

## Crystal chemistry and proposed nomenclature for sulfosalts intermediate in the system bismuthinite–aikinite ( $\text{Bi}_2\text{S}_3$ – $\text{CuPbBiS}_3$ )

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### Abstract

Five ordered phases ( $\text{CuPbBi}_3\text{S}_6$ ,  $\text{CuPbBi}_{11}\text{S}_{18}$ ,  $\text{CuPbBi}_5\text{S}_9$ ,  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ ,  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ ) have recently been discovered as minerals intermediate to bismuthinite,  $\text{Bi}_2\text{S}_3$ , and aikinite,  $\text{CuPbBiS}_3$ . Early work of Johansson (1924) proposed "lindströmite" as  $\text{CuPbBi}_3\text{S}_6$  from Gladhammar, Sweden. Re-examination of type material (Welin, 1966) showed the composition to actually be  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ . It is proposed that the name lindströmite be retained for this mineral. Recent work (Large and Mumme, 1975; Žák, Syneček and Hybler, 1974) has established  $\text{CuPbBi}_3\text{S}_6$  as a distinct species, to which the name krupkaite has been given.

The  $Z^n$  principle (Moore, 1967) proposed for classification of bismuthinite derivatives has not been followed by the crystal structures found for krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , and pekoite,  $\text{CuPbBi}_{11}\text{S}_{18}$ , because Pb tends to order into the maximum permitted number of  $\text{Bi}_4\text{S}_6$  chains and form  $\text{CuPbBi}_3\text{S}_6$  ribbons. A similar quadruple ribbon has also been found to occur in the structure of gladite,  $\text{CuPbBi}_5\text{S}_9$ . It is therefore proposed that the  $Z^n$  classification be abandoned. Parent structures have now been established which consist solely of  $\text{Bi}_4\text{S}_6$  (bismuthinite),  $\text{CuPbBi}_3\text{S}_6$  (krupkaite), or  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$  (aikinite) quadruple ribbons within a unit cell of the same geometry. It is therefore proposed that generic names of these structure types be used to designate similar structural units when they occur in other bismuthinite derivatives, or in more complex sulfosalts.

### Introduction

Bismuthinite,  $\text{Bi}_2\text{S}_3$ , has a chain structure (Hofmann, 1933; Kupčík and Veselá-Nováková, 1970) which is isostructural with that of stibnite,  $\text{Sb}_2\text{S}_3$  (Hofmann, 1933; Ščavničar, 1960; Bayliss and Nowacki, 1972). A pair of Bi with [1+2+2] square pyramidal coordination shares an apical edge to form a double chain. An additional pair of Bi with 3-fold pyramidal coordination flanks this double chain to build a 4-membered ribbon. The structure of aikinite,  $\text{CuPbBiS}_3$ , was shown by Wickman (1953) to possess the same space group as bismuthinite and to contain similar quadruple chains; the Cu atom occupies a

tetrahedral interstice among a bismuthinite-like array of atoms. Recent reinvestigations of aikinite (Ohmasa and Nowacki, 1970a; Kohatsu and Wuensch, 1971) established that aikinite is a derivative of the structure of bismuthinite in which Pb replaces the interior 5-coordinated Bi atom in the quadruple chain. The atomic positions in aikinite remain remarkably similar to those in bismuthinite in spite of these substitutions (Kohatsu and Wuensch, 1971).

Descriptions of several additional Pb-Cu-Bi sulfosalts from Gladhammar, Sweden, appear in earlier mineralogical literature (Lindström, 1887, 1889; Flink, 1910; Johansson, 1924). Chemical analyses

were produced in support of the definition of these species, but crystal data were not provided. Paděra (1955) considered these minerals to be solid solutions intermediate to bismuthinite and aikinite. Attempts to synthesize intermediate compounds at temperatures as low as 300°C produced, in fact, only disordered solid solutions (Springer, 1971).

