THE CRYSTAL STRUCTURE OF Ag–Bi-BEARING HEYROVSKYITE

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Abstract

The crystal structure of Ag- and Bi-substituted heyrovskyite from La Roche Balue, west of Nantes, France, has been refined using 341 independent reflections to an R value of 0.06. An electron-microprobe analysis of heyrovskyite yields Pb3.67Cd0.05Ag1.15Bi3.13S9.19 (Moëlo et al., 1987), and the structure determination gave Pb3.36Ag1.32Bi3.32S9 for the crystal studied. Cell parameters are a 4.110(1), b 13.600(3), c 30.485(12) Å, space group Cmcn. Trigonal prismatic sites Me1 on planes of unit-cell twinning are fully occupied by Pb, octahedral sites Me2 and Me3 in central slab portions by ~80% Pb, ~20% Bi, semi-marginal octahedral site Me5 by Bi; Ag substitution takes place in the marginal octahedral site Me4: 0.657 Ag + 0.343 Bi. Departures from the PbS-like archetype in slabs are small, with the largest departures occurring in marginal sites Me4 and Me5.

Keywords: heyrovskyite, Ag and Bi substitution, crystal structure.

SOMMAIRE

La structure cristalline d’un échantillon de heyrovskyite provenant de La Roche Balue, située à l’ouest de Nantes (France), a été affinée jusqu’à un résidu R de 0.06 en utilisant 341 réflexions indépendantes. Les analyses à la microsonde électronique mènent à la composition Pb3.67Cd0.05Ag1.15Bi3.13S9.19 (Moëlo et al., 1987); l’affinement de la structure donne Pb3.36Ag1.32Bi3.32S9 pour l’échantillon que nous avons étudié. Ses paramètres réticulaires sont a 4.110(1), b 13.600(3), c 30.485(12) A, et le groupe spatial, Cmcn. Le plomb occupe les sites trigonaux prismatiques Me1 dans les plans de macle des mailles élémentaires; les sites octaédriques Me2 et Me3 de la couche centrale de la structure contiennent Pb (environ 80%) et Bi (20%). Le site octaédrique semi-marginal Me5 contient le Bi. Le remplacement par l’Ag affecte le site octaédrique marginal Me4 (0.657 Ag + 0.343 Bi). Les écarts structuraux de l’archétype PbS sont mineurs au sein des couches; les plus importants impliquent les sites Me4 et Me5.

Mots-clés: heyrovskyite, remplacement par Ag et Bi, structure cristalline.

INTRODUCTION

Heyrovskyite, Pb5.16(Ag,Cu)0.24Bi2.48S9, was described by Klominsky et al. (1971) as a natural analogue of Phase II, Pb6-pi2+2"73Se, synthesized and characterized by Otto & Strunz (1968). This characterization included a proposal of the schematic structure, which was confirmed and refined by Takéuchi & Takagi (1974) in their determination of the crystal structure of natural heyrovskyite, Pb5.40Ag0.16Bi2.42S9.

Considerable evidence has accumulated that heyrovskyite can contain appreciable amounts of silver, in the form of a coupled substitution Ag + Bi = 2Pb (Czamanske & Hall 1915). In 1977, Makovicky & Karup-Møller (1977b) defined heyrovskyite as the seventh member of the lillianite homologous series, PbN-x2rBi2**AgrS1,'a 2, where N is the order of the homologue, and x is the coefficient of Ag and Bi substitution, with the maximum value xmax = (N-2)/2. For heyrovskyite, the range of substitution can be conveniently expressed as the percentage of the maximally substituted end-member, PbBi4.5Ag2.5S9 (defined as Ag,BiHey100, but generally used in the simplified form Hey100), and the complementary percentage.
of the unsubstituted end-member, Pb$_5$Bi$_3$S$_9$, denoted as $^{3}$PbHey in the original paper (and usually omitted in the symbols used today). Thus, the material of Czamanske & Hall (1975) from Darwin, California, represents a selenan Ag- and Bi-substituted heyrovskyite Hey$_{58-60}$, whereas the heyrovskyite from Castelgar, British Columbia is Hey$_{71}$ (Karup-Møller & Makovicky 1981), and the present material from La Roche Balue is Hey$_{33-34}$ (Moëlo et al. 1987). The original heyrovskyite from Hurky, Bohemia, corresponds to Hey$_{8-19}$ (Klominský et al. 1971), and that from the Yakuki mine, Fukushima, Japan, is Hey$_{10}$ (Karup-Møller 1977).

