Zeitschrift für Kristallographie, Bd. 130, S. 254–260 (1969)

On the crystal structures of seligmannite, $PbCuAsS_3$, and related minerals

By **Y. Takéuchi** and **N. Haga**

Mineralogical Institute, Faculty of Science, University of Tokyo,
Hongo, Tokyo

(Received 19 April 1969)

Auszug

Die Verfeinerung der Kristallstruktur von Seligmannit ergab, daß die Abstände Cu–S mit 2,21 bis 2,39 Å sehr ähnlich den Abständen in den CuS_4-Tetraedern der Kupfersulfosalze sind, und daß die Abstände As–S 2,28 und 2,35 Å betragen, wie sie in AsS_3-Pyramiden üblicherweise gefunden werden. Diese Ergebnisse führen zu der Auffassung, daß die Struktur von Seligmannit im wesentlichen aus einem Gerüst von CuS_4-Tetraedern und AsS_3-Pyramiden aufgebaut ist, und daß die Pb-Atome in den großen Hohlräumen eingelagert sind. So können Seligmannit, Bournonit und vielleicht Aikinit in die gleiche Kategorie von Kupfersulfosalzen eingeordnet werden wie Tetraedrit und Wolfsbergit, deren Strukturen denen von Zinkblende und Wurtzit nah verwandt sind. Das Strukturgerüst besteht aus Schichten, die weitgehend den Schichten aus Cu- und As-Tetraedern des Enargits gleichen, der eine Struktur vom Wurtzittyp hat.

Abstract

A refinement of the crystal structure of seligmannite has revealed that the Cu–S distances lie in the range between 2.21 and 2.39 Å and are very close to those in the CuS_4 tetrahedra of copper sulfosalts, and the As–S distances have values commonly found in the AsS_3 pyramids of sulfosalts, the values being 2.28 and 2.35 Å. These results lead us to a view namely, that the structure of seligmannite is built up essentially of a framework of CuS_4 tetrahedra and AsS_3 pyramids, with lead atoms inserted in the large holes. Therefore seligmannite, bournonite and possibly aikinite may be classified into the same category as copper sulfosalts, like tetrahedrite and wolfsbergite, which have structures closely related to those of sphalerite or wurtzite. In fact the framework consists of a sheet which is closely related to the sheets of Cu and As tetrahedra in enargite, which has a wurtzite-type structure.

Introduction

Seligmannite, bournonite and aikinite are lead sulfosalts containing copper, and they have respectively the following lattice constants and space groups:

seligmannite	bournonite	aikinite
$a = 8.081$ Å	$a = 8.162$	$a = 11.30$
$b = 8.747$	$b = 8.710_5$	$b = 11.64$
$c = 7.636$	$c = 7.810_5$	$c = 4.00$
$Pn2_1m$	$Pn2_1m$	$Pnma$

The crystal structures of seligmannite, $PbCuAsS_3$, and bournonite, $PbCuSbS_3$, have been determined by LEINEWEBER (1956) and by HELLNER and LEINEWEBER (1956) and that of aikinite, $PbCuBiS_3$, by WICKMAN (1952), who pointed out that the structure of aikinite is similar to that of stibnite, Sb_2S_3, Pb and Bi forming a linkage similar to the Sb—S linkage in stibnite, tetrahedral holes of which are filled with copper. Moreover, HELLNER and LEINEWEBER stated that the structures of seligmannite and bournonite are also closely related to that of stibnite.

In our investigation into the systematization of the structural relationships of sulfosalts, we noticed that the characteristics of the structures of sulfosalts are basically controlled by the dimensional relationships between metal polyhedra and the pyramids of trivalent atoms (TAKÉUCHI and SADANAGA, 1969). In connection with this, we had made a survey of bond lengths in sulfosalts and found that some of the Cu—S and As—S bond lengths in seligmannite showed considerable deviations from those of other sulfosalts. We therefore refined the structure of seligmannite using the data of HELLNER and LEINEWEBER, and the result led us to the view that, instead of the linkage of Pb, As and S, the framework consisting of CuS_4 tetrahedra and AsS_3 pyramids is the essential feature of the structure of seligmannite. Since we considered it necessary for our report on the structural scheme of sulfosalts (TAKÉUCHI and SADANAGA, 1969) to describe our new view of the structure of seligmannite separately, it is reported in the present paper.

