

Polytypism in baumhauerite

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ABSTRACT

High-resolution transmission electron microscope studies reveal the origin and nature of polytypism in baumhauerite. The polytypes are stacking variants of the basic baumhauerite structure, $a = 22.80$, $b = 8.36$, $c = 7.89$ Å, $\beta = 97.27^\circ$, and involve inversion of the Pb and As distribution about **b** and lead to multiplicity along **a**. A new polytype of baumhauerite is reported: baumhauerite- $\Psi O3abc$, $a = 68.3$, $b = 8.4$, $c = 7.9$ Å. The mineral baumhauerite- $2a$ is also considered to be a member of this polytypic family. Stacking disorder was observed in crystals of the longer period polytypes. The long-period polytypes baumhauerite- $2a$ and baumhauerite- $\Psi O3abc$ contain up to one atom of Ag pfu, and it appears that Ag may play a role in stabilizing the longer period polytypes.

INTRODUCTION

Baumhauerite, $Pb_{16}As_{12}S_{36}$, was first described as a new mineral from Lengenbach, Binntal, Switzerland, by Solly and Jackson (1902). At this locality the mineral occurs with a series of closely related lead arsenic sulfide minerals. Baumhauerite has since been found at a number of other localities (Graeser et al., 1986; Anthony et al., 1990). Recently Pring et al. (1990) described baumhauerite- $2a$, a Ag-bearing mineral with a superstructure derived from baumhauerite and with an average composition $Pb_{11.1}Ag_{0.7}As_{17.2}Sb_{0.4}S_{36}$. This mineral occurs intergrown on the unit-cell level with Ag-free baumhauerite at Lengenbach, Switzerland, and at Quiruvilca, Peru (Pring et al., 1990; Robinson and Harris, 1987). Pring (1990) also described the occurrence of disordered polysomatic intergrowths in the lead arsenic sulfide minerals at Lengenbach. Further HRTEM studies, which are reported here, show that these disordered polysomatic intergrowths are, in fact, products of stacking disorder in baumhauerite polytypes. In this reexamination a new baumhauerite polytype has been identified. Interestingly, the concept of polytypism was introduced by H. A. Baumhauer, for whom baumhauerite was named, to explain the many structural modifications of SiC formed by different stacking sequences of apparently structurally and stoichiometrically identical layers or units (Baumhauer, 1915).

STRUCTURE AND COMPOSITION OF BAUMHAUERITE

The structure of baumhauerite was determined in detail by Engel and Nowacki (1969) following the earlier approximate determination by Le Bihan (1962). Details of the unit-cell parameters and symmetry are given in Table 1. Baumhauerite is a member of the sartorite group, a series of polysomatic lead arsenic sulfide minerals. The

structures of the sartorite group minerals, in broad detail, consist of edge-sharing chains of PbS_5 polyhedra (truncated trigonal prisms) with a 7.9 Å repeat. These chains are linked by strips of Pb and As polyhedra (monocapped trigonal prisms and highly distorted octahedra, respectively), which form $(Pb,As)S_5$ slabs. The $(Pb,As)S_5$ slabs are arranged about the PbS_5 chains in a zig-zag or chemically twinned manner (Fig. 1). Slabs of two widths occur, either two As polyhedra wide or three As polyhedra wide. The slabs two polyhedra wide are similar to those found in sartorite (S-type units), and those three polyhedra wide are similar to those found in dufrenoyite (D-type units). The structure of sartorite contains two S units, and dufrenoyite two D units (Pring, 1990). In baumhauerite the sequence is DS (although because of Pb-As substitutions the S and D units have compositions slightly different from those found in dufrenoyite and sartorite, respectively). Sartorite has a 4.2-Å *b* repeat, which corresponds with the height of a PbS_5 truncated trigonal prism. In all the other sartorite group minerals, including baumhauerite, the *b* repeat is doubled to 8.4 Å because of the ordering of Pb and As in the $(Pb,As)S_5$ slab, and the structures can be considered as consisting of two layers. In baumhauerite the arrangement of Pb and As in these two layers is quite different (Fig. 2).