The full extent of heyrovskyite solid-solution toward Hey$_{100}$ is not known. Synthetic studies do not seem to contribute unambiguously to this problem. Hoda & Chang (1975) found no solubility of Ag in heyrovskyite at 400°C and 500°C, whereas Chang et al. (1988), in their study of the system Ag$_2$S-Cu$_2$S-PbS-Bi$_2$S$_3$ at 500°C, reported a field of solid solution between Ag- and Cu-free heyrovskyite and a substituted heyrovkykite with a composition that shows Cu contents higher than Ag contents. However, the end-member composition they gave, Ag$_{0.76}$Cu$_{1.31}$Pb$_{3.18}$Bi$_{3.18}$S$_9$, represents a lillianite homologue with $N = 14.2$ and 61% substitution. The order $N$ is too high even if we assume the presence of Cu-for-Bi substitution, which could cause excessively high apparent values of $N$; obviously, more analytical work is needed on these synthetic products.

Possible compositional gaps in the heyrovskyite solid-solution at geologically interesting temperatures are not known, and all crystallographically studied cases display the same X-ray symmetry. The electron-microprobe data of Patrnick (1984) from Corrie Byue, Scotland (Hey$_{50}$), and unpublished data of W.H. Paar and collaborators on material from the Alps (oral comm.), have narrowed considerably the previously existing compositional gap between Hey$_{50}$ and the original material (and that of Paar et al. 1980), which show a limited extent of Ag and Bi substitution. No compositional pairs or exsolution phenomena, which would suggest a compositional gap, have been found as yet. On the other hand, the above maximal extent of substitution, slightly above 70%, has not been exceeded to date.

Unsubstituted synthetic heyrovskyite (“Phase II”), Pb$_5$Bi$_3$(x$_{2-4}$)S$_9$, displays a compositional field toward values richer in Bi (Salanci & Moh 1969). The presence of cation vacancies has been postulated for Phase II by Otto & Strunz (1968), but this claim still awaits crystallographic confirmation (see Makovicky 1977). The distribution of Ag atoms and of the associated ‘‘additional’’ Bi atoms in the structure has not been studied either. The distribution of Pb and Bi in the only heyrovskyite structure published, that of Pb$_{5.48}$Ag$_{0.18}$Bi$_{5.42}$S$_9$ (Hey$_{71-73}$) from Yakuki mine, Japan by Takéuchi & Takagi (1974), is assumed to be largely statistical. Pb occupies the central zones of slabs (311) PbS, and mixed occupancies occur in the marginal zones of these slabs, closer to the planes of unit-cell twinning; an assumption was made that Ag atoms occur in the marginal areas as well. It is quite possible that the crystal structure of heyrovskyite, with its large PbS-like areas, is stable only if Pb and Bi are statistically distributed in quasi-octahedral coordination. Heyrovskyite is presumed to be a high-temperature phase that is unstable at lower temperature (Klominský et al. 1971), combined with higher sulfur fugacities (Salanci & Moh 1969). Therefore, the discovery of aschamalmite, Pb$_{3.3}$Bi$_{2.1}$S$_9$ (Mumme et al. 1983), which shows evidence of cation ordering and ensuing distortion of the heyrovskyite-like anion framework, to a monoclinic symmetry, opens a new, as yet unexplored possibility of Pb-Bi cation ordering in lillianite homologues in the absence of Ag and Bi substitution as a possible means of stabilization at lower temperatures.

For at least a narrow range of heyrovskyite compositions, $\sim$Pb$_{2.5}$Ag$_{1.8}$Bi$_{3.8}$S$_9$ (~Hey$_{71}$) (Karup-Møller & Makovicky 1981), a monoclinic dimorph, eskimoite, exists ($N_1$:$N_2$ = 5:9 instead of $N_1$:$N_2$ = 7:7 where $N_1$ and $N_2$ are the order parameters for a pair of adjacent, alternating PbS-like slabs) with the compositions $\sim$Cu$_{0.2}$Pb$_{2.4-2.6}$Ag$_{1.8}$,Bi$_{3.4-3.7}$S$_9$ (Esk$_{71-68}$) (Makovicky & Karup-Møller 1977b). Differences in pressure-temperature conditions, kinetics of crystallization, or minor-element concentrations may lie behind this dimorphism; nothing is known about these factors at present. Eskimoite (unanalyzed) overgrows in trace amounts heyrovskyite(50) from La Roche Balue; disordered material with both heyrovskyite and eskimoite domains present, besides disordered portions, was found by one of the authors (W.G.M.) in NMNH specimen 127023 (“neyite" from Alice Arm, British Columbia, kindly provided for study by Dr J.S. White, Smithsonian Institute, Washington). For many occurrences, e.g., Corrie Byue (Patrnick 1984), only microprobe data exist, so that material can only be assumed to be heyrovskyite and not eskimoite.