Refinement

The structural analysis of seligmannite by LEINEWEBER (1956) was carried out in the c-axis and the b-axis projections. Among the 179 reflections which they reported, nine were non-observable and 004 was largely affected by secondary extinctions. If these reflections were excluded, the discrepancy factor R was calculated to be 0.216 for 169 reflections, 0.252 for $F(hk0)$ and 0.165 for $F(h0l)$. Since a least-squares refinement using structure factors of two projections was successful for the refinement of the structure of wallisite, $PbTlCuAs_2S_5$ (Takéuchi *et al.*, 1968), an attempt to refine the structure of seligmannite in a similar manner was undertaken.

Starting from the atomic coordinates given by Hellner and Leineweber (1956), refinement has been accomplished by means of full-matrix least-squares program, ORFLS (Busing *et al.*, 1962) which was modified by Iitaka for HITAC 5020E at the Computing Center of the University of Tokyo. Form factors for non-ionized atoms based, upon the Thomas-Fermi-Dirac statistical method, were employed for Pb, and those given by Freeman and Watson and by Dawson were used for As and S respectively (*International tables for x-ray crystallography*, Vol. III, pp. 201—212). The R value has been reduced in the refinement to 0.170 for the 169 reflections. Positional parameters and isotropic temperature factors are listed in Table 1. Since the temperature factors of the arsenic and sulfur atoms became negative at the final stage of the refinement, they were fixed at the low values listed and were not varied for the final calculations. Therefore their actual values are not significant. Fairly large shifts of the light atoms from the parameters given by Hellner and Leineweber (1956) are observed, especially along the polar axis; e.g., the shifts of y parameters of S(4), S(2) and As(2) amount to 0.5, 0.415 and 0.41 Å respectively. As a result, the Cu—S and As—S bond lengths varied as listed in Table 2, which clearly indicates that the copper and sulfur polyhedra are almost regular tetrahedra, and

Table 1. *Atomic parameters for seligmannite*

Atom	x		y		z		B	
Pb(1)	.0762	± .0007	.0000		.0000		.97	± .16
Pb(2)	.5558	7	.1923	± .0020	.5000		.78	.15
As(1)	.0716	16	.0773	36	.5000		.20	
As(2)	.5068	18	.1570	35	.0000		.20	
Cu	.2786	20	.4287	35	.2419	± .0032	.18	.30
S(1)	.2555	41	.2761	82	.0000		.10	
S(2)	.2257	43	.2960	76	.5000		.10	
S(3)	.1012	30	.6475	33	.2351	45	.10	
S(4)	.5601	27	.4970	39	.2631	48	.10	

Table 2. *Bond lenghts and bond angles in seligmannite*

	(Leineweber)		(Present work)			(Present work)	
Cu–S					S(1)–Cu–S(2)	112.2 ± 1.4°	
	Cu–S(1)	2.27 Å	2.29 ± .047 Å		S(1)–Cu–S(3)	113.6	1.7
	–S(2)	2.28	2.33	38	S(1)–Cu–S(4)	106.4	1.3
	–S(3)	2.65	2.39	37	S(2)–Cu–S(3)	107.9	1.6
	–S(4)	2.25	2.36	33	S(2)–Cu–S(4)	104.2	1.4
As–S					S(3)–Cu–S(4)	112.2	1.5
	As(1)–S(2)	2.16	2.28	60	S(3)–As(1)–S(2)	96.0	1.7 (2)
	–S(3)	2.36 (2)	2.35	36 (2)	S(3)–As(1)–S(3)	99.2	0.9
	As(2)–S(1)	2.77	2.28	45	S(4)–As(2)–S(1)	93.9	1.2 (2)
	–S(4)	2.37 (2)	2.35	37 (2)	S(4)–As(2)–S(4)	100.1	0.4

Figures in parentheses indicate the number of equivalent bonds. The Pb–S and S–S distances are not enumerated because further refinement of the structure based upon new intensity data has been undertaken in collaboration with Prof. W. Nowacki (Edenharter, Nowacki and Takéuchi, 1970).

that the arsenic and sulfur polyhedra are the trigonal pyramids commonly found in sulfonats (Takéuchi and Sadanaga, 1969). Since it was decided that these results are sufficient for a discussion of the general feature of the structure, further refinement of the structure was not attempted for the present purpose.

