

## Ordered Chemical Twinning in the $\text{Bi}_2\text{S}_3$ - $\text{CuPbBiS}_3$ Series

JAN-OLOV BOVIN\* AND JEAN GALY

*Laboratoire de Chimie de Coordination du C.N.R.S., B.P. 4142, 310 30 Toulouse Cedex, France*

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Ordered chemical twinning on the unit cell level is used to describe the structures of the  $\text{Bi}_2\text{S}_3$ - $\text{CuPbBiS}_3$  series. A possible mechanism, chemical twinning growth, is introduced to explain the exsolution textures found in crystals from this system.

### Introduction

The crystal structures of the minerals in the system bismuthinite-aikinite ( $\text{Bi}_2\text{S}_3$ - $\text{CuPbBiS}_3$ ) have been subjects of many publications concerning their nomenclature and classification. Most facts are summarized by Harris and Chen (1) and by Mumme and Watts (2). In the following note another approach will be taken to describe and to relate the structures to other ones on the basis of structure building operations such as chemical twinning (3), stereochemical effects of lone pairs (4, 5) and swinging twinning (6).

The coordination polyhedra of sulfur around Bi(III) and Pb(II) are generally described as distorted octahedra with a "split vertex" or as a square pyramid with one or two more-distant sulfurs, Bi and Pb are always situated off-centre in the octahedra or above the square face of the pyramid. The structural relationships between bismuthinite ( $\text{Bi}_2\text{S}_3$ ), pekoite ( $\text{CuPbBi}_{11}\text{S}_{18}$ ), gladite ( $\text{CuPbBi}_5\text{S}_9$ ), krupkaite ( $\text{CuPbBi}_3\text{S}_6$ ), hammarite ( $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ ), and aikinite

( $\text{CuPbBiS}_3$ ) are usually described in terms of three different ribbons  $\text{Bi}_4\text{S}_6$ ,  $\text{CuPbBi}_3\text{S}_6$  and  $\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ .

### Structural Relations

The coordination polyhedra of Bi and Pb can instead be described as more or less distorted one-capped trigonal prisms; in this way it is easier to understand structural relationships to other compounds. There are two kinds of one-capped trigonal prism in the structures—one which always contains the bismuth atom as is shown in Fig. 1a, and one which can contain either Pb(II) or Bi(III) and this can be seen in Fig. 1b. The bond between the capping sulfur and Bi/Pb is marked with dotted lines. The trigonal prisms share corners and edges in a way illustrated in Fig. 1c, d, e, and the prisms of Fig. 1b also share faces along the *c*-axis.

It was pointed out long ago (7) that the structure of  $\text{U}_2\text{S}_3$  (Fig. 1c) was essentially isostructural with that of  $\text{Sb}_2\text{S}_3$  (and  $\text{Bi}_2\text{S}_3$  in Fig. 1d) and later on Wickman (8) showed that  $\text{CuPbBiS}_3$  (Fig. 1e) was also. The only difference was a slight displacement of the Sb (Bi or Pb) atom compared with the position of the uranium atom in  $\text{U}_2\text{S}_3$  structure. The

\* Permanent address: Inorganic Chemistry 2, Chemical Center, P.O. Box 740, S-220 07 Lund 7, Sweden.

