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THE ORDERING SCHEME FOR METAL ATOMS IN THE CRYSTAL STRUCTURE OF HAMMARITE, $Cu_2Pb_2Bi_4S_9$

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ABSTRACT

Hammarite, $Cu_2Pb_2Bi_4S_9$, is orthorhombic, space group *Pbnm*, with *a* 33.7726(8), *b* 11.5857(3), *c* 4.01Å, and $D_{calc}=7.05$ g/cm³ for $Z=4$. The structure was solved in projection from visually–estimated *hk*0 reflections. Least-squares refinement was carried to $R=16.9\%$. The structure is a superstructure with *a* triple that of Bi_2S_3 and consists of krupkaite and aikinite ribbons in ratio 2:1. If only sites involved in substitutions are considered, hammarite is the anti-structure of gladite.

SOMMAIRE

L'hammarite, $Cu_2Pb_2Bi_4S_9$, appartient au groupe spatial orthorhombique *Pbnm* avec *a* 33.7726(8), *b* 11.5857(3), *c* 4.01Å; $d_{calc}=7.05$ pour $Z=4$. La structure cristalline a été résolue en projection, à partir des réflexions *hk*0 estimées visuellement, et affinée par la méthode des moindres carrés jusqu'au résidu $R=16.9\%$. La structure cristalline est une surstructure dont le paramètre *a* vaut trois fois celui de Bi_2S_3; elle consiste en rubans de krupkaite et d'aikinite dans le rapport 2:1. L'hammarite est l'anti-structure de la gladite, si l'on ne considère que les sites impliqués dans les substitutions.

(Traduit par la Rédaction)

INTRODUCTION

Bismuthinite, Bi_2S_3 (isostructural with stibnite, Sb_2S_3) has a structure which consists of 4-membered Bi_4S_6 ribbons (Kupčík & Veselá-Nováková 1970). Aikinite, $CuPbBiS_3$ (Ohmasa & Nowacki 1970a; Kohatsu & Wuensch 1971) is a derivative of this atomic arrangement: the interior pair of Bi atoms is replaced by Pb, and Cu atoms are added to entirely fill an available set of tetrahedral interstices.

Five ordered phases have been discovered as superstructures intermediate to bismuthinite and aikinite. Structures (in order of increasing Pb:Bi) have been established for pekoite, $CuPbBi_{11}S_{18}$ (Mumme & Watts 1976); gladite, $CuPbBi_5S_9$ (Kohatsu & Wuensch 1973a, 1976; Syneček & Hybler 1974) and krupkaite, $CuPbBi_3S_6$ (Syneček & Hybler 1974; Mumme 1975). Review of the crystal chemistry of these phases and proposals for nomenclature have been given by Mumme *et al.* (1976) and by Harris & Chen (1976). In the phases examined thus far, there is ordered partial replacement of Bi by Pb atoms, and only a fraction of the tetrahedral interstices are filled by Cu. The following crystal-chemical principles have emerged: the Pb atoms appear always to replace an interior Bi in the bismuthinite chain as in aikinite. The interstitial Cu atom occupies the interstice which is adjacent to Pb and on the same side of the ribbon. The Pb atoms tend to distribute among as many chains as possible. Thus, krupkaite consists entirely of $CuPbBi_3S_6$ ribbons, rather than being comprised of a mixture of Bi_4S_6, bismuthinite-like, and $Cu_2Pb_2Bi_2S_6$, aikinite-like, units. Similarly, pekoite and gladite have been found to consist of mixtures of $CuPbBi_3S_6$ and Bi_4S_6 ribbons in ratios 1:2 and 2:1, respectively.

Structures have not, as yet, been determined for lindströmite, $Cu_3Pb_3Bi_7S_{15}$, or hammarite, $Cu_2Pb_2Bi_4S_9$. The structural models permitted by the subgroup-supergroup relation have been enumerated, however, by Ohmasa & Nowacki (1970b). Being the most Pb-rich of the intermediate superstructures, the arrangement of Pb and Cu in their structures is of great interest toward complete understanding of the crystal chemistry of this series of minerals. We here report the results of a preliminary study of the crystal structure of hammarite which, though conducted with visually-estimated intensities, establishes the ordering scheme with certainty.