In a reinvestigation of Gladhammar material preserved in the Swedish Museum of Natural History, Welin (1966) provided crystallographic data and chemical analyses which established the existence of three distinct intermediate phases: gladite,  $\text{CuPbBi}_5\text{S}_9$ ; hammarite,  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ ; and  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ . Diffraction patterns showed these minerals to be superstructures based upon bismuthinite with one lattice constant equal to 3, 3, and 5 times, respectively, that of a corresponding 11.115 Å translation in bismuthinite. On the basis of this relationship, Moore (1967) proposed  $\text{Cu}_x\text{Pb}_x\text{Bi}_{8Z-x}\text{S}_{12Z}$  as a generalized formula for these minerals, where  $Z$  is the integral multiple of the bismuthinite translation, and  $x$  is assumed to be a multiple of 4 in accord with the equipoint requirements of the orthorhombic space groups found for all derivatives discovered to that time. A restriction  $4Z > x$  must obtain, since 4 Cu ( $\equiv$  Pb) represents the number of tetrahedral interstices available in each bismuthinite subcell. Compositions and cell geometries were predicted for an extensive series of hypothetical compounds on this basis. Rather than admit a separate mineral name for each specie, Moore (1967) proposed the designation  $Z^n$ , where  $Z$ , defined above, is the multiplicity of the 11.115 Å translation, and  $n = x/4$  is the number of Cu ( $\equiv$  Pb) atoms contained in the asymmetric unit of a particular structure. Thus gladite and hammarite became  $3^1$  and  $3^2$ , respectively, and Welin's third phase became  $5^3$ . Ohmasa and Nowacki (1970b) used subgroup-supergroup relationships to fix the space group of " $5^3$ ", and to enumerate the configurations permitted to each derivative. These considerations showed three types of quadruple chains to be permitted by symmetry: (a) =  $\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$  (aikinite-like), (b) =  $\text{Bi}_4\text{S}_6$  (bismuthinite-like), and (c) =  $\text{CuPbBi}_3\text{S}_6$ . As only bismuthinite-like and aikinite-like chains were then known to exist, structures consisting of mixtures of (a) and (b) ribbons were considered to be the practical possibilities. However, the crystal structure of gladite,  $\text{CuPbBi}_5\text{S}_9$ , when subsequently established (Kohatsu, 1971; Kohatsu and Wuensch, 1972), unexpectedly was found to consist of a mixture of  $\text{Bi}_4\text{S}_6$  and  $\text{CuPbBi}_3\text{S}_6$  ribbons, rather than a combination of

the structural units known in bismuthinite and aikinite.

Several new minerals intermediate to bismuthinite and aikinite have been identified from the Juno Mine at Tennant Creek, Northern Territory, Australia. (Large and Mumme, 1975; Mumme, 1975; Mumme and Watts, to be published). The crystal structure of  $\text{CuPbBi}_3\text{S}_6$  has been established by Mumme (1975) and independently by Syneček and Hybler (1974). The new minerals discovered at Tennant Creek create ambiguities in the names presently assigned to some of these sulfosalts. Further, the recent structure determinations appear to contradict the basis for classification of these derivative structures as proposed by Moore (1967). The present joint paper accordingly presents the data currently available, and proposes revisions in nomenclature and terminology to resolve the ambiguities which have been created by recent results.

#### Summary of established species and problems in nomenclature

Table 1 summarizes the chemical, crystallographic, and structural data presently available for sulfosalts intermediate in the series bismuthinite–aikinite. Projections of crystal structures thus far established for these phases are presented in Figure 1<sup>1</sup>. These recent results have created two problems: the identity of the mineral "lindströmite," and the validity of the " $Z^n$ " system of nomenclature.

#### The lindströmite problem

The bulk wet-chemical analysis provided by Johansson (1924) in establishing the identity of lindströmite corresponds quite closely to  $\text{CuPbBi}_3\text{S}_6$ , as shown in Table 2. The single-crystal study of Welin (1966) established the existence of a 5-fold superstructure in material (RM 24100:3) obtained from the same hand specimen studied by Johansson, but spectrographic analysis showed the composition to be  $\text{Cu}_{2.40}\text{Pb}_{2.40}\text{Bi}_{5.60}\text{S}_{12} \approx \text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ . This result is close to the analysis of Johansson (Table 2) although  $\text{CuPbBi}_3\text{S}_6$  fits Johansson's analysis more satisfactorily. Several recent compilations (e.g., Strunz, 1970; Povarennykh, 1972) have incorporated the

<sup>1</sup> Different labels have been assigned to cell edges by various workers. To avoid confusion, Figure 1 maintains the setting employed in the reference cited for each structure. To facilitate comparison of the structures, however, the origin of the cell depicted in Figure 1 has been shifted from that of the study cited to 0½ for bismuthinite, ¼00 for krupkaite, 00½ for aikinite, and 00¼ for pekoite.

