CRYSTALLOGRAPHIC DATA, UNIT CELL AND SPACE GROUP FOR BERTHIERITE ($FeSb_2S_4$)

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ABSTRACT

Crystallographic data are lacking for berthierite because its imperfect morphological development prevents optical goniometric study. These data, however, have been easily obtained by Weissenberg methods. An equi-inclination study leads to the following results:

Centrosymmetrical symmetry: $mmm = V_h$
Crystal system: orthorhombic
Unit cell:

absolute	ratio
$a = 11.44$ Å	0.810
$b = 14.12$	1.000
$c = 3.76$	0.266_3

$Z = 4$ formula weights per cell.
Diffraction symbol: *mmmPna-*.
Space group: *Pna* (C_{2v}^9) or *Pnam* (V_h^{16}).

The general geometry allows for 58 possible structures, but a simple intensity relation eliminates all but one, and definitely fixes the space group as *Pnam*. All atoms are on reflection planes (4*c*) with different parameters. Although an intensity-parameter study has not yet been made, a structure has been suggested based upon a substituted sphalerite type framework.

INTRODUCTION

Not only is the crystal structure of berthierite unknown, but crystallographic information is also lacking for this species because of its imperfect morphological development. The mineral occurs characteristically as small needles of irregular diamond-shaped cross-section and without faceted terminations. The needles are minutely striated parallel to their lengths. A crystal, therefore, yields only a continuous band of reflections and spectral effects in the needle axis zone when examined by optical goniometric methods. Crystallographic information regarding berthierite may, however, be easily obtained with the aid of the new Weissenberg *x*-ray methods.[1,2,3]

Excellent coördinated density and analytical determinations have been made for the Carpathian Kisbánya berthierite by Zsivny and

[1] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Zeit. Krist.*, vol. **88**, pp. 356–380, 1934.

[2] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeit. Krist.*, vol. **91**, pp. 255–289, 1935.

[3] Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Zeit. Krist.*, vol. **94**, pp. 87–99, 1936.

Zombory,[4] who have kindly made some of their original material available to the writer for the present investigation. The pertinent data for this berthierite are presented in Table 1. The analysis evidently indicates a slight excess of iron over antimony for the ideal formula $FeSb_2S_4$.

General Cell Characteristics

Method.—Crystals such as berthierite, whose optical reflections are confined to a confused band in the needle axis zone, may be accurately oriented by optical goniometric means for rotation about the needle axis. The reciprocal lattice can then be completely determined with the aid of a rotation photograph about this axis, together with the Weissenberg resolutions of several adjacent levels. Appropriate crystallographic axes may be chosen according to the symmetries, patterns and dimensions of these reciprocal lattice projections.[2]

To obtain further data of crystal structural importance, it is necessary to rotate the crystal about one (in the case of a monoclinic crystal) or both of the two crystallographic axes so selected. For space group determinative purposes, only axes in a plane at right angles to the needle axis need be investigated. If such an axis exists (i.e., if the crystal is not triclinic), it can be located by either of two methods. In either case, the crystal is remounted with the needle axis at right angles to the rotation axis, which keeps this perpendicular plane in the rotation axis; the needle axis is also placed parallel with one of the adjusting arc axes of the adjusting crystal holder.[3] This allows the crystal to be rolled about its long axis without disturbing its normality with the rotation axis. The amount of rolling required to rotate a crystallographic axis lying in the normal plane, into parallelism with the rotation axis, is controlled in either of two ways:

(a) A very general method may be used if the band of optical reflections and spectra given by the needle axis zone contains peculiarities which can be mapped or otherwise recognized again after the mounting is changed. In this case, a careful map of such peculiarities is prepared before the mounting is changed, using the optical goniometer rotation angles as coördinates. The relation between the optical goniometer zero rotation setting and the Weissenberg rotation zero setting is assumed to be known. It is then possible to refer the map of optical reflection peculiarities to the ω coördinates of the Weissenberg photographs, and therefore to the crystallographic axes which appear on the Weissenberg, needle axis, zero-layer, film. This enables the crystallographic axes to be tied in to optical peculiarities. After remounting as indicated above,

[4] Zsivny, Victor and Zombory, László, Berthierite from Kisbánya, Carpathians: *Mineral. Mag.*, vol. **23**, pp. 566–568, 1934.

the optical reflections are again studied. When the peculiarities have been identified, the band map locates the crystallographic axes in the new orientation and the arc may be adjusted until a crystallographic axis is parallel with the rotation axis.