In the current program of study of the heyrovskyite solid-solution, we intend to perform crystal-structure refinements on several members: synthetic Phase II, natural low-Ag heyrovkykite, aschamalmite and selected samples of Ag- and Bi-substituted heyrovskyite. These studies should elucidate the distribution of cation vacancies,
Pb–Bi ordering or disorder, the cation sites influenced by Ag and Bi substitution, as well as deformations of the ideal heyrovskyite framework connected with these phenomena. Furthermore, the changes in the bonding scheme of Bi as a result of substitution processes will be examined.

As the first contribution in this series, the crystal structure of Ag- and Bi-substituted heyrovskyite from La Roche Balue (Loire Valley, France) is described.

**EXPERIMENTAL**

The analyzed crystals have been extracted from a polished section used in the study of the W–As–(Pb, Bi, Ag) mineralization at La Roche Balue, west of Nantes, France by Moëlo et al. (1987). At this deposit, heyrovskyite (with traces of eskimoite) has been deposited together with quartz, scheelite, arsenopyrite, gustavite, vikingite and galena at 350–400°C. The average of five microprobe analyses, closely spaced within the area Hey33–Hey54 of the phase diagram Pb5S3–Bi5S3–Ag5S5, gives (in wt. %): Pb 41.24, Cd 0.27, Ag 6.73, Bi 35.52, Sb 0.04, S 15.96, Se 0.03, total 99.79, giving a formula Pb3.67Cd0.65Ag1.15Bi3.13Se0.16 (Moëlo et al. 1987, Table III), which corresponds to Heyrovsky of the phase diagram Pb2S2-Bi2S3-

A Weissenberg study of heyrovskyite crystals gave starting unit-cell parameters: \( a = 13.61(1) \) Å, \( b = 30.47(2) \) Å, and \( c = 4.08(2) \) Å. From extinction rules and relationships among X-ray intensities, the applicable space-groups are \( Bbmm \) and \( Bb21m \) (Moëlo et al. 1987).

X-ray intensities were collected on an Enraf-Nonius CAD-4F diffractometer at the University of Melbourne with graphite-monochromated Mo radiation (\( \lambda = 0.710687 \) Å) using the \( \omega/2\theta \) mode. A total of 1988 measured reflections were merged into 1138 unique reflections (agreement factor \( R_{int} = \sum_{\text{Iobs}} - I_{av} \) \( \sum \text{Iobs} \) is equal to 4.7%). Application of absorption corrections for the crystal examined (0.04 \( \times 0.10 \times 0.01 \) mm) did not improve the subsequent refinement; therefore, no absorption correction for the final set of data was undertaken. Unit-cell parameters were refined using 25 reflections.

The refined unit-cell parameters and the space group used are listed in Table 1. The crystal structure of heyrovskyite solid-solution approximates closely a PbS-like array twinned periodically on \((311)_{PbS}\) (Otto & Strunz 1968, Takéuchi & Takagi 1974, Makovicky & Karup-Møller 1977a). Therefore, its weighted reciprocal lattice displays strong- to medium-intensity reflections at the loci of nodes of the two “twin-related” PbS-like reciprocal sublattices, and weak to very weak reflections for the majority of the true-lattice nodes (Fig. 4 in Makovicky & Karup-Møller 1977a). In this situation, all 1138 unique reflections were used throughout the refinement except for the final cycle, where only 341 reflections with the cut-off value \( I \geq 3\sigma(I) \) were used.

Initial positional parameters used for the refinement were those given for \( \text{Pb}_{5.4}\text{Ag}_{0.4}\text{Bi}_{2.2}\text{S}_{9} \) by Takéuchi & Takagi (1974). The program set SHELX76 (Sheldrick 1976) was used for the refinement, and corrections for anomalous dispersion were included. Fourier and difference-Fourier maps were used in the search for possible Ag positions outside those occupied in Ag-poor heyrovskyite; suspect peaks have all been tried in the least-squares refinement. No additional positions for cations (or anions) have been found.

