Zeitschrift: Archives des sciences et compte rendu des séances de la Société
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 47 (1994)
Heft: 2: Archives des Sciences

Artikel: A note on the crystal structure of schulenbergite
Autor: Mumme, William G. / Sarp, Halil / Chiappero, Pierre J.
DOI: https://doi.org/10.5169/seals-740178

Archs Sci. Genève	Vol. 47	Fasc. 2	pp. 117-124	Septembre 1994

A NOTE ON THE CRYSTAL STRUCTURE OF SCHULENBERGITE

BY

William G. MUMME*, Halil SARP & Pierre J. CHIAPPERO*****

(Ms reçu le 3.2.1994, accepté le 31.5.1994)

ABSTRACT

A note on the crystal structure of schulenbergite. - The ratio Cu:Zn in schulenbergite, described originally by Hodenberg, is 1.3. In a Cu-rich variety of schulenbergite from the Cap Garonne mine, the ratio Cu:Zn is 6. This difference in chemical composition strongly modifies the reported refractive indices. Furthermore, Weissenberg X-ray films exposed over a long duration indicate that the a=8.27 x c=7.11 Å cell ascribed to schulenbergite represents a subcell of the Cu-rich variety, and the unit cell of Cu-rich schulenbergite is actually much larger. Although it has not been possible to define this cell accurately, the structure of the sub-cell of Cu-rich schulenbergite has been determined using a combination of the Patterson method and atomic site restrictions. This structure, which is based on brucite-like layers, represents a ideal model for Cu-rich schulenbergite. If schulenbergite as previously described by Hodenberg does not possess the superlattice found in the Cu-rich variety, then it probably constitutes a different mineral phase.

INTRODUCTION

Schulenbergite was originally described by Hodenberg *et al.* (1984) as (ideally) $(Cu, Zn)_7(SO_4, CO_3)_2(OH)_{10}.3H_2O$, with the proportion of Cu:Zn not varying much from 1:1. Carbonate was found to substitute in small amounts for sulphate in this material.

More recently a sample which contains Cu-rich schulenbergite, with idealized formula $Cu_6Zn(SO_4)_2(OH)_{10}.3H_2O$, has been collected in the mine at Cap Garonne (Var, .France). The mineral is associated with brochantite, serpierite, linarite, and Co-Ni ktenasite (Sarp *et al.*, 199O). Schulenbergite from Cap Galonne is emerald-green and forms aggregates or spherules (diameter ~ 0.25 mm) made up of thin platy hexagonal crystals.

Physical and optical properties

The crystals are transparent with vitreous lustre, pale green streak and perfect basal cleavage {00 1}. The measured density obtained using heavy liquids is 3.42(2)gm/cm^3;

* CSIRO, Division of Mineral Products, P.O.Box 124, Port Melbourne, Victoria 3207, Australia.

** Département de Minéralogie du Muséum d'Histoire naturelle, C.P. 6434, CH-1211 Genève 6.

*** 27, Rue du Pressoir Neuf, 45000 Orléans, France.

the calculated density using the formula $Cu_6Zn(SO_4)_2(OH)_{10}.3H_2O$ is 3.45 gm/cm^3. Cu-rich schulenbergite is highly pleochroic, uniaxial (–) with ϵ =1.666 and ω =1.707 (both measured at 590 nm). ϵ is colourless to clear green: ω is emerald-green to green. The material described by Hodenberg *et al.* (1984) has ϵ =1.623 and ω =1.640. The large difference between these two sets of refractive indices is due to the high Cu content in the present material, Cu/Zn ~ 6, whereas for the first reported occurrence Cu/Zn ~ 1.3.