TABLE 1. Crystallographic Data and Structural Results for Ordered Minerals in the Series Bismuthinite-Aikinite

Order of Supercell	Mineral and Composition	Lattice constants (Å)			Space group	Structure	Reference
1-fold	Bismuthinite, $\text{Bi}_2\text{S}_3$	$a = 11.115(20)$	$b = 11.25(2)$	$c = 3.97(1)$	Pbnm	$\text{Bi}_4\text{S}_6$ ribbons	Kupčík and Veselá-Nováková (1970)
	Krupkaite, $\text{CuPbBi}_3\text{S}_6$	$a = 11.20$	$b = 11.56$	$c = 4.00$	$Pb2_1m^*$	$\text{CuPbBi}_3\text{S}_6$ ribbons	Mumme (1975)
	Aikinite, $\text{CuPbBiS}_3$	$a = 11.275(2)$	$b = 11.608(1)$	$c = 4.0279(3)$	Pbnm*	$\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ ribbons	Kohatsu and Wuensch (1971)
3-fold	Pekoite $\text{CuPbBi}_{11}\text{S}_{14}\text{Se}_4$ $\text{CuPbBi}_{11}\text{S}_{16}$	$b = 3 \times 11.248(2)$ $b = 3 \times 11.168(2)$	$a = 11.472(2)$ $a = 11.322(2)$	$c = 4.016(1)$ $c = 3.987(1)$	$P2_1am^*$	1 $\text{CuPbBi}_3\text{S}_6$ : 2 $\text{Bi}_4\text{S}_6$ ribbons	Mumme and Watts (to be published)
	Gladite, $\text{CuPbBi}_5\text{S}_9$	$b = 33.531(6)$ $= 3 \times 11.177$	$a = 11.486(2)$	$c = 4.003(2)$	Pnam*	2 $\text{CuPbBi}_3\text{S}_6$ : 1 $\text{Bi}_4\text{S}_6$ ribbon	Kohatsu and Wuensch (1972)
	Hammarite $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$	$b = 33.45$ $= 3 \times 11.15$	$a = 11.58$	$c = 4.01$	Pnam*	--	Welin (1966)
5-fold	Lindströmite, $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$	$b = 56.07$ $= 5 \times 11.21$	$a = 11.57$	$c = 4.01$	$P2_1am^*$	--	Welin (1966)**

\* Labeling of cell edges and space group setting of cited reference has been transposed to the convention  $b > a > c$

\*\* Probable space group established by Ohmasa and Nowacki (1970b)

crystal data of Welin for "lindströmite" while retaining Johansson's earlier chemical composition. The name has become even more ambiguous now that Large and Mumme (1975), and Žák, Syneček, and Hybler (1974) have shown that  $\text{CuPbBi}_3\text{S}_6$  does exist as a distinct specie with quite different crystallography.

#### The $Z^n$ nomenclature

According to the model proposed by Moore (1967),  $\text{CuPbBi}_3\text{S}_6$  should be  $2^1$ , a 2-fold superstructure based upon bismuthinite. This mineral instead has the cell of bismuthinite, and a space group of lower symmetry ( $Pb2_1m$ ) which permits the rank of the equipoints occupied by the metals to be less than 4 as assumed by Moore (Mumme, 1975). Similarly, the new mineral pekoite<sup>2</sup>,  $\text{CuPbBi}_{11}\text{S}_{18}$  (Mumme and Watts, to be published) has a 3-fold superstructure and is not  $6^1$  as in Moore's proposal. This unanticipated behavior is apparently caused by the tendency of Pb to order among as many distinct bismuthinite chains as possible. A chain of composition  $\text{CuPbBi}_3\text{S}_6$ , also found in gladite (Kohatsu and Wuensch, 1972), appears to be the predominant structural feature in the bismuthinite de-

rivatives despite the close dimensional similarity (Kohatsu and Wuensch, 1971) of the aikinite, ( $\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ ) and bismuthinite ( $\text{Bi}_4\text{S}_6$ ) ribbons.

#### Proposed nomenclature

The following conventions are proposed to standardize the terminology used to describe the structures of minerals intermediate to bismuthinite and aikinite, and to clarify the names assigned to particular species.

