50. **On the Structure of Galenobismutite**

By Yoshio TAKÉUCHI and Junkou TAKAGI*

Mineralogical Institute, Faculty of Science, University of Tokyo

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With increasings of Bi/Pb ratio, the structures of the crystalline phases on the PbS-Bi₂S₃ join vary in an interesting manner. The structure of phase III (Bi/Pb=2/3) (Otto and Strunz, 1968) is built on the same principle as that of phase II (Bi/Pb=1/3) which we discussed in our previous report. Basic difference between the two structures is only in the thickness of slabs; that of phase III is two-third that of phase II. Owing to the smaller dimensions of the slabs and higher Bi/Pb ratio, metal atoms in the structure of phase III are statistically distributed over the metal positions (Takagi and Takéuchi, 1972), while in phase II they are partially ordered.

On the other hand, the structure of phase IV (Bi/Pb=2) bears, in appearance, no relation with those of phase II and phase III. However, a closer examination into the structure (Iitaka and Nowacki, 1962) reveals that it is in fact made up of fragments of a galena type structure, though they are fairly distorted owing to higher Bi/Pb ratio.

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Fig. 1. (a) The structure of galenobismutite schematically illustrated using fragments of the galena structure. Fragments F and F' are symmetrically related to each other by glide reflections of the space group Pnam.

(b) The structure of galenobismutite projected along the c axis.

* Present address: Central Research Laboratory, SHARP Corporation, Tenri, Nara.
ratio in the structure. This situation is depicted in Fig. 1. Fig. 1(a) shows a set of fragments having ideal galena structure which are mutually related by glide reflections in the space group Pnam. If each pair of closer metal atoms, which have been so placed in such an arrangement of fragments, is replaced by one metal atom as indicated by an arrow, and a pair of sulfur atoms S₁ and S₁' are shifted, along the c axis, by 1/2, the resulting structure is essentially the same as that of galenobismutite (Fig. 1b). One of the constituent galena fragments in the structure of galenobismutite is indicated in Fig. 1(b) by shadings, showing its distortion due to formation of Bi-S covalent bonds.

In the very similar way, it is possible to represent the structures of cosalite (Bi/Pb=1) and even bismuthinite (phase VI, B₂S₃) by assemblies of galena fragments. Both cosalite and bismuthinite have the same space group Pbnm which is in fact equivalent to Pnam for galenobismutite. If therefore the a and b axes of galenobismutite are interchanged, the three minerals, now discussing, have a common space group Pbnm. Their unit cell dimensions are compared below:

![Fig. 2. (a) The structure of cosalite schematically illustrated using fragments of the galena structure. To complete structure, M1 and M2 must be replaced by a metal atom at T, M3 and M4 by a metal atom T', and S2 must be eliminated. (b) The c axis projection of the structure of cosalite.](image-url)
As will be conceivable from the above table, the dimensions of fragments in the cosalite structure are larger than those in galenobismutite, and those of bismuthinite are smaller. The arrangement of ideal galena fragments which corresponds to the structure of cosalite...
(Weitz and Hellner, 1960) is shown in Fig. 2(a). As will be observed in this figure, for this particular case, additional pairs of sulfur atoms have to be introduced in the intersticies of fragments to complete the structure corresponding to that of cosalite. The arrangement of fragments which corresponds to the structure of bismuthinite (Kupčík and Veselá-Nováková, 1970) is shown in Fig. 3(a). A salient feature common to the above three structures is that the glide planes which relate one fragment to another are parallel to (311) plane of their constituent galena fragments.

As the result, the structures of naturally occurring phases in the PbS-Bi$_2$S$_3$ join may be classified into two categories:

1. Those in which Bi/Pb<1. They consist of polysynthetic twins of galena slabs taken place on (311).
2. Those in which Bi/Pb≥1. In their structures galena slabs are broken into fragments and they are joined together by glide reflections which are again parallel to (311) plane of galena fragments.

In the structures of the both categories, dimensions of slabs or fragments decrease with increasings of Bi/Pb ratios. It is to be noted that the structures which belong to the first category occur in the high temperature phase V though its Bi/Pb ratio has a large value of 4. The structure of phase V will be discussed in the subsequent paper of a series of our studies on the PbS-Bi$_2$S$_3$ join.

References

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