In order to reduce the relative weight of the strongest reflections, the weights \( w \) used in the refinement were taken to be inversely proportional to \( \sigma^2(F) + 0.001F^2 \). This weighting scheme equalized substantially the distribution of \( w\Delta F^2 \) over the \( F/F_{max} \) categories. In the final cycles, for 1138 reflections, an approximately even distribution of \( w\Delta F^2 \) for all reflections \( F/F_{max} > 0.04 \) was achieved (\( R = 0.20 \), weighted \( R = 0.10 \)), which was considered justified in light of the large \( \sigma(I)/I \) for the very weak reflections. In the final step of the refinement, a very even distribution of \( w\Delta F^2 \) over the entire range \( F/F_{max} \) was achieved, except for the sixty strongest reflections, which were assigned values of \( w\Delta F^2 \) larger by about 1/3 than the rest. This difference is considered negligible because the final agreement factor \( R \) for 341 nonequivalent observed reflections is 0.062, compared to weighted \( R_w = 0.060 \). Anisotropic temperature-factors were refined for metal atoms; only isotropic temperature-factors were used for sulfur. Atomic parameters are given in Table 2, RMS displacements for metal atoms in Table 3, and interatomic angles and distances in Table 4. Tables of structure factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Canada K1A 0S2.
The crystal structure of heyrovskyite (Fig. 1) has five independent cation sites, four of which are octahedral or quasi-octahedral; the fifth site represents a bicapped trigonal coordination prism. The numbering scheme of the sites used here is that used by Takéuchi & Takagi (1974) for Ag-poor heyrovskyite.

The bicapped coordination prism (site Me1) is situated on the planes (311) of unit-cell twinning by the coordination polyhedra of Me4, in which the Ag–Bi substitution in heyrovskyite(50) takes place. This substitution appears to influence the position of S4 atoms, which cap the prism so that the distance Me1–S4 is equal to 3.21 Å instead of 3.48 Å observed by Takéuchi & Takagi (1974) in the Ag-poor structure. It also influences the S3 atoms, which acquire high “temperature-factors”, i.e., positional disorder. The RMS displacement for Me1 is appreciable in the direction perpendicular to vertical mirror planes, similar to the results of Takéuchi & Takagi (1974) for heyrovskyite and to those of Takagi & Takéuchi (1972) for lillianite.

In Pb$_{5.6}$Ag$_{0.9}$Bi$_{2.2}$S$_9$ (Takéuchi & Takagi 1974), the central zone of the PbS-like slab is occupied by lead atoms; the averages of six Me–S distances are 2.94 Å and 2.97 Å for Me2 and Me3, respectively. The situation is altered for both sites in the present structure of heyrovskyite(50). The respective averages are smaller, 2.90 Å for Me2 and 2.93 Å for Me3. The shortest Me–S distances are appreciably shorter as well: 2.87(×2) Å for Me2 and 2.85(×1) Å for Me3–S5. Averages of three shortest distances are 2.88 Å for Me2 and 2.89 Å for Me3. Therefore, besides accommodating potentially the trace amounts of Cd detected in microprobe analyses (this assignment can be disputed), these positions display partial Bi replacement for Pb. The conclusion is supported by higher appropriate mean-square displacements (Table 3) and a higher “temperature-factor” of S2. Such a replacement brings about a reduction in the size of Me2 and
The crystal structure of Ag-Bi bearing heyrovskyite. In the order of decreasing size, the circles denote atoms of S, Pb (and Pb$_{0.6}$Bi$_{0.2}$), Bi, and (Ag,Bi). Empty circles denote atoms at $x = 0$, filled circles atoms at $x = 1/2$.

Me3 coordination octahedra and may be necessary to alleviate potential misfit.

Toward the slab margins, the next cation site, with the coordination octahedron still wedged between octahedra and the trigonal prismatic site, has been denoted Me5 by Takéuchi & Takagi (1974). The average of three shortest distances for this site is 2.73 Å, the shortest (Me5–S1) distance is 2.54 Å, whereas the average for the entire coordination octahedron, 2.89 Å, is similar to those of Me2 and Me3. It represents a pure Bi site, situated within the cluster of pure-Bi sites in the plot of bond-distance ratios devised by Hummel & Armbruster (1987, Fig. 1).

According to the results of the present refinement, all detectable Ag substitution takes place in the site Me4, which is the closest to the margin of the PbS-like slab. Only a single maximum was found, refined as 0.657 Ag + 0.343 Bi. Its RMS displacement values are not markedly higher than those of the other atoms (Table 3); the principal displacement occurs along the line of the largest (Me4–S2 = 3.04 Å) and shortest (Me4–S3 = 2.48 Å) bonds in the coordination quasi-octahedron (Table 4). As mentioned above, S3 displays the largest displacements of all S atoms in the structure, undoubtedly owing to two different cation coordinations in the site Me4.