Although the structural formula of baumhauerite was determined as $Pb_{11.6}As_{15.7}Ag_{0.6}S_{36}$ by Engel and Nowacki (1969), published chemical analyses rarely correspond exactly with this composition. This may in part be due to the difficulty of obtaining accurate S analyses in these minerals by electron microprobe analyses. However the variation may also be due to the compositional flexibility of the $(Pb,As)S_5$ slabs, which can accommodate substitution of As for Pb and vice versa. It should be noted, however, that these are not simple substitutions on the

TABLE 1. Unit-cell data from the baumhauerite polytypes

Mineral	Composition	Structure	Unit cell
Baumhauerite	$Pb_{12}As_{16}S_{36}$	↑	$a = 22.80, b = 8.36, c = 7.89 \text{ \AA}, \beta = 97.27^\circ$
Baumhauerite-2a	$Pb_{22}Ag_{14}As_{34}S_{72}$	↑ ↓	$a = 44.75, b = 8.48, c = 7.89 \text{ \AA}, \beta = 93.63^\circ$
Baumhauerite-ψO3abc	$Pb_{38.1}Ag_9As_{51.9}Sb_{0.9}S_{96}$	↑ ↑ ↓	$a = 68.3, b = 8.48, c = 7.89 \text{ \AA}, \beta = 90^\circ$

same site but are instead the result of major displacements in the coordinating S atoms: the Pb and As atoms occupy different sites. Kutoglu (1969) determined the phase diagram for the Pb-As-S system and found the baumhauerite structure to be stable over the range 55–60 mol% PbS ($Pb_{12}As_{16}S_{36}$ to $Pb_{10.4}As_{17}S_{36}$). At the Pb-rich end of the compositional field, baumhauerite overlaps with liveingite, and at the lower end it overlaps with rathite (a phase not found synthetically by Kutoglu, 1969). Ag and Tl have been observed substituting into the sartorite minerals. This substitution takes the form $2Pb = Ag(Tl) + As$, and it contributes to considerable variation from the ideal stoichiometry. A systematic study of the variation of baumhauerite crystal chemistry with stoichiometry is yet to be undertaken, and the exact nature of these substitutions remains unclear.

EXPERIMENTAL METHODS

Crystals of the baumhauerite polytypes from Lenggenbach, Binntal, Switzerland, were obtained from the collections of the South Australian Museum, Adelaide, the Museum of Victoria, Melbourne, and the Natural History Museum, Basel.

Material was prepared for examination in the electron microscope by grinding under acetone or *n*-butanol in an agate mortar and then by dispersal on Cu grids coated with holey carbon support films. The specimens were examined in several transmission microscopes but mainly in a JEOL 200 CX at 200 kV, a Philips EM 430, and a CM 30 operating at 300 kV with theoretical point-to-point resolutions in the range 2.0–2.8 Å. Simulations of high-resolution images were performed by the conventional multislice method (Goodman and Moodie, 1974) using local programs based on the routines by G. R. Anstis (personal communication).

RESULTS

Reexamination of baumhauerite-2a and disordered intergrowths

Figure 3 shows a set of [001] zone electron diffraction patterns for baumhauerite, baumhauerite-2a, and the so-called disordered liveingite of Pring (1990). Note the strong baumhauerite subcell reflections, which are present in all four diffraction patterns. Figure 3a shows a simple orthogonal $22.62 \times 8.4 \text{ \AA}$ net corresponding with the