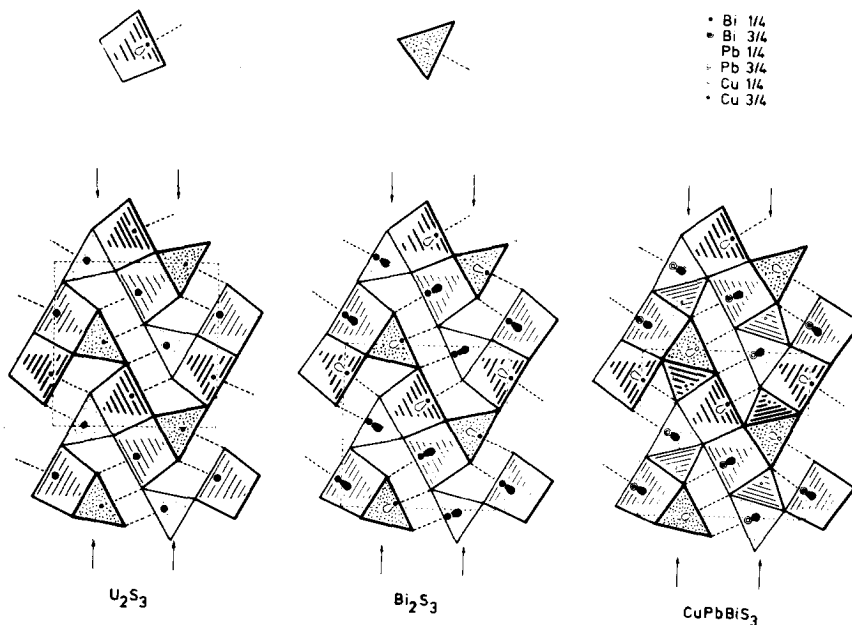


FIG. 1. The structures of  $U_2S_3$  (c), bismuthinite ( $Bi_2S_3$ ) (d), and aikinite ( $CuPbBiS_3$ ) (e) projected along their shortest axis. Uranium atoms are at  $\frac{1}{4}$  and  $\frac{3}{4}$  as are Pb and Bi in the other structures. The sulfur atoms are situated at the corners of the polyhedra at  $\frac{1}{4}$  and  $\frac{3}{4}$ . The stereochemically active lone pairs of Pb(II) and Bi(III) are marked as circle sectors. The trigonal prism which always contains Bi(III) are shown in (a) and the one which can contain Bi(III) or Pb(II) in (b).

difference can be explained by assuming that the lone pairs of electrons of Bi(III) and Pb(II), which usually require space comparable with that of anion (4, 5), push the Bi or Pb atoms towards the one-capped square face in order to make enough space in the trigonal prism (cf. Fig. 1c, d, e).

Swinging twinning on the unit cell level was introduced as a structure-building operation in the solid state (6) on the basis of the definitions of chemical twinning (3) and swinging crystallographic shear (9). It was found that with a certain direction (swing) of the twin planes in the structure of YO(OH) (closely related to the important TII structure type), the structure of  $Bi_2S_3$  could be derived by the twin operation (6). The twin operation can be visualized in the following way: copy the structure on transparent paper; cut out every second of the twin blocks along the twin planes (marked with arrows in Fig. 1c, d, e); rotate  $\pi/2$  rad around the twin axis

(perpendicular to the twin planes in this case); join them together along the edges of the trigonal prism and the parent structure YO(OH) of  $Bi_2S_3$  is obtained. It is worth noting that with another swing of the twin planes in the parent structure YO(OH) the structure type of  $Cr_3C_2$  (or  $K_2AgI_3$ ) is produced with almost the same twinning blocks as in the  $Bi_2S_3$  structure (6).

#### Ordered Occupancy of the Twin Planes

In almost all chemical twinings on the unit cell level, the twin planes contain coordination polyhedra which are different from those found in the parent structure (3). The twin planes of  $Bi_2S_3$  contain tetrahedra and trigonal prisms of another orientation than the parent structure (cf. Fig. 1). The twin planes can in this way accommodate ions which normally do not fit the parent structure as in this case Cu(I), which enter the tetra-

hedral site at the same time as Pb(II) enter the nearest trigonal prism in order to balance the charge. The compounds of the  $\text{Bi}_2\text{S}_3\text{-CuPbBiS}_3$  series known up to now can thus be understood as ordered chemical twinings with different occupancy of Cu(I) and Pb(II) in the twinning planes (cf. Fig. 2). The recently published structure of Lindströmite (10),  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$  (not included in Fig. 2), show also the same chemical twinning planes containing the Cu(I) atoms in an ordered way.