Structural principles

Based upon the results described above, the structure of seligmannite, illustrated in Fig. 1, is a framework consisting of Cu tetrahedra and As pyramids, the lead atoms being merely inserted in the large spaces in the framework. This way of looking at the structure of seligmannite appears to be more reasonable than pointing out the similarity between seligmannite and stibnite. The latter view implies that the structure is based upon the framework of Pb and As polyhedra, copper atoms being locating in the tetrahedral spaces of the framework. Although the structure of aikinite is indeed strikingly similar to that of stibnite, the similarity between seligmannite and stibnite is not clear. If the Pb and As framework is essential to the structure, the copper tetrahedra could be distorted. However, as has been argued, both the Cu tetrahedra and As pyramids are close to their regular shapes, and the lead polyhedra are irregular. Thus it can be decided that the Cu, As and S framework is the essential feature which characterizes the structure of seligmannite. This feature can also be seen in bournonite

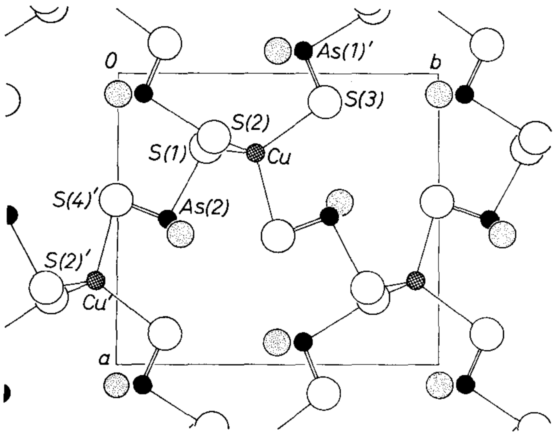

Fig. 1. The crystal structure of seligmannite projected along the *c* axis. The linkage of CuS_4 tetrahedra, and AsS_3 pyramids is indicated, large open circles, solid circles, shaded circles and dotted circles being respectively S, As, Cu and Pb

and possibly in aikinite. Therefore these mineral species may well be classified into the same category of copper sulfosalts as tetrahedrite, $Cu_{12}As_4S_{13}$, and wolfsbergite $CuSbS_2$ whose structures are closely related to the simple tetrahedral structures of sulfides such as sphalerite or wurtzite.

In fact a closer examination of the Cu, As and S framework reveals that it is built up of sheets closely related to the tetrahedral sheets in enargite, Cu_3AsS_4 (PAULING and WEINBAUM, 1934), having a wurtzite-type structure. As indicated in Fig. 1, if we take an array of the As(1)′, Cu, As(2) and Cu′ polyhedra, we notice that they form a sheet parallel to (110). Though the sulfur array, S(3)—S(2)—S(1)—S(4)′—S(2)′, in the sheet is, in fact, corrugated, if it were idealized so that the sulfur array formed a flat plane, the sheet could be schematically depicted in Fig. 2*a* which should be compared with a sheet of enargite of Fig. 2*b*. The enargite sheet contains two different kinds of tetrahedral chains along the *c* axis. The first of these consists of only Cu tetrahedra, and the second is an alternating arrangement of Cu and As tetrahedra. These two kinds of chains are alternately joined together into a sheet so that each tetrahedron shares its three corner sulfur atoms, and the fourth vertices all point in the same direction. If the copper atoms in the second type of chains in a sheet are taken away, and the As tetrahedra are replaced by As paramids, the seligmannite sheet is obtained. In the structure of seligmannite these sheets are joined together by As pyra-