EXPERIMENTAL

The original single-crystal[1] of hammarite from Gladhammar, Sweden which had been isolated by Welin (1966) was employed for study. The specimen consisted of a prismatic fragment measuring 0.34×0.17×0.15mm, whose shape could be satisfactorily approximated by a collection of eight planar surfaces. Diffraction

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[1] Naturhistoriska Riksmuseet Stockholm. Catalogue No. RM 24098:1.

patterns showed hammarite to be orthorhombic with systematic absences of reflections characteristic of space groups $Pbn2_1$ (C^9_{2v}) or $Pbnm$ (D^{16}_{2h}). The latter proved satisfactory for structural analysis. Lattice constants *a* 33.7726(8) and *b* 11.5857(3) were determined from least-squares fit to 86 *hk*0 reflections recorded in Cu$K\alpha$ radiation with a back-reflection Weissenberg camera. A value *c* 4.01Å was measured from a rotation photograph. These data provide $D_{calc}=7.05$ g/cm³ for $Z=4$ ideal formula units.

Intensity data were photographically recorded with Ni-filtered Cu$K\alpha$ radiation ($\mu_l=1394\text{cm}^{-1}$) using an equi-inclination Weissenberg camera and the multiple-film technique. Intensities were visually estimated by comparison with a standard density wedge which had been prepared with the same specimen. Of 222 independent accessible *hk*0 reflections within $2\theta<42°$, a total of 35 was undetectable. Standard corrections for Lorentz, polarization and absorption factors were applied in converting the data to structure factors.

DETERMINATION OF THE STRUCTURE

It was anticipated that the atomic arrangement in hammarite would be a derivative of the bismuthinite structure (Ohmasa & Nowacki 1970b). This requires 6 heavy-metal atoms (2 Pb and 4 Bi), 2 Cu and 9 S atoms in the asymmetric unit of the structure, all in position 4(*c*)*m xy*¼ of space group *Pbnm*. The Cu atoms must occupy two of three available sites: *A*(0.236 0.232,¼), *B*(.569, .232,¼) or *C*(.903, .232,¼). Models for the three possible configurations of Cu (*AB,BC,AC*) were examined, using all 222 accessible *hk*0 reflections, and with the following initial conditions: coordinates derived from the structure of Bi_2S_3 (Kupčík & Veselá-Nováková 1970), Bi arbitrarily assigned to all heavy-metal positions, and an overall isotropic temperature factor of 0.4Å².

Four cycles of least-squares refinement of the metal atom coordinates with equal weight for all data, were performed with the full-matrix program RFINE2 (Finger & Prince 1975) and reduced *R* from initial values of 65% for all three models to 47.3% for Cu distribution *AB*, 43.4% for *AC*, but 30.9% for Cu placed in positions *B* and *C*. The last configuration was accordingly adopted as most probable.

At this stage the 35 unobserved intensities were removed from the data set as were six very intense substructure reflections which were found to be overexposed. Further cycles of refinement of coordinates for all atoms and adjustment of a single overall temperature factor to 1.3Å² provided convergence at $R=18.6\%$. Computation of interatomic distances revealed one minimum metal-sulfur separation characteristic of Pb (2.96Å) and the shorter length typical for Bi for three others (2.57, 2.68 and 2.71Å); intermediate and similar distances of 2.83 and 2.84Å were found for the remaining pair of heavy-metal atoms. One of these had trigonal prismatic coordination and, moreover, was an interior position in the bismuthinite chain of the sort which is usually replaced by Pb. This site was accordingly assumed to contain the second Pb atom. Upon assignment of Pb to these sites, further refinement of coordinates for all atoms and of separate temperature factors for the metal atoms produced a value of $R=16.9\%$. As the essential features of the structure seemed firmly established, refinement was suspended at this stage.

TABLE 1. ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR HAMMARITE (Estimated standard deviations in parentheses; z=¼ for all atoms)