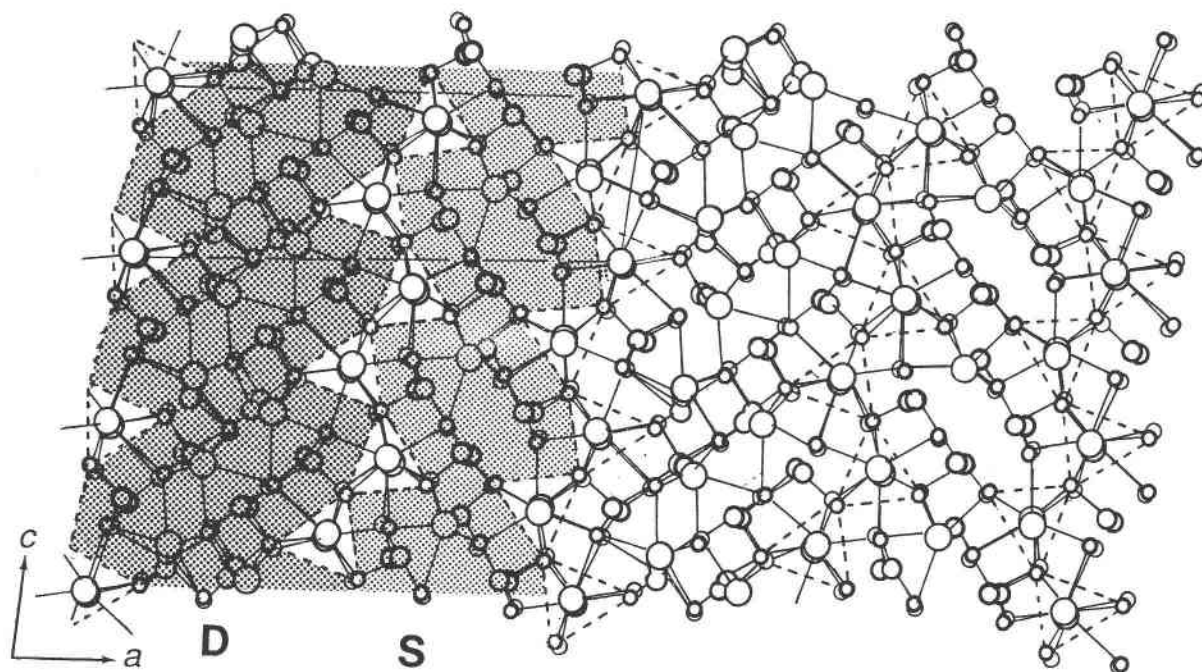


Fig. 1. The structure of baumhauerite projected down [010] showing the two types of structural units (S-type slabs and D-type slabs) arranged about the PbS, edge-sharing polyhedra chains. The circles in order of decreasing size: Pb, As, S.

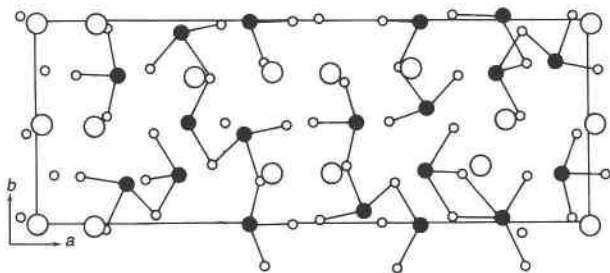


Fig. 2. The baumhauerite structure projected down [001]. Note that Pb and As in the $(\text{Pb,As})\text{S}_3$ slabs are ordered along b and that the structure can be considered as two layers. The composition of the lower layer ($0.0 \leq z \leq 0.4999$) is $\text{Pb}_7\text{As}_7\text{S}_{17}$, and that of the upper layer ($0.5 \leq z \leq 0.9999$) is $\text{Pb}_5\text{As}_5\text{S}_{19}$, based on the refinement of Engel and Nowacki (1969). In the longer period baumhauerite polytypes the order of Pb and As between the layers is periodically reversed. Pb = large open circles, As = solid circles, S = small open circles.