Chemical composition

The chemical composition was determined by electronprobe microanalysis (EPMA) using a Cameca microprobe. Preliminary investigation using qualitative methods indicated the presence of Cu, Zn, Co, Ni, S and very small amounts of C. Quantitative analyses using the wavelength dispersive spectrometers were carried out at 15 KV operating voltage and 9na incident current. The standards used were Cu, Co and Ni metals, and ZnS . The result of nine analyses and their average are presented in Table 1. The average composition may be best expressed by the formula

$CU_{5.7}Zn_{1.3}(SO_4)_{1.8}(OH)_{10.4}.3H_2O$, which requires CuO, 53.28; ZnO, 12.44; SO_3, 16.93; H_2O, 17.35.

X ray crystallography

A powder X ray pattern of Cu-rich schulenbergite was obtained using a 114.6 mm diameter Gandolfi camera and Ni-filtered CuKα radiation. An acceptable monocrystal was also studied using precession and Weissenberg cameras. The symmetry determined from the single crystal is trigonal, space group P3 or P$\bar{3}$. Lattice constants are a = 8.211(2), c=7.106(2)Å and the values of d_{calc} and d_{obs} resulting from the least squares refinement and indexing procedure are listed in Table 2. However rotation films indicate that Cu-rich schulenbergite has a **c** axis which is greater than 7. 1 Å because very weak intermediate layer lines are visible on long film exposures. In addition weak reflections intermediate to the a=8.21Å hexagonal reciprocal lattice are also visible on the Weissenberg films of the 0, 1, 2, and 3rd levels of the 7. 1Å axis, indicating a larger **a** cell dimension. It is suggested therefore that for the present case the 8.21x7.11Å hexagonal cell represents only the subcell of one which is much larger, and not readily determined at this stage.

Gladstone-Dale calculations

Using the relationships in Mandarino (1981), with ϵ =1.666, ω =1.707 and $\bar{n}$=1.693,

$$K_p = \frac{1.693 - 1}{d_{meas}} = 0.203$$

For the average formula derived from EPMA, K_c = 0.202; for the idealized formula $CU_6Zn(SO_4)_2(OH)_{10}.3H_2O$, K_c = 0.199. These values result in $1 - K_p/K_c$ = 0.005 and

