7	2.706	2.708	112	2.237	121
112	2.4414	2.4416	3	2			2.703	021	1.956	005
113	<i>o</i>	2.1350	2	2	5	2.525	2.523	103	1.954	114
104	2.0918	2.0922	1	1	6	2.445	2.445	004	1.953	201
200	1.9885	1.9886	7	4			2.438	022	1.879	210
005		1.9681		0.2	4	2.129	2.129	023	1.878	123
201		1.9492		0.02	3	2.087	2.084	104	1.875	030
114	1.8515	1.8516	3	3			2.080	122	1.756	105
202		1.8437		0.03	7	1.991	1.992	200	1.754	212
210		1.7786		0.2	6	1.847	1.847	015	1.750	032
205		1.7640		0.02			1.846	202	1.696	130
211		1.7503		0.1			1.845	024	1.630	006
203	1.7004	1.7005	0.4	0.7			1.845	211	1.628	213
212	1.6727	1.6727	4	3			1.841	031	1.626	220
006	<i>o</i>	1.6401	0.4	0.8	1	1.786	(Inexplicable)		1.625	033
115	1.6124	1.6125	1	1	5	1.673	1.676	115	1.545	204
213	1.5635	1.5636	1	1			1.674	124	1.543	222
204		1.5465		0.2			1.671	131	1.509	106
106		1.5162		0.4	3	1.609	1.606	025	1.505	133
214	<i>o</i>	1.4414	1	0.8			1.604	221	1.490	214
116		1.4168		0.06	3		1.603	132	1.489	125
220	1.4061	1.4061	2	2		1.565	1.565	016	1.488	034
007		1.4058		0.06	3	1.406	1.410	026	1.457	116
205		1.3988		0.3			1.406	040	1.455	223
221		1.3920		0.01					1.397	007
222		1.3520		0.02					1.396	205
300		1.3257		0.05					1.394	134
107		1.3254		0.4					1.392	041

Table 2. (Continuation)

TiCu ₄ Se ₃ (tetragonal model)					Sabatierite (orthorhombic model)					
<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs}	<i>I</i> _{calc}	Observations related to model				Missing reflexions	
					<i>I</i> _{obs}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>	<i>d</i> _{calc} (Å)	<i>hkl</i>
215		1.3196		0.02					1.366	230
301		1.3138		0.03					1.356	017
223		1.2924		0.3					1.355	215
302	0	1.2801		1					1.354	224
206	1.2653	1.2653	1	2					1.353	035
310		1.2577		0.2					1.352	231
117		1.2574		0.2					1.351	042
311	0	1.2475		1	2	1.266	1.262	206	1.329	126
008		1.2301		0.02			1.259	233	1.329	300
303		1.2291		0.4					1.326	140
224	0	1.2208		0.2					1.318	107
312		1.2185		0.7					1.317	301
									1.315	232
									1.314	141
									1.293	310
									1.291	043
									1.284	117
									1.282	302

to prepare it with syntheses in the range TiCu₄Se₃–TiCu₇Se₄. The latter phase may be copper-deficient, as exemplified by crookesite, but not to the extent of making $x = 1$ in the formula TiCu_{7-x}Se₄.

Makovicky et al. (1980) and Klepp et al. (1980) discussed the structure series AM_{2n}X_{n+1}, with sulphides and selenides as members, such as TiCu₂Se₂ ($n = 1$) and TiCu₄Se₃ ($n = 2$). The composition TiCu₆Se₄ would thus represent $n = 3$. The structural principles of the known first end members disclose that n represents the number of layers of tetrahedrally coordinating copper inserted between layers of cubically coordinating thallium with respect to the chalcogen. The ultimate end member for an infinite number of copper-containing layers is then Cu₂X (X = S, Se), which may, indeed, crystallize in the anti-fluorite structure.

Exploring the consequences of these principles further, one expects tetragonal cells which have a fairly constant a -axis and which are I-centred when n is odd and primitive when n is even. The c -axis is determined from the layer sequence. Thus, with C and T representing the thickness of cubic and tetrahedral layers, respectively, one obtains $c_1(n_{\text{odd}}) = 2(C + nT)$ and $c_1(n_{\text{even}}) = C + nT$. Furthermore, if the coordination about thallium is taken as strictly cubic, then $C = a_1$. Accordingly, the a -axis of (hypothetical?)

TiCu_6Se_4 may be estimated as $c_t = 2(a_t + 3T) = 3(a_t + 2T) - a_t = 3c_t[\text{TiCu}_4\text{Se}_3] - a_t = 25.54 \text{ \AA}$. For the analogue TiCu_6S_4 , using the parameters of TiCu_4S_3 , one obtains $c_t = 24.15 \text{ \AA}$.

This estimation emerges to be very good. TiCu_6S_4 was obtained when heat-treating a sample of nominally $\text{TiCu}_{6.4}\text{S}_{3.8}$ at 625 K for one week. Extremely thin plate-like crystals were found. These were investigated in a Weissenberg camera and showed an I-centred tetragonal cell. The refined parameters (powder diffraction) are $a = 3.9465(1) \text{ \AA}$ and $c = 24.230(1) \text{ \AA}$. Intensity calculations based on an $I4/mmm$ structure built of layers in the prescribed manner as above showed very good agreement with the observed values. In view of the success of this model for the sulphur system and the fact that these sulphides and selenides are very similar, there is reason to believe that an estimation of the cell parameters for TiCu_6Se_4 – if the substance exists in this form – would be equally effective. Therefore, intensity calculations were performed for a cell with parameters $a_t = 3.99 \text{ \AA}$ and $c = 25.6 \text{ \AA}$, showing that the strongest powder line would be due at $d(105) = 3.15 \text{ \AA}$. Other prominent lines would occur at 2.76, 2.00, 1.90 and 1.69 \AA , values that do not occur for *sabatierite* (Table 2: Johan et al. 1978). The density of such a modification of TiCu_6Se_4 becomes 7.35 g/cm^3 , which fits very well with expectations.

To conclude, the new crystallographic and chemical analysis data prove that *crookesite* is a slightly copper-deficient member of the $\text{NH}_4\text{Cu}_7\text{S}_4$ structure type. On the other hand, the true composition of *sabatierite* could not be determined. The published diffraction data are definitely due to TiCu_4Se_3 , which thus occurs as a mineral. If another mineral exists with the composition TiCu_6Se_4 , it is probably isostructural with TiCu_6S_4 . Accordingly, it is strongly recommended that the mineral sample be reinvestigated for a better characterization of the species.

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