cell of baumhauerite. The diffraction pattern of baumhauerite- $2a$ (Fig. 3b) shows a $44.5 \times 8.4 \text{ \AA}$ net; the reflections are streaked along a , indicating some degree of stacking disorder in this direction. The diffraction pat-

terns in Figure 3c and 3d are from specimen M35933, the disordered liveingite of Pring (1990). Figure 3c is heavily streaked along a , indicating a high degree of stacking disorder in this direction. It was suggested by Pring (1990) that this stacking disorder was due to polytypic disorder between sartorite-like (S) and dufrénoyite-like (D) structural units; however, Figure 3d, which is from an adjacent section of the same crystal fragment, shows rows of sharp reflections that define an orthogonal $68.3 \times 8.4 \text{ \AA}$ net, a lattice. This lattice corresponds geometrically with a $3a$ superstructure of baumhauerite. Figure 4a shows that the structure repeat is $3 \times a_{\text{baum}} \sin \beta = 68.3 \text{ \AA}$. A disordered part of the same crystal is shown in Figure 4b. The detail of the image motif in both images is very similar to that of baumhauerite and baumhauerite- $2a$ (Fig. 5). Although the baumhauerite lattice is orthogonal viewed down [001], the image motif shows a pronounced diagonal along [101]; this reflects the distribution of the Pb atoms in the cell. This feature is also prominent in disordered and ordered images (Fig. 4) but at the prominent planar defects the diagonality of motif is reversed. In the 68.3-\AA phase (Fig. 4a), the diagonality of the image motif is reversed every third strip. Attempts