Atom	Gladite	Hammarite	x	y	B(Å²)
M(1)	Bi(1)	Bi(1)	.0633(4)	.0194(12)	2.1(3)
M(2)	Bi(2)	Bi(2)	.3935(3)	.0234(11)	1.5(3)
M(3)	Bi(3)	Bi(3)	.7241(3)	.0182(11)	1.8(3)
M(4)	Pb	Bi(4)	.3202(3)	.3465(11)	2.1(3)
M(5)	Bi(4)	Pb(1)	.6662(3)	.3226(11)	1.7(3)
M(6)	Bi(5)	Pb(2)	.9970(4)	.3307(14)	2.6(4)
Cu(A)	Cu	-			
Cu(B)	-	Cu(1)	.5662(12)	.239(3)	0.9(11)
Cu(C)	-	Cu(2)	.9027(11)	.235(3)	0.5(11)
S(1)			.213(2)	.047(6)	1.3
S(2)			.546(2)	.044(7)	
S(3)			.876(2)	.050(6)	
S(4)			.189(2)	.368(7)	
S(5)			.519(2)	.372(6)	
S(6)			.846(2)	.366(6)	
S(7)			.100(2)	.228(6)	
S(8)			.440(2)	.225(6)	
S(9)			.764(2)	.220(6)	

DISCUSSION

Temperature factors and coordinates for the 17 atoms contained in the asymmetric unit of hammarite are presented in Table 1. A projection of the electron density in the structure is given in Figure 1. Noteworthy is the fact that there is no evidence for electron density in the unoccupied tetrahedral interstice at (0.236, 0.232). Interatomic distances for the Pb and Bi atoms (Table 2) are similar to those found in other bismuthinite derivatives. One Cu-S separation of 2.22Å is short for a Cu atom in tetrahedral coordination. This polyhedron is actually intermediate to tetrahedral and triangular coordination. A similar geometry occurs in gladite (Kohatsu & Wuensch 1976).

The structure of hammarite consists of a mixture of aikinite-like $Cu_2Pb_2Bi_2S_6$ ribbons and krupkaite $CuPbBi_3S_6$ chains in ratio 1:2. Hammarite, because of its high Pb content, is the first intermediate bismuthinite derivative found to contain an aikinite unit, although this chain has been found in nuffieldite, $CuPb_2(Pb,Bi)Bi_2S_7$,

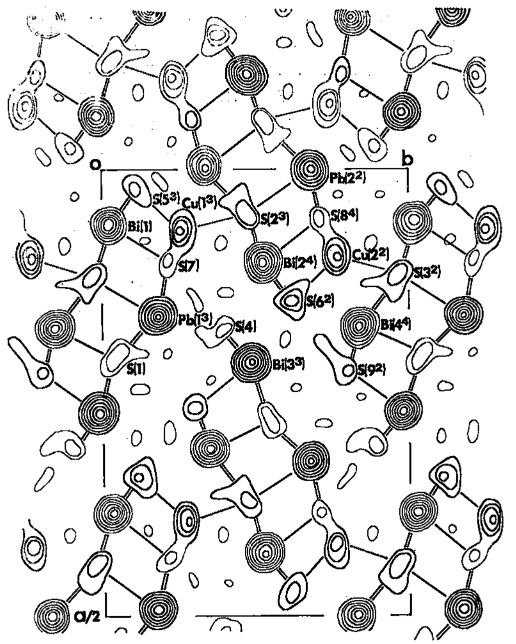

FIG. 1. Electron density in hammarite projected along *c*. Contours begin at 8 $e/Å^2$; intervals of 8 $e/Å^2$ for heavy-metal atoms, 4 e/A^2 elsewhere. Bold contours arise from atoms at $z = 3/4$, the lighter contours from atoms at $z = 1/4$.

another Pb-rich bismuth sulfosalt (Kohatsu & Wuensch 1973b).

The crystal-chemical features found in other superstructures of the bismuthinite-aikinite series are followed in hammarite; the Pb atoms are distributed among the maximum possible number of ribbons (i.e., the structure does not consist of a combination of bismuthinite and aikinite units) and the tetrahedral interstice which is occupied by Cu is again found to be adjacent to the substituted Pb atom. Of interest is that if one considers only the tetrahedral interstices and the two interior Bi positions for which Pb substitutes, hammarite turns out to be the anti-structure of gladite (Table 1). That is, vacant tetrahedral sites in one structure are occupied in the other, and interior chain positions occupied by Bi in one structure are occupied by Pb in the other. Detailed discussion of the coordination polyhedra in hammarite and comparison of the configuration with that of other bismuthinite derivatives will be deferred until refinement of the structure with 3-dimensional diffractometer data is completed.