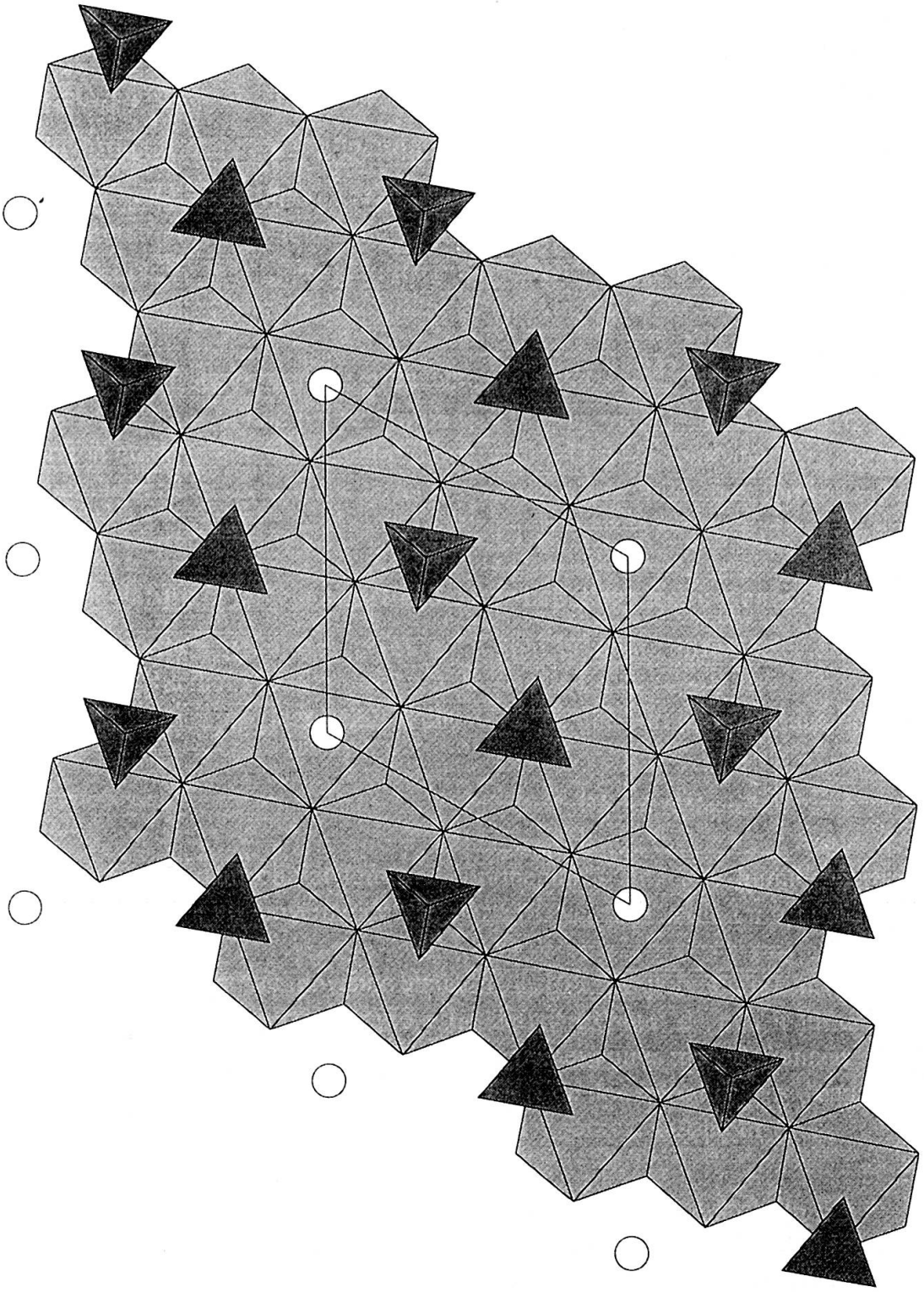

FIG. 1. Projection onto (001) of the structure of schulenbergite.