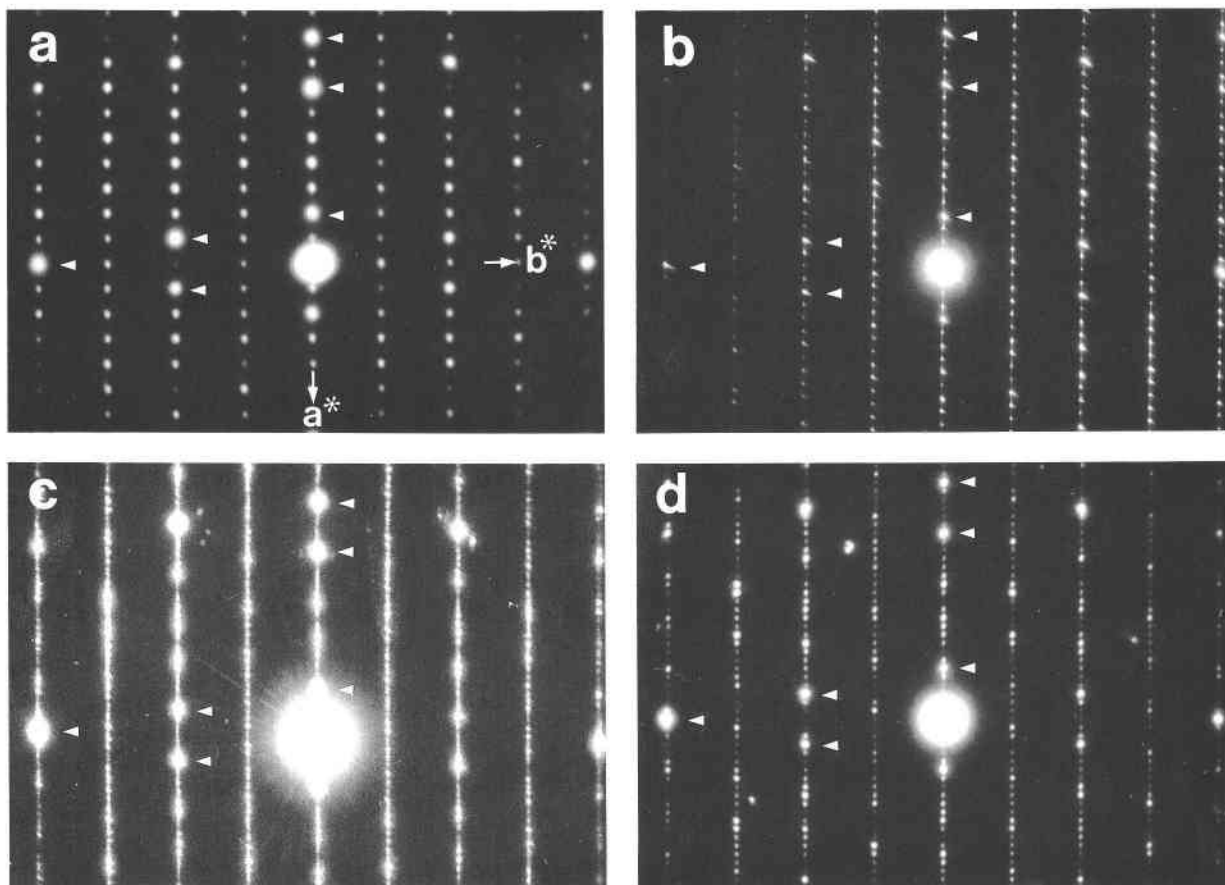


Fig. 3. The [001] zone electron diffraction patterns of baumhauerite polytypes. Common subcell reflections are indicated. (a) Baumhauerite, showing a rectangular net $22.62 \times 8.4 \text{ \AA}$. (b) Baumhauerite- $2a$, showing a rectangular net $44.5 \times 8.4 \text{ \AA}$. (c) Disordered liveingite M35933, showing streaking along a^* due to polytypic disorder. (d) Baumhauerite- $\psi\text{O}3abc$, showing a rectangular net $68.3 \times 8.4 \text{ \AA}$ (M35933).

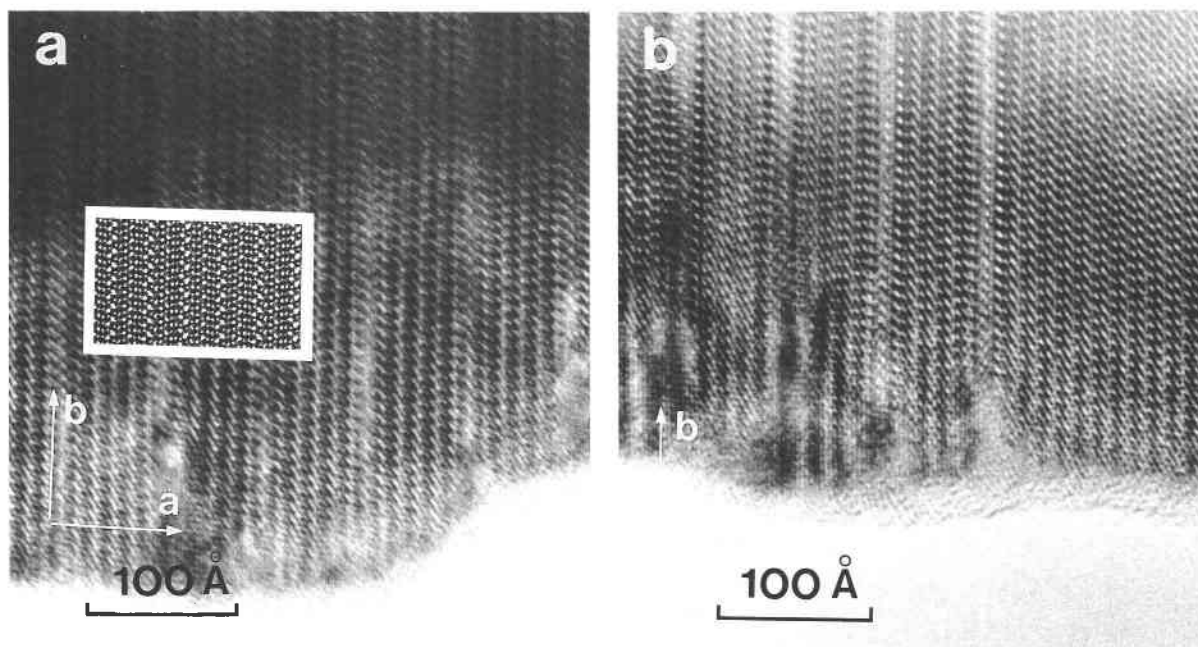


Fig. 4. (a) Lattice image of baumhauerite- $\Psi O3abc$ down [001], corresponding to diffraction Fig. 3d. Note that the diagonal direction of the image motif is reversed every third baumhauerite cell. The computer image simulation is inset. The image simulation was calculated for a foil thickness of 60 Å and a defocus of -840 Å. (b) Lattice image showing a disordered intergrowth of baumhauerite and baumhauerite- $\Psi O3abc$. Part of the same crystal shown in a.

to derive a model for this structure using the model proposed by Pring (1990) for disordered livingite were unsuccessful. It is not possible to have a six-unit structure with a 68.3-Å repeat using the S and D layers of appropriate composition as defined by Pring (1990). However a model based on the periodic inversion of the baumhauerite cell about the b repeat gave a satisfactory match (see insert on Fig. 4a). This is equivalent to inversion,

about the b repeat, of the Pb-As ordering in the baumhauerite cell.