TABLE 2. INTERATOMIC DISTANCES IN HAMMARITE

Bi(1) -	S(7)	2.71Å		Pb(1) -	S(1^3)	2.96Å	2X
	S(5^3)	2.80	2X		S(7^3)	3.07	2X
	S(3^2)	2.95	2X		S(3^4)	3.01	
	S(5^4)	3.26			S(4^3)	3.08	2X
Bi(2) -	S(8)	2.83		Pb(2) -	S(8^3)	2.84	2X
	S(6^3)	2.87	2X		S(2^4)	2.86	
	S(2^2)	2.97	2X		S(2^3)	2.98	2X
	S(4^4)	3.31			S(5^3)	3.18	2X
Bi(3) -	S(4^3)	2.68	2X	Cu(1) -	S(5)	2.22	
	S(9)	2.70			S(7^3)	2.33	2X
	S(6^4)	2.95			S(2)	2.36	
	S(1^2)	3.02	2X				
Bi(4) -	S(1^4)	2.57		Cu(2) -	S(3)	2.31	
	S(9^3)	2.87	2X		S(8^3)	2.42	2X
	S(3^3)	3.03	2X		S(6)	2.44	
	S(6^3)	3.29	2X				

A superscript identifies an atom related by symmetry to an atom in the asymmetric unit. The value of this integer corresponds to the position of the coordinates of the atom in the list of equivalent positions for space group Pbnm in "International Tables for x-ray Crystallography", Vol. 1.

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REFERENCES

FINGER, L. W. & PRINCE, E. (1975): A system of Fortran IV computer programs for crystal structure computations. *U.S. Nat. Bur. Stand. Tech. Note* 854.

HARRIS, D. C. & CHEN, T. T. (1976): Crystal chemistry and re-examination of nomenclature of sulfosalts in the aikinite-bismuthinite series. *Can. Mineral.* 14, 194-205.

KOHATSU, I. & WUENSCH, B. J. (1971): The crystal structure of aikinite, PbCuBiS$_3$. *Acta Cryst.* **B27**, 1245-1252.

——— & ——— (1973a): The crystal structure of gladite, PbCuBi$_5$S$_9$. *Amer. Mineral.* **58**, 1098 (Abstr.)

——— & ——— (1973b): The crystal structure of nuffieldite, Pb$_2$Cu(Pb,Bi)Bi$_2$S$_7$. *Z. Krist.* **138**, 343-365.

——— & ——— (1976): The crystal structure of gladite, PbCuBi$_5$S$_9$, a superstructure intermediate in the series Bi$_2$S$_3$-PbCuBiS$_3$ (bismuthinite-aikinite). *Acta Cryst.* **B32**, in press.

KUPČÍK, V. & VESELÁ-NOVÁKOVÁ, L. (1970): Zur Kristallstruktur des Bismuthinits, Bi$_2$S$_3$. *Tschermaks Mineral. Petrog. Mitt.* **14**, 55-59.

MUMME, W. G. (1975): The crystal structure of krupkaite, CuPbBi$_3$S$_6$, from the Juno Mine at Tennant Creek, Northern Territory, Australia. *Amer. Mineral.* **60**, 300-308.

——— & WATTS, J. A. (1976): Pekoite, CuPbBi$_{11}$S$_{18}$, a new member of the bismuthinite-aikinite mineral series: its crystal structure and relationship with natural and synthetically-formed members. *Can. Mineral.* **14**, 322-333.

———, WELIN, E. & WUENSCH, B. J. (1976): Crystal chemistry and proposed nomenclature for sulfosalts intermediate in the system bismuthinite-aikinite (Bi$_2$S$_3$-CuPbBiS$_3$). *Amer. Mineral.* **61**, 15-20.

OHMASA, M. & NOWACKI, W. (1970a): A redetermination of the crystal structure of aikinite [$BiS_2|S|Cu^{IV}Pb^{VII}$]. *Z. Krist.* 132, 71-86.

——— & ——— (1970b): Note on the space group and on the structure of aikinite derivatives. *Neues Jahrb. Mineral. Monatsh.*, 158-162.

SYNEČEK, V. & HYBLER, J. (1974): The crystal structures of krupkaite, $CuPbBi_3S_6$, and of gladite, $CuPbBi_5S_9$, and the classification of superstructures in the bismuthinite-aikinite group. *Neues Jahrb. Mineral. Monatsh.*, 541-560.

WELIN, E. (1966): Notes on the mineralogy of Sweden, 5. Bismuth-bearing sulfosalts from Gladhammar, a revision. *Arkiv Mineral. Geol.* 4, 377-386.

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