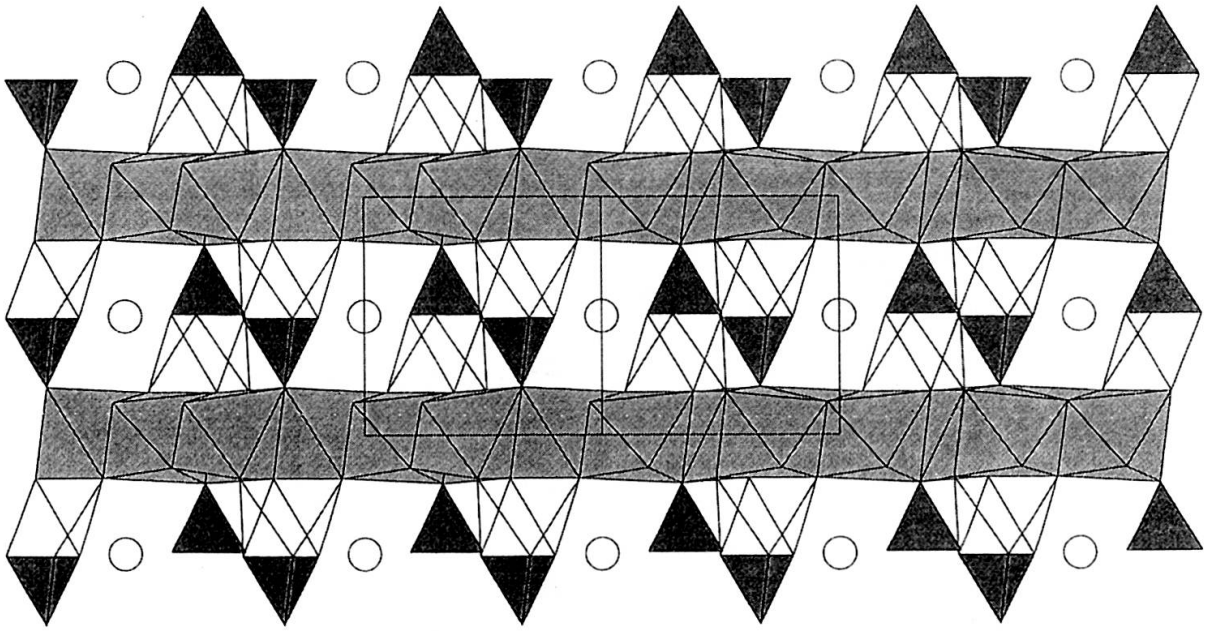

FIG. 2. Projection onto (110) of the atomic structure of schulenbergite showing the brucite-like layers of edge-shared CuO_6 octahedra which are joined together mostly via the SO_4 groups and their attached hydrogen bonds.

0.020 which (respectively) indicate superiour and excellent compatability index agreements relating the refractive indices, densities and chemical composition.

Crystal structure determination and description

X ray data were collected using a Siemens AED single crystal diffractometer with Mo radiation, Θ-2 Θ scans, and a standard reflection was measured every 50 reflections. In all, 1200 reflections were merged to yield 505 unique reflections.

The substructure was solved using a combination of the Patterson method and atomic site restrictions due to the overall mineral chemistry which suggests that one Cu atom occupies the origin in P3. Atom positions are given in Table 3; bond lengths in Table 4. The crystal structure proposed for Cu-rich schulenbergite (subcell only) is illustrated in Figs. 1 and 2 which are projections onto (001) and (110). The structure consists of brucite-like layers of edge-shared (predominently) CuO_6 octahedra which are joined together mostly via the SO_4 groups and their attached hydrogen bonds. For the purposes of the illustrated structure the free water located above Cu, Zn2 is placed at 001/2 although it is apparently disordered around this site in the subcell described here. Cu, Zn ordering could not be determined.

The proposed structure must be regarded as an idealized model for the structure of schulenbergite. Sites containing some electron density were also observed in the Fourier maps at levels between the octahedral layers, reflecting the ordering of more complicated layer sequences and displacements in the larger true cell. Apart from this