The use of twin planes to accommodate ions which normally do not fit into the parent structures gives rise to the question of whether even macroscopic twinings in minerals are caused by ion impurities (3). If this is the case different ions or combinations of ions should yield different twin laws in the same mineral. One possible way to investigate such twinings is by means of high resolution electron microscopy.

### Possible Defects and Crystal Growth

Progressive filling of the tetrahedral sites of the twin planes with Cu(I) and a consequent exchange of Bi(III) for Pb(II) in the trigonal prisms can produce any solid solution between  $\text{Bi}_2\text{S}_3$  and  $\text{CuPbBiS}_3$ . This has been stated to occur (11, 2) for synthetic members made at temperatures above  $300^\circ\text{C}$ . It is believed that in the case of the minerals, which are thought to be crystallized at lower temperatures, the filling of the twinning planes is mainly ordered (cf. Fig. 2), even if some streaks have been reported along  $a$  (1) which indicates different occupancy in the twin planes or different width of the slabs between the twin planes. One possibility is that such a crystal could contain some of the different twinning planes shown in Fig. 2.

The exsolution texture existing in the  $\text{Bi}_2\text{S}_3\text{-CuPbBiS}_3$  series and described by

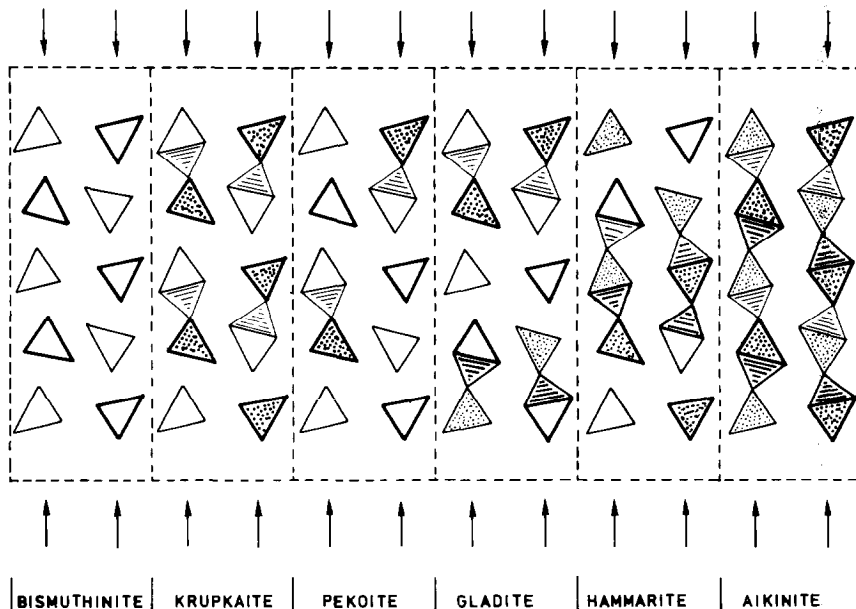


FIG. 2. Idealized drawing of the occupancy of the tetrahedral and trigonal prism sites of the twin planes found in the  $\text{Bi}_2\text{S}_3\text{-CuPbBiS}_3$  series. Dotted triangles are Pb(II)-centered trigonal prisms. Open triangles are Bi(III)-centered ones. Triangles marked with lines are tetrahedra centered by Cu(I). Polyhedra situated at different levels are drawn with thin and heavy outlines. The Bi(III)-centered trigonal prisms which make up the twin blocks between the twinning planes are omitted in the figure.

several authors (i.e. 2) can be understood as *chemical twinning growth* which has taken place in a direction perpendicular to the twin planes. The crystallization process proceeds twin block after twin block over twin planes which have a Cu(I) and Pb(II) occupancy depending of the variation in the Cu(I) (and Pb(II)) concentration. The exsolution texture is a macroscopic growth texture probably yielded by chemical twinning growth.

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