(b) If, for any reason, it is inconvenient to proceed as above, the new needle orientation may be corrected so that a crystallographic axis is parallel with a rotation axis, by the following method: The crystal holder is placed in position on the Weissenberg or other similar apparatus with the needle approximately normal with the *x*-ray beam. Laue photographs are then made for a sequence of settings of the crystal holder adjusting arc. These exposures ordinarily need not exceed fifteen minutes and may be made on tiny dental films held in a special holder just behind the crystal. If the crystallographic axis sought is in a symmetry axis or symmetry plane of the crystal (multiplied, if necessary, by a symmetry center, in the case of non-centrosymmetrical crystals), the Laue photograph will show the position pattern which is the cross-sectional projection of this symmetry,[2] as the correct arc setting is attained. By this means, the crystallographic axis (except in the case of triclinic crystals whose projected symmetry is nil) may be located to within one or two degrees. The accuracy may be still further refined by taking several short rotation photographs in the correct region with a series of settings varying by about half a degree. The correct setting has been attained when the reflections of the several planes of a form record as the same spot on the rotation film.

Symmetry.—For determining the general cell characteristics, use was made of cobalt radiation, to which iron minerals offer little absorption.

The needle axis in berthierite has been designated as the *c*-axis. Rotation photographs and zero-layer Weissenberg photographs were prepared for rotations about all three crystallographic axes. In addition, first and second layer photographs were made for rotations about both the *c*- and *b*-axes.

All Weissenberg photographs agree in displaying the level symmetry C_{2l}. This proves that the crystal system of berthierite is orthorhombic, but does not distinguish between the crystal classes *mmm*, *2mm* and 222. (Some intensity data to be introduced later prove, however, that the crystal class is holohedral, *mmm*.)

Space Lattice Type.—Each of the *n*-level equi-inclination Weissenberg photographs displays a rectangular level pattern, and the level stacking sequence[2] is 9 (coincident rectangles). The space lattice type is consequently simple orthorhombic.

Unit cell.—The *n*-level equi-inclination patterns lead to a set of cell dimensions (checked by the three axial rotation photographs, and re-

fined by ξ_w measurements of high-order pinacoid reflections appearing on zero-level Weissenberg photographs) as follows:

absolute	ratio
$a = 11.44$Å	0.810
$b = 14.12$	1.000
$c = 3.76$	0.266_3
V = 607Å^3	

In the introduction it was noted that the cross-section of a berthierite needle is rudely diamond shaped. It is important to point out that the long diagonal of this diamond is in the direction of the *a*-axis and not the *b*-axis as might be expected.

The cell contents may be calculated with the aid of the relation:

$$\text{measured density} = \frac{\text{cell mass}}{\text{cell volume}}$$

$$d = \frac{Z \times f \times 1.649 \times 10^{-24}}{V \times 10^{-24}}$$

where d = measured density
Z = number of formula weights per unit cell
f = chemical formula weight
V = cell volume in cubic Ångstroms

Substitution of the appropriate values of d, f, and V for berthierite in this relation leads to a value of Z close to 4 formula weights per unit cell.

Space group.—Comparison of reciprocal cell translations[2] on *n* level and zero level equi-inclination Weissenberg photographs shows that in the (100) plane both *b* and *c* reciprocal translations are doubled, and that in the (010) plane the *a* translation is doubled. These multiple translations indicate a glide plane with glide components $b/2+c/2$ normal to *a*, and a glide plane of glide component $a/2$ normal to *b*. The sum total of information obtainable from diffraction patterns may be expressed by the diffraction effect formula[2] *mmmPna*—. The space group is therefore either *Pna*— $\simeq$ *Pna* Mauguin (C_{2v}^9) or *Pnam* (V_h^{16}). It will be shown beyond that certain simplicities in the *z* coördinates of the atoms are indicated by the spectra from (001) which require space group *Pnam*.