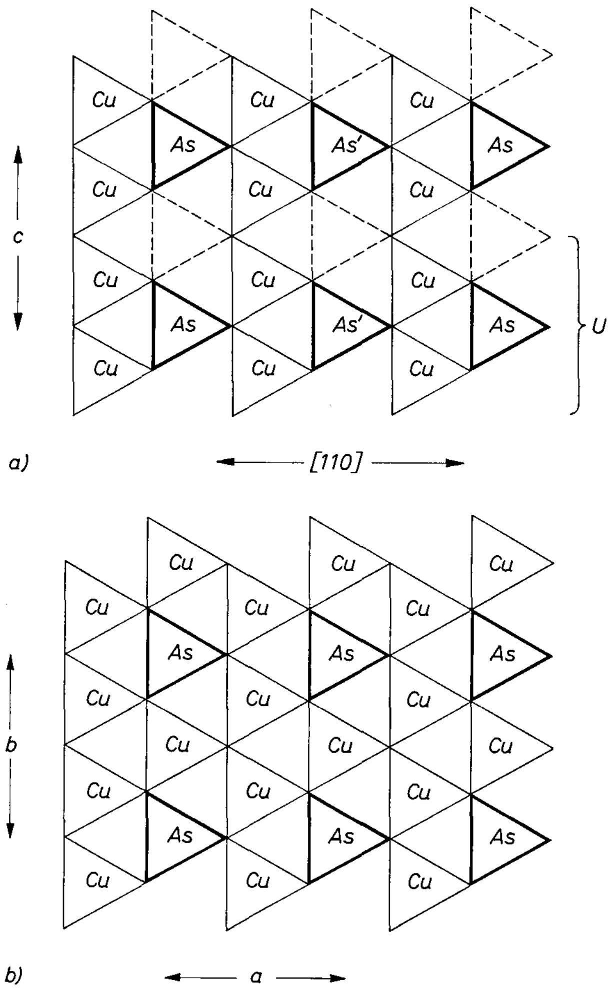

Fig. 2. (a) A sheet of CuS_4 tetrahedra and AsS_3 pyramids of seligmannite. The apices of tetrahedra and pyramids are pointing upwards, except As′ pyramids, whose apices are pointing downwards. If Cu and As are respectively replaced by Fe and Cu in the unit slab *U* of this sheet, a slab closely related to that of cubanite, $CuFe_2S_3$ (BUERGER, 1947) is derived. (*b*) A sheet of CuS_4 and AsS_4 tetrahedra of enargite. All apices are pointing same direction. In the both illustrations, apical sulfurs are omitted

mids to form the bulk of the structure. But the pyramids which join the sheets together, and the Cu tetrahedra in the sheets, again form similar sheets parallel to $(1\bar{1}0)$. Thus, the structure of seligmannite is actually built up of an intersecting network of sheets parallel to (110) and of sheets parallel to ($1\bar{1}0$).

The authors wish to thank Professor R. Sadanaga for his interest in this work, and Dr. A. L. Mackay for reading manuscript.

References

M. J. Buerger (1947), The crystal structure of cubanite. Amer. Min. **32**, 415—425.

W. R. Busing, K. O. Martin and H. A. Levy (1962), ORFLS, a FORTRAN crystallographic least-squares program, ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

A. Edenharter, W. Nowacki und Y. Takéuchi (1970), Verfeinerung der Kristallstruktur von Bournonit $[(SbS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$ und von Seligmannit $[(AsS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$. Z. Kristallogr. **131** [im Druck].

Erwin Hellner und Günter Leineweber (1956), Über komplex zusammengesetzte sulfidische Erze. I. Zu den Strukturen des Bournonits, $CuPbSbS_3$, und Seligmannits, $CuPbAsS_3$. Z. Kristallogr. **107**, 150—154.

Günter Leineweber (1956), Struktur-Analyse des Bournonits und Seligmannits mit Hilfe der Superpositionsmethoden. Z. Kristallogr. **108**, 161—184.

L. Pauling and S. Weinbaum (1934), The crystal structure of enargite, Cu_3AsS_4. Z. Kristallogr. **88**, 48—53.

Y. Takéuchi, M. Ohmasa and W. Nowacki (1968), The crystal structure of wallisite, $PbTlCuAs_2S_5$. Z. Kristallogr. **127**, 349—365.

Y. Takéuchi and R. Sadanaga (1969), Structural principles and classification of sulfosalts. Z. Kristallogr. **130**, 346—368.

F. W. Wickman (1953), The crystal structure of aikinite, $CuPbBiS_3$. Arkiv Mineralog. Geol. **1**, 501—507.