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

Rolf A. Berger

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Crookesite | Sabatierite | Thallium copper chalcogenides | Crystal structure

Abstract. Natural *crookesite* from Skrikerum, Sweden, is slightly copper-deficient ($TlCu_{6.8}Se_4$) as compared with the synthetic material $TlCu_7Se_4$, which is isostructural with $NH_4Cu_7S_4$. 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 $TlCu_{6.8}Se_4$ (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 $TlCu_{7-x}Se_4$ 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 $NH_4Cu_7S_4$ (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 $TlSe-Cu_2Se$, 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 $NH_4Cu_7S_4$. 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	3.682	3.72	3.684	3.679
4	6	220	3.6955	3.6960				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	2.612	2.60	2.6078	2.6065
28 }		400	2.6131	2.6133			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	2.333	2.32	2.3330	2.3322
18 }		420	2.3372	2.3374				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	1.8501	1.8503	1.845	1.837	1.8448	1.8448
35 }		431						
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	1.735[c]	1.729	1.7394	1.7395
2 }		600	1.7421					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	1.574	1.566	1.5707	1.5704
19	38	611	1.5772	1.5771			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	1.508	1.498	1.5040	1.5039
10	12	541	1.5099	1.5098			1.5065	1.5067
5 }	6	550	1.4782	1.4781	1.477		1.4775	1.4772
1 }		710						
17 }	21	631	1.4506	1.4503	1.449	1.442	1.4480	1.4477
2 }		640	1.4495					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		1.349			1.3458
5	—	721	1.3503					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	TlCu$_1$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 }		802	1.0917	1.0914				1.0876
9 }	38	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 TlCu$_7$Se$_4$ and TlCu$_9$Se$_5$. 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 (TlCu$_4$Se$_3$) and the other for the chemical analysis results (TlCu$_6$Se$_4$).

Synthesis of a possible product TlCu$_6$Se$_4$ at 673 K (Berger, 1987) yielded a three-phase mixture with TlCu$_4$Se$_3$ as the main constituent. Tédénac et al. (1981) cast some doubt on the existence of TlCu$_6$Se$_4$ and tried in vain

Table 2. Comparison between X-ray data of $TlCu_4Se_3$ and sabatierite (Johan et al., 1978). Orthorhombic indexing (see text) was used for the latter. The data for $TlCu_4Se_3$ were collected from a powder film on three-phase material obtained at the nominal composition $TlCu_6Se_4$ (claimed for sabatierite). Some reflexions were overlapped (given as o in the column of d-values) by the other phases, mainly by copper-deficient $TlCu_5Se_3$ having the cell parameters $a = 12.9034(4)$ Å and $c = 3.9776(2)$ Å. The cell for $TlCu_4Se_3$ was $a = 3.9771(2)$ Å and $c = 9.8406(7)$ Å. The observed intensities from overlapped reflexions were obtained from samples at other compositions containing this phase.

$TlCu_4Se_3$ (tetragonal model)				Sabatierite (orthorhombic model)					
				Observations related to model				Missing reflexions	
hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkl	d_{calc} (Å)	hkl
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	o	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	o	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	o	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	o	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)

TlCu₄Se₃ (tetragonal model)					Sabatierite (orthorhombic model)					
hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}	Observations related to model				Missing reflexions	
					I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkl	d_{calc} (Å)	hkl
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 o		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 o		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 o		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 $TlCu_4Se_3 - TlCu_7Se_4$. The latter phase may be copper-deficient, as exemplified by crookesite, but not to the extent of making $x = 1$ in the formula $TlCu_{7-x}Se_4$.

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 $TlCu_2Se_2$ ($n = 1$) and $TlCu_4Se_3$ ($n = 2$). The composition $TlCu_6Se_4$ 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 Cu_2X ($X = S$, 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 $c_t(n_{odd}) = 2(C + nT)$ and $c_t(n_{even}) = C + nT$. Furthermore, if the coordination about thallium is taken as strictly cubic, then $C = a_t$. Accordingly, the a-axis of (hypothetical?)

$TlCu_6Se_4$ may be estimated as $c_t = 2(a_t + 3T) = 3(a_t + 2T) - a_t = 3c_t[TlCu_4Se_3] - a_t = 25.54$ Å. For the analogue $TlCu_6S_4$, using the parameters of $TlCu_4S_3$, one obtains $c_t = 24.15$ Å.

This estimation emerges to be very good. $TlCu_6S_4$ was obtained when heat-treating a sample of nominally $TlCu_{6.4}S_{3.8}$ 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 $a = 3.9465(1)$ Å and $c = 24.230(1)$ Å. 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 $TlCu_6Se_4$ — if the substance exists in this form — would be equally effective. Therefore, intensity calculations were performed for a cell with parameters $a_t = 3.99$ Å and $c = 25.6$ Å, showing that the strongest powder line would be due at $d(105) = 3.15$ Å. Other prominent lines would occur at 2.76, 2.00, 1.90 and 1.69 Å, values that do not occur for sabatierite (Table 2: Johan et al. 1978). The density of such a modification of $TlCu_6Se_4$ 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 $NH_4Cu_7S_4$ structure type. On the other hand, the true composition of sabatierite could not be determined. The published diffraction data are definitely due to $TlCu_4Se_3$, which thus occurs as a mineral. If another mineral exists with the composition $TlCu_6Se_4$, it is probably isostructural with $TlCu_6Se_4$. Accordingly, it is strongly recommended that the mineral sample be reinvestigated for a better characterization of the species.

References

Berger, R.: A phase-analytical study of the Tl-Cu-Se system. J. Solid State Chem. **70** (1987) 65–70.

Berger, R. A., Sobott, R. J.: Characterization of $TlCu_7S_4$, a crookesite analogue. Monatsh. Chem. **118** (1987) 967–972.

Earley, J. W.: Description and synthesis of the selenide minerals. Am. Mineral. **35** (1950) 337–364.

Gattow, G.: Die Kristallstruktur von $NH_4Cu_7S_4$. Acta Crystallogr. **10** (1957) 549–553.

Hiller, J. E.: The lattice constants of crookesite, argyrodite and canfieldite. Zentralbl. Mineral. **1940 A**, 138–142.

Johan, Z., Kvaček, M., Picot, P.: La sabatierite, un noveau séléniure de cuivre et du thallium. Bull. Minéral. **101** (1978) 557 — 560.

Klepp, K., Boller, H., Völlenkle, H.: Neue Verbindungen mit KCu_4S_3-struktur. Monatsh. Chem. **111** (1980) 727 — 733.

Kvaček, M.: Selenides from the deposits of Western Moravia, Czechoslovakia — part 2. Acta Univ. Carol.-Geol. **1 — 2** (1979) 15 — 38.

Makovicky, E., Johan, Z., Karup-Møller, S.: New data on bukovite, thalcusite, chalcothallite and rohaite, Neues Jahrb. Mineral. Abh. **138** (1980) 122 — 146.

Nordenskiöld, A. E.: Undersökning af Selenmineralierna från Skrikerum. Öfv. Kgl. Vet.-Akad. Förhandl. **23** (1866) 361 — 367.

Sobott, R.: Das System $Tl_oS — Cu_2S$. Monatsh. Chem. **115** (1984) 1397 — 1400.

Tédénac, J.-C., Brun, G., Maurin, M.: Propriétés physico-chimiques des phases du ternaire cuivre-thallium-sélénium. Rev. Chim. Fr. minér. **18** (1981) 69 — 73