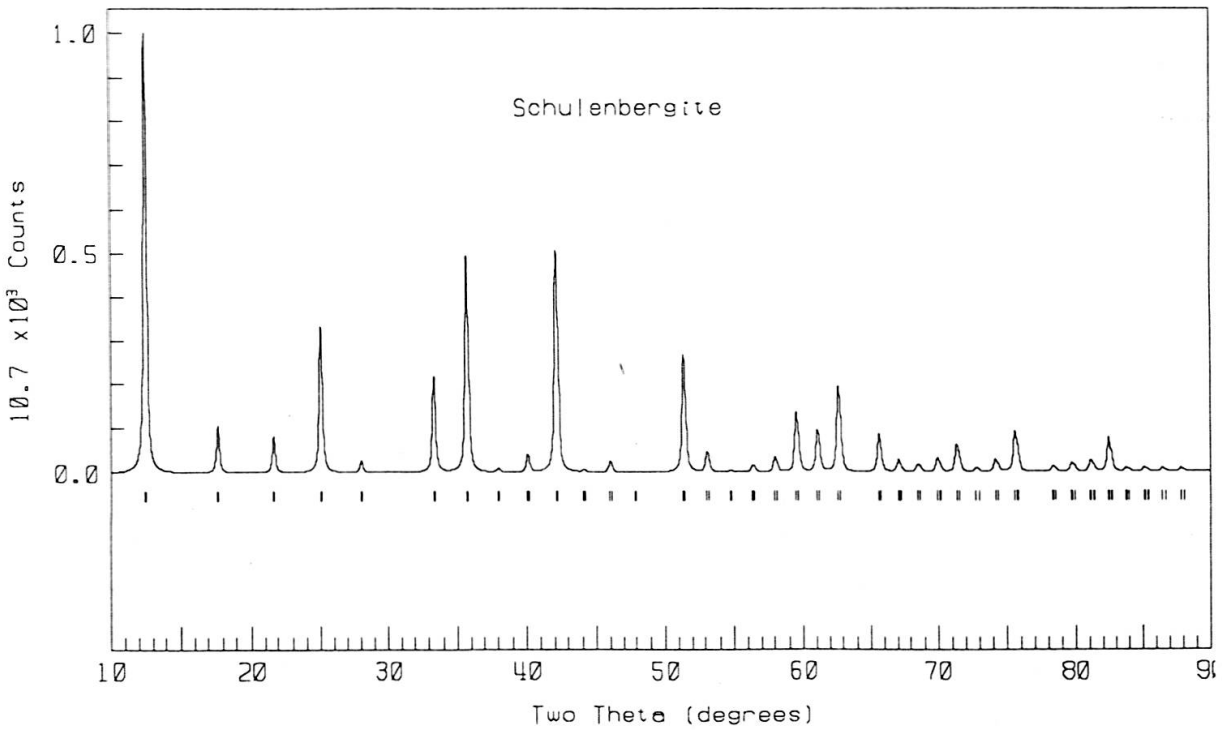

FIG. 3. Calculated powder pattern for Cu-riche schulenbergite.

aspect, stacking faults also probably exist in this type of structure. Refinements in P3 symmetry which incorporated some of these partially occupied sites into a subcell structure resulted in an improved agreement. It is not known whether the Zn richer variety described by Hodenberg *et al.* (1984) similarly displays intermediate layer lines in rotation films or whether the Cu-rich variety described here in effect represents a new mineral variety because it actually has a larger unit cell.

A powder pattern for Cu-rich schulenbergite has been calculated by the Rietveld method (Hill and Howard, 1986) for the P3 parameters given in Table 3 and is illustrated in Fig. 3. Comparison of this calculated pattern with the observed powder X ray intensities in Table 2 indicates that the overall agreement is good, confirming the structure proposed in this report.

RÉSUMÉ

La schulenbergite décrite originalement par Hodenberg a une proportion Cu:Zn ~ 1,3. Or, dans la Cu-riche schulenbergite de la mine de Cap Garonne que nous avons étudiée, ce rapport Cu:Zn est de 6.

Cette différence de composition chimique crée également une très large différence sur les indices de réfraction. En plus, les films de rotation de Weissenberg longuement exposés montrent que la maille 8.27 x 7.11 Å est un subcell et que la maille de Cu-riche

schulenbergite est plus large. Cette maille n'a pas pu être déterminée à ce stade du fait de la très faible intensité des spots.

Néanmoins, la substructure atomique de Cu-riche schulenbergite a pu être résolue en combinant la méthode de Patterson et la restriction de site atomique.

Cette structure représente un modèle idéalisé de la structure de schulenbergite qui n'a pas encore été résolue jusqu'à maintenant.

Si la schulenbergite décrite par Hodenberg ne possède pas une large maille, la Cu-riche schulenbergite décrite ici doit être un nouveau minéral.

TABLE 1. Quantitative analyses in wt% for schulenbergite.

	1	2	3	4	5	6	7	8	9	Aver.
CuO	54.21	54.37	53.77	50.97	54.50	52.61	52.23	52.43	53.54	53.18
ZnO	10.94	11.65	9.43	12.47	12.73	12.50	11.75	9.78	11.34	11.39
CoO	1.03	1.03	0.87	0.93	0.73	0.87	0.85	0.59	0.69	0.84
NiO	1.06	0.70	0.85	0.91	0.84	0.52	0.71	0.67	0.75	0.78
SO3	13.26	14.89	16.08	14.22	16.39	15.09	14.66	16.64	14.94	15.13
H2O by diff.	19.50	17.36	19.00	20.50	14.81	18.41	19.80	19.89	18.74	18.68

TABLE 3. Atomic coordinates for schulenbergite.