(1) The crystal structure of aikinite is itself a derivative of the simpler structure of bismuthinite. It is therefore proposed that the intermediate Cu-Pb-Bi sulfosalts be referred to as "bismuthinite derivatives" rather than "aikinite derivatives" as has been the case in several preceding papers.

(2) It is proposed that the name "lindströmite" be used to designate the 5-fold superstructure of composition  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$  (Welin, 1966) identified in the same material which was originally studied by Johansson (1924)<sup>3</sup>. The new name krupkaite<sup>4</sup> has been

<sup>3</sup> Proposal approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. (September, 1975).

<sup>4</sup> Approved by Commission on New Minerals and Mineral Names, International Mineralogical Association (name proposed by Lubor Žák of Charles University, Prague).

<sup>2</sup> Name approved (July, 1975) by Commission on New Minerals and Mineral Names, International Mineralogical Association.

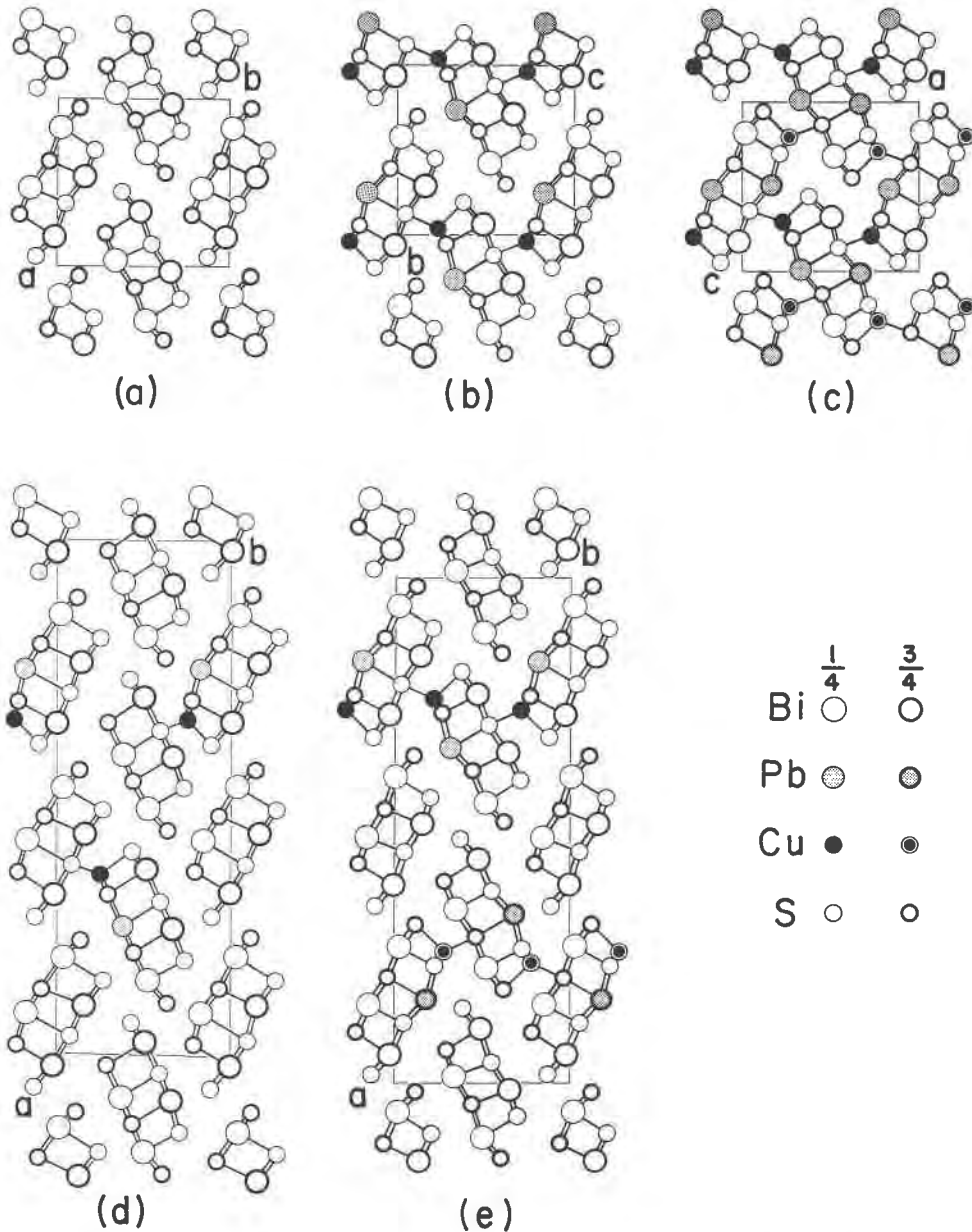


FIG. 1. Projections along their common 4 Å translation of those crystal structures presently known in the bismuthinite-aikinite series. (a) bismuthinite,  $\text{Bi}_2\text{S}_3$  (Kupčik and Veselá-Nováková, 1970); (b) krupkaite,  $\text{CuPbBi}_3\text{S}_6$  (Mumme, 1975); (c) aikinite,  $\text{CuPbBiS}_6$  (Kohatsu and Wuensch, 1971); (d) pekoite,  $\text{CuPbBi}_{11}\text{S}_{18}$  (Mumme and Watts, to be published); (e) gladite,  $\text{CuPbBi}_6\text{S}_6$  (Kohatsu and Wuensch, 1972). A single line indicates a bond to an atom at the same elevation. Double lines represent a pair of bonds to two atoms which are related by the lattice translation normal to the projection, and which superpose in projection. Indication of the weaker, secondary bonds which exist between the four-membered ribbons has been omitted for clarity.

given to the mineral  $\text{CuPbBi}_3\text{S}_6$  recently discovered at Tennant Creek (Large and Mumme, 1975) and at Krupka in the Krušné hory Mountains in Northwestern Bohemia, by Žák, Syneček, and Hy-

ler (1974). This leaves unresolved the question of whether Johansson's 1924 analysis might have been performed on a collection of fragments which actually consisted of  $\text{CuPbBi}_3\text{S}_6$ . In view of Welin's