With arrows to denote the relative orientation of the baumhauerite cells (about b) the sequence is $\uparrow \uparrow \downarrow$. In accordance with the guidelines for polytype nomenclature (Guinier et al., 1984) this polytype is baumhauerite- $\Psi O3abc$, where ΨO indicates that symmetry is pseudo-orthorhombic. Confirmation of this interpretation of the

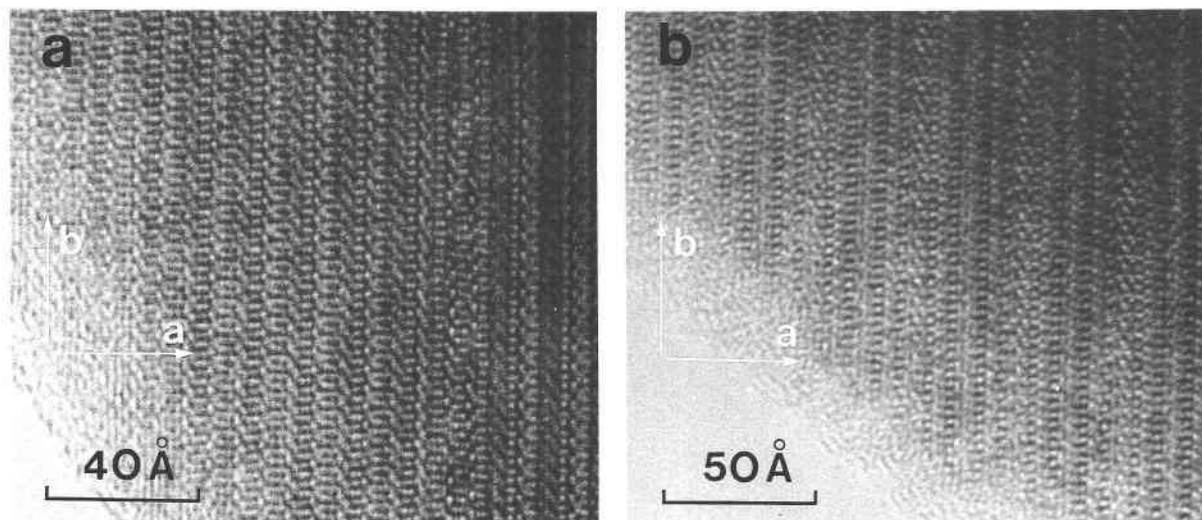


Fig. 5. Lattice images of (a) baumhauerite and (b) baumhauerite-2a, showing the similarity of lattice motifs. Note the strong diagonality of the lattice motifs.