Atom	x/a	y/b	z/c	Occup.	U
Cul	0.4369	0.1761	0.0009	1.0	0.011
Cu2	0.0000	0.0000	0.0000	0.167	0.011
Sl	0.6667	0.3333	0.4280	0.333	0.011
O1	0.2453	0.1938	0.1382	1.0	0.051
O2	0.4853	0.3997	0.8396	1.0	0.051
O3	0.6667	0.3333	0.2183	0.333	0.051
O4	0.4937	0.1946	0.4919	1.0	0.051
O5	0.0000	0.0000	0.5000	0.167	0.051

TABLE 4. Bond lengths for schulenbergite in Å.

Cul	O2	2.02	Sl	O3	1.48
	O3	2.26		O4	1.37
	O2'	2.15			
	O2"	2.30	O4	O2	2.99
	O1	1.91		O2'	2.89
	O1'	2.16		O2"	3.09
Cu2	O1	2.07	O1	O5	3.14

TABLE 2. X-ray powder diffraction data of Cu-rich schulenbergite

h k l	dc.	dobs.	Ivis.
0 0 1	7.106	7.11	100
1 0 1	5.026	5.025	10
1 1 0	4.105	4.109	10
1 1 1	3.555	3.554	60
0 0 2	3.553		
2 0 1	3.180	3.179	60
1 0 2	3.178		
2 1 0	2.688	2.687	80
1 1 2	2.687		
2 1 1	2.514	2.513	90
2 0 2	2.513		
0 0 3	2.369	2.367	<5
3 0 1	2.249	2.248	10
1 0 3	2.247		
2 1 2	2.144	2.143	35
2 2 0	2.053	2.052	<5
1 1 3	2.052		
3 1 0	1.972	1.972	10
2 2 1	1.972		
3 0 2	1.972		
2 0 3	1.971		
3 1 1	1.900	1.903	5
2 2 2	1.777	1.777	35
2 1 3	1.777		
0 0 4	1.776		
4 0 1	1.725	1.724	10
3 1 2	1.724		
1 0 4	1.724		
3 2 0	1.631	1.629	<5
1 1 4	1.630		
3 2 1	1.590	1.591	5
4 0 2	1.590		
4 1 0	1.552	1.554	30
2 2 3	1.551		
4 1 1	1.516	1.518	25
3 1 3	1.516		
3 2 2	1.483	1.482	30
2 1 4	1.482		
4 1 2	1.422	1.423	5
4 0 3	1.422		
3 0 4	1.422		
0 0 5	1.421		
4 2 0	1.344	1.345	10
3 3 1	1.344		
3 2 3	1.344		
4 2 1	1.320	1.322	10
5 0 2	1.320		
3 1 4	1.320		
4 1 3	1.298	1.298	5
5 1 0	1.277	1.276	<5
3 3 2	1.277		
4 2 2	1.257	1.256	10
4 0 4	1.257		
2 1 5	1.256		

REFERENCES

HILL, R.J & HOWARD, C.J. (1986): *Aust. Atomic Energy Commission Report No. M112*, Lucas Heights Res. Labs, NSW, Australia.

HODENBERG, R.V., KRAUSE, W. & TAUBER, H. (1984): Schulenbergite, (Cu, Zn)$_7$(SO_4,CO_3)$_2$(OH)$_{10}$.3H_2O, a new mineral. N. Jb. Miner. Mh. 1984, 17-24.

MANDARINO, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatability concept and its application. Canad. Miner. 19, 441-450.

SARP, H., PERROUD, P. & CAMEROLA, M. (1990): Cobalt nickel-ktenasite de la mine de Cap Garonne (Var), France, nouvelle variété de ktenasite. *Schweiz Mineral. Petrogr. Mitt.* 70, 333-335.