The Crystal Structure

Equipoints.—The space group must accomodate 4 formula weights of $FeSb_2S_4$ per unit cell. The 4 Fe, 8 Sb and 16 S can only be distributed individually among the several equipoints of the two possible space groups, *Pna* and *Pnam*, as shown in Table 2. The permissible combinations of these equipoints is given in Table 3; their number is very large.

Fortunately, the extremely simple intensity series for the reflections from (001) permits a selection of the correct equipoint combination from the 58 possibilities available. These reflections appear only in even orders and their intensities form a regularly declining series. That the series is one of "regular decline" and not just some kind of gradual decline is attested by the fact that each of its reflections is the most intense on the film for its own $\sin\theta$ region; i.e., the atoms are all in phase for these reflections and are confined to identically populated (001) sheets. The appearance of the spectra only in even orders indicates that these sheets are spaced at $c/2$ intervals. Referred to an appropriate origin, then, each atom must have a z coördinate of $\pm\frac{1}{4}$. This exact coördinate can only be attained by the occupation of a special position which is without z parameters. This eliminates *Pna* immediately, for this space group has no special positions. The only equipoint combination capable of giving all atoms a z coördinate of $\frac{1}{4}$ is combination 47, Table 3. The berthierite structure thus has all atoms occupying the equipoint 4*c* of space group *Pnam*, i.e., all atoms are on the reflection plane with different parameters.

It should be observed that this intensity discussion incidentally proves the holohedral nature of the symmetry of berthierite.

Structure.—The structure of berthierite involves 14 parameters which must be determined 7 at a time. A systematic study of parameter-intensity relations has not, as yet, been carried out. A tentative structure based upon certain reasonable assumptions has, however, been suggested.[5]

TABLE 1

Original analytical results		Results after deduction of insoluble and reduction to 100%	Atomic ratios
S	29.46%	29.78	4.000
Sb	56.06	56.65	2.009
Fe	13.43	13.57	1.049
Mn	trace	—	—
Insoluble	0.33	—	—
	99.28	100.00	

$d_4^{20} = 4.65_2$.

[5] Buerger, M. J., The crystal structure of berthierite, *Am. Mineral.*, vol. **21**, pp. 205–206, 1936.

TABLE 2. EQUIPOINT POSSIBILITIES FOR ATOMS IN BERTHIERITE

Space Group	4 Fe	8 Sb	16 S
Pna	4*a*	4*a*+4*a*	4*a*+4*a*+4*a*+4*a*
Pnam	4*a* 4*b* 4*c*	4*a*+4*b* 4*a*+4*c* 4*b*+4*c* 4*c*+4*c* 8*d*	4*a*+4*b*+4*c*+4*c* 4*a*+4*b*+8*d* 4*a*+4*c*+4*c*+4*c* 4*a*+4*c*+8*d* 4*b*+4*c*+4*c*+4*c* 4*b*+4*c*+8*d* 4*c*+4*c*+4*c*+4*c* 4*c*+4*c*+8*d* 8*d*+8*d*