TABLE 2. Chemical Analyses of Lindströmite and Krupkaite\*

Element	CuPbBi <sub>3</sub> S <sub>6</sub>	Johansson (1924)	Krupkaite		Lindströmite (Welin, 1966)	Cu <sub>3</sub> Pb <sub>3</sub> Bi <sub>7</sub> S <sub>15</sub>
			Large and Mumme (1975)	Žák et al. (1974)		
Cu	5.83	5.84	5.95	5.0	6.5	6.92
Pb	19.01	18.95	19.3	21.1	22.1	22.57
Bi	57.51	57.13	59.8	55.4	53	53.04
S	17.65	[17.88]	17.25	18.5	[18.4]	17.47
Se	--	--	0.95	--	--	--

\* (in weight percent).

observation (1966) that grains of this material contain abundant exsolutions, this seems extremely unlikely.

(3) The  $Z^n$  classification proposed by Moore is based upon the assumption that bismuthinite derivatives should assume space groups in which the rank of available equipoints is a multiple of 4. This is not borne out by the crystal data for the new minerals krupkaite (CuPbBi<sub>3</sub>S<sub>6</sub>) and pekoite (CuPbBi<sub>11</sub>S<sub>18</sub>) and appears to be due to the tendency of Pb to form CuPbBi<sub>3</sub>S<sub>6</sub> ribbons rather than to segregate into solely aikinite and bismuthinite-like units. Accordingly, we propose that the  $Z^n$  classification be discontinued. The known bismuthinite derivatives are composed of three distinct structural units and have subgroups which are less directly related than anticipated. We therefore feel that the establishment of distinct names for these ordered mineral species, in accord with traditional mineralogical practice, is justified.

(4) Bismuthinite, krupkaite, and aikinite have provided examples, within a cell of virtually identical geometry, of structures composed solely of four-membered ribbons of composition Bi<sub>4</sub>S<sub>6</sub>, CuPbBi<sub>3</sub>S<sub>6</sub>, and Cu<sub>2</sub>Pb<sub>2</sub>Bi<sub>2</sub>S<sub>6</sub>, respectively. Accordingly, we propose that, in description of the structures of the more complex derivatives, the structural units be designated as "bismuthinite"- (or stibnite-), "krupkaite"- or "aikinite"-like ribbons, respectively, according to the name of the parent structure which consists solely of such units. The designations (b), (c), and (a) ribbons for these units, as introduced by Ohmasa and Nowacki (1970b), are arbitrary labels. Such nomenclature is less informative now that representative structures are known for each type of ribbon.

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