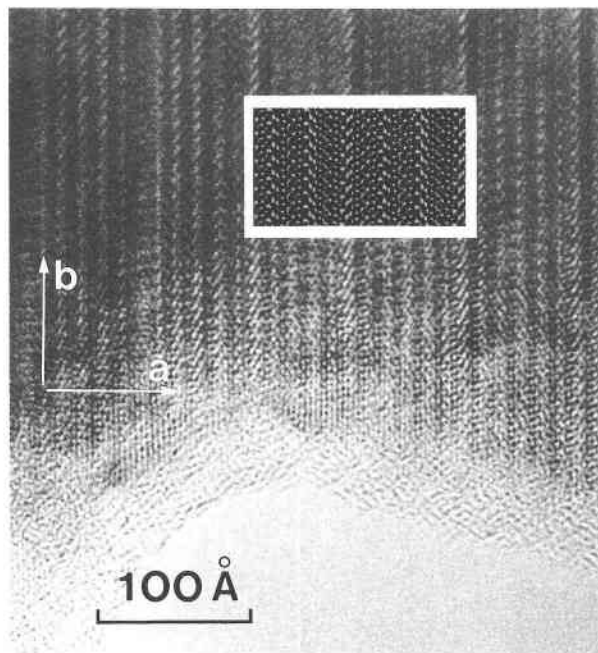


Fig. 6. Part of the original lattice image of disordered liveingite from Pring (1990) with a new image simulation based on the baumhauerite polytype model. The disorder evident in the image is not polysomatic but due to the stacking disorder of baumhauerite cells. The image simulation was calculated for a foil thickness of 60 Å and a defocus of -570 Å.

structural nature of the disordered liveingite is shown in Figure 6, part of the original image of disorder shown in Pring (1990), together with new image simulations based on the baumhauerite polytype model. These new image simulations are a more satisfactory match than those based on the disordered intergrowth of D and S type units. The cell and approximate compositional data for baumhauerite- $\Psi O3abc$ are summarized in Table 1. It was not possible to determine accurately the composition or cell of baumhauerite- $\Psi O3abc$ because of the disordered nature of the specimen, but the average composition was determined to be $Pb_{12.7}AgAs_{17.3}Sb_{0.3}S_{36}$, which has a slight excess of Pb and As over baumhauerite, a feature which is probably a reflection of the accuracy of the S analysis (Pring et al., 1990).

Reexamination of the baumhauerite-2a images (Fig. 5b) in the light of these findings suggests that its structure is based on the same principle, and the sequence is $\uparrow \downarrow$ (Pring et al., 1990). However the ubiquitous presence of Ag or Tl in baumhauerite-2a indicates that these monovalent ions play an important role in structural stabilization.

DISCUSSION

A summary of the cell and compositional data for the baumhauerite polytypes is presented in Table 1. The a repeats for the various polytypes are, or are very close to, simple multiples of the a repeat of baumhauerite. In ad-

dition to these three polytypes, it appears, on the basis of cell-parameter data, that the 115-Å phase of Ozawa and Takéuchi (1983) may also be a baumhauerite polytype. Ozawa and Takéuchi (1983) considered the phase to be a new polysome between liveingite and rathite; however, the 115.4-Å a repeat is similar to $5 \times a$ baumhauerite (114 Å). Ozawa and Nowacki (1974) reported a long-period lead arsenic sulfide mineral, rathite IV, with an a repeat of 138.3 Å. This repeat is similar to the spacing of six layers of baumhauerite ($6 \times a_{\text{baum}} \sin \beta = 136.6$ Å), and it appears possible that rathite IV is a polytype of baumhauerite rather than of rathite. Further work, recently initiated, is underway in an attempt to clarify the nature of this phase.

The structural mechanism for polytypism in baumhauerite is clear from the HRTEM images: the reversal of the Pb-As order along b in the (Pb,As) S_3 slabs (inversion of the structure about b). However, it is likely that other, more subtle, structural processes may also be involved. The higher polytypes of baumhauerite are characterized by the presence of approximately one Ag atom pfu (36S). Baumhauerite has been observed to have a variable composition with respect to the presence of Ag. Both Ag-bearing and Ag-free baumhauerite have been reported from Lengenbach, and Rösch and Hellner (1959) synthesized both baumhauerite and baumhauerite-2a from Ag-free compositions, but natural baumhauerite-2a always contains approximately one atom pfu of Ag or Tl. It seems likely that Ag or other monovalent cations such as Tl play a role in stabilizing some of the baumhauerite polytypes, although the exact structural role is yet to be resolved. Price and Yeomans (1984) noted that, in many polytypic systems, phases are stabilized by impurities, thus obscuring any correlation of structure with variables such as temperature and pressure.

Detailed studies of the structure and composition of the baumhauerite polytypes are required before their relationships can be understood. Such an understanding, however, could also shed considerable light on the complex paragenesis of the lead arsenic sulfide minerals at Lengenbach.

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