TABLE 3. EQUIPOINT COMBINATION POSSIBILITIES FOR ATOMS IN BERTHIERITE

Combination designation	Space Group	4 Fe	8 Sb	16 S	Number of Parameters *x* *y* *z*
1	*Pna* (C_{2v}^9)	4*a*	4*a*+4*a*	4*a*+4*a*+4*a*+4*a*	7 7 7
2	*Pnam* (V_h^{16})	4*a*	4*b*+4*c*	4*c*+4*c*+4*c*+4*c*	5 5 —
3	"	"	"	4*c*+4*c*+8*d*	4 4 1
4	"	"	"	8*d*+8*d*	3 3 2
5	"	"	4*c*+4*c*	4*b*+4*c*+4*c*+4*c*	5 5 —
6	"	"	"	4*b*+4*c*+8*d*	4 4 1
7	"	"	"	4*c*+4*c*+4*c*+4*c*	6 6 —
8	"	"	"	4*c*+4*c*+8*d*	5 5 1
9	"	"	"	8*d*+8*d*	4 4 2
10	"	"	8*d*	4*b*+4*c*+4*c*+4*c*	4 4 1
11	"	"	"	4*b*+4*c*+8*d*	3 3 2
12	"	"	"	4*c*+4*c*+4*c*+4*c*	5 5 1
13	"	"	"	4*c*+4*c*+8*d*	4 4 2
14	"	"	"	8*d*+8*d*	3 3 3
15	"	4*b*	4*a*+4*c*	4*c*+4*c*+4*c*+4*c*	5 5 —
16	"	"	"	4*c*+4*c*+8*d*	4 4 1
17	"	"	"	8*d*+8*d*	3 3 2
18	"	"	4*c*+4*c*	4*a*+4*c*+4*c*+4*c*	5 5 —
19	"	"	"	4*a*+4*c*+8*d*	4 4 1
20	"	"	"	4*c*+4*c*+4*c*+4*c*	6 6 —
21	"	"	"	4*c*+4*c*+8*d*	5 5 1
22	"	"	"	8*d*+8*d*	4 4 2
23	"	"	8*d*	4*a*+4*c*+4*c*+4*c*	4 4 1
24	"	"	"	4*a*+4*c*+8*d*	3 3 2
25	"	"	"	4*c*+4*c*+4*c*+4*c*	5 5 1
26	"	"	"	4*c*+4*c*+8*d*	4 4 2

TABLE 3. (*Cont.*)

Combination designation	Space Group	4 Fe	8 Sb	16 S	Number of Parameters *x*	*y*	*z*
27		"	8*d*	8*d*+8*d*	3	3	3
28		4*c*	4*a*+4*b*	4*c*+4*c*+4*c*+4*c*	5	5	—
29		"	"	4*c*+4*c*+4*d*	4	4	1
30		"	"	8*d*+8*d*	3	3	2
31		"	4*a*+4*c*	4*b*+4*c*+4*c*+4*c*	5	5	—
32		"	"	4*b*+4*c*+8*d*	4	4	1
33		"	"	4*c*+4*c*+4*c*+4*c*	6	6	—
34		"	"	4*c*+4*c*+8*d*	5	5	1
35		"	"	8*d*+8*d*	4	4	2
36		"	4*b*+4*c*	4*a*+4*c*+4*c*+4*c*	5	5	—
37		"	"	4*a*+4*c*+8*d*	4	4	1
38		"	"	4*c*+4*c*+4*c*+4*c*	6	6	—
39		"	"	4*c*+4*c*+8*d*	5	5	1
40		"	"	8*d*+8*d*	4	4	2
41		"	4*c*+4*c*	4*a*+4*b*+4*c*+4*c*	5	5	—
42		"	"	4*a*+4*b*+8*d*	4	4	1
43	*Pnam* (V_h^{16})	4*c*	4*c*+4*c*	4*a*+4*c*+4*c*+4*c*	6	6	—
44		"	"	4*a*+4*c*+8*d*	5	5	1
45		"	"	4*b*+4*c*+4*c*+4*c*	6	6	—
46		"	"	4*b*+4*c*+8*d*	4	4	1
47		"	"	4*c*+4*c*+4*c*+4*c*	7	7	—
48		"	"	4*c*+4*c*+8*d*	6	6	1
49		"	"	8*d*+8*d*	5	5	2
50		"	8*d*	4*a*+4*b*+4*c*+4*c*	4	4	1
51		"	"	4*a*+4*b*+8*d*	3	3	2
52		"	"	4*a*+4*c*+4*c*+4*c*	5	5	1
53		"	"	4*a*+4*c*+8*d*	4	4	2
54		"	"	4*b*+4*c*+4*c*+4*c*	5	5	1
55		"	"	4*b*+4*c*+8*d*	4	4	2
56		"	"	4*c*+4*c*+4*c*+4*c*	6	6	1
57		"	"	4*c*+4*c*+8*d*	5	5	2
58		"	"	8*d*+8*d*	4	4	3