If we select a similarly situated Me5 (Bi) from the crystal structure of unsubstituted benjaminite (Herbert & Mumme 1981) as one mixing component for the combined Me4 site in heyrovskyite (50), and that of Ag in trechmannite (Matsumoto & Nowacki 1969) as the other component, and weigh the observed maximum in terms of products of occupancies with respective atomic numbers (Makovicky & Nérestam 1985) [i.e., (0.657 × 47 + 0.343 × 83)/130], the observed position represents, in terms of electron density, 52% Ag and 48% Bi. By multiplying the model Me–S distances defined above with these "weighted percentages", we can build a composite model coordination polyhedron and compare it with the observed one. The calculated Me4–S4 distance is 3.03 Å, observed 3.04 Å; Me4–S1 calc. 2.72 Å, obs. 2.76 Å; Me4–S3 calc. 2.63 Å, obs. 2.48 Å; and Me4–S2 calc. 2.92 Å, obs. 3.04 Å. Taking into account a rather arbitrary choice of the Ag
example, the agreement is satisfactory. On the one hand, rather varied Ag coordinations [3 + 1] are
given in the literature, and on the other hand S2 and S3 have large displacement parameters, and
Me4 atoms show anisotropic displacement along the S2-S3 line. With only averages of the three
shortest bonds (2.77 Å for Bi 5 in benjaminite and 2.62 Å for Ag in trechmannite), their weighted
average, 2.69 Å, is close to the observed one, 2.67 Å.

The Ag/Bi ratio in the Me4 site determines the
chemical composition of the analyzed crystal as
Pb6.70Ag2.6Bi6.63S16, assuring that the traces of Cd
are located elsewhere and added in the formula to Pb. Bi from the Me5 and Me4 sites add up to
5.37 Bi. The remaining 1.26 Bi per formula is
distributed among the two Me2 and four Me3 sites;
Me1 is assumed to be occupied entirely by Pb. This
assumption gives an average occupancy for an
octahedron from the central slab portions (Me2 or
Me3) of 79% Pb and 21% Bi, in good quantitative
agreement with their Me–S distances. Least-squares
refinement using these Pb/Bi ratios did not give
results that differ significantly from those obtained
using pure Pb in these positions.

The extent of Ag- and Bi-substitution derived
from the present determination of the crystal
structure is 52.60% if the traces of Cd occur in Me*
sites. Comparing this value with the percentage of
substitution determined from the electron-
microprobe analyses, equal to 45% for the average
of all crystals analyzed, a Ag- and Bi-substitution
of 50% represents a good estimate for the material
studied.

The crystal structure of heyrovskyite(50) is
similar to that of Ag-poor heyrovskyite studied by
Takeuchi & Takagi (1974) and deviates only a little
from the regular PbS archetype. Average sizes of
all coordination octahedra are very consistent,
except for the marginal Me4 site, with an average
bond-length of only 2.86 Å. However, without the
shortest outwardly directed bond, Me4–S3, this
polyhedron attains the average bond-length of 2.93 Å. In heyrovskyite(50), as has been generally
observed for sulfofalsats (Makovicky 1981), for those
bond directions that impinge at larger angles upon
slab boundaries, an appreciable separation into
outward, shorter bonds and inward, longer distan-
tces takes place (Table 5), with lone pairs of
electrons of (primarily) Bi playing a stereochemical
role. Similar separation for bonds running at low
angles to the slab boundaries is much less
pronounced (Table 5). Further geometrical and
structural correlations are deferred until our
analysis of the entire span of heyrovskyite struc-
tures is completed.

TABLE 5. ME4 S BOND DISTANCE SEPARATIONS FOR MARGINAL
COORDINATION POLYHEDRA IN HEYROVSKYITE(50)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bonds at high angle to slab boundary</th>
<th>Direction relative to slab edge</th>
<th>Bonds at low angle to slab boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me4</td>
<td>S3 2.479 x 1</td>
<td>outward pointing</td>
<td>S1 2.758 x 2</td>
</tr>
<tr>
<td></td>
<td>S2 3.043 x 1</td>
<td>inward pointing</td>
<td>S4 3.057 x 2</td>
</tr>
<tr>
<td>Me5</td>
<td>S1 2.541 x 1</td>
<td>outward pointing</td>
<td>S4 2.821 x 2</td>
</tr>
<tr>
<td></td>
<td>S5 3.218 x 1</td>
<td>inward pointing</td>
<td>S2 2.966 x 2</td>
</tr>
</tbody>
</table>

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