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Abstract

Full Text

Crystallography

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Crystal Structure of Beryllonite $NaBePO_4$

(Presented by Academician N. V. Belov, 7 VI 1961)

Beryllonite, $NaBePO_4$, was first described by Dana (^{1}), and then by Dana and Wells (^{2}) in 1888-1889 as an orthorhombic mineral. Much later (1934), Gossner and Besslein (^{3}), on the basis of X-ray data, showed that beryllonite should be assigned to the monoclinic space group $C_{2h}^5 = P2_1/n$. They also determined the unit-cell parameters of beryllonite as $a = 8.13$, $b = 7.76$, $c = 14.17$ Å and $\beta \approx 90°$, as well as the number of formula units in the cell, equal to 12. In 1954, by Vrenberg (^{4}), the cell parameters were corrected to $a = 8.16$, $b = 7.79$, $c = 14.08$ Å at $\beta \approx 90°$.

We had at our disposal samples of beryllonite from a deposit near Stonham (Maine, USA), obtained from the Mineralogical Museum of the Academy of Sciences of the USSR. Laue photographs and rotation X-ray photographs confirmed that beryllonite belongs to the monoclinic system and the cell dimensions given by Vrenberg, while the systematic extinctions of reflections on Weissenberg layer-line photographs obtained with a Weissenberg goniometer correspond to the space group C_{2h}^5 in the setting $P2_1/n$.

Fig. 1. Projection of the interatomic-vector function $P(xz)$

The very pronounced pseudohexagonality of the zero-layer-line Weissenberg photograph along the b axis, with an axial ratio $a = 8.16$ and $c = 14.08$ Å that differs little from the axial ratio a and b in an orthorhombic cell $(1 : \sqrt{3})$, and also the pseudocentered character of this cell, caused by the glide plane n, make the projection of the structure onto the XZ plane very close to hexagonal. However, there is no complete coincidence of the intensities of reflections associated with the pseudohexagonal axis.

From the squares of the structure factors obtained from Weissenberg photographs taken with copper radiation, projections of the interatomic-vector function onto three coordinate planes were calculated, as well as Harker sections $P(x0z)$ and $P(x^1/_2z)$. One of these projections, $P(xz)$, is shown in Fig. 1. The large peaks of this projection are located at the vertices of regular triangles

Fig. 2. Projection of the electron density $\rho(xz)$ (half of the reduced cell)

Figure 2: Fig. 2. Projection of the electron density $\rho(xz)$ (half of the reduced cell)

filling the entire plane. At the centers of these

of the triangles there are smaller peaks. In the Harker section $P(x\frac{1}{2}z)$, the projection peaks designated by the number 1 are also matched by strong peaks, while peaks 2 are almost absent in it. In the section $P(x0z)$, on the contrary, peaks 2 are present, but peaks 1 are absent. Peaks 3 of the projection in both sections correspond to peaks of considerably smaller magnitude. On the basis of the Belov—Butuzov theorem (^{5}), it was assumed that peaks 1 correspond to the actual positions of the P atoms, with sextets of atoms arranged according to the law of the screw threefold axis 6_3 around halves of the 2_1 axes. The projections $P(yz)$ and $P(xy)$ do not contradict the proposed arrangement of the P atoms. In the projection $P(xy)$, the strongest of the peaks lying on the line $x = 0.5$, where the ends of vectors connecting atoms related by a glide plane are concentrated, has a y coordinate close to zero. In the projection $P(yz)$ the same holds for peaks lying on the line $z = 0.5$. It follows from this that the P atoms are located not far from the glide planes, i.e., have y coordinates close to $\frac{1}{4}$ and $\frac{3}{4}$.

Fig. 2. Projection of the electron density $\rho(xz)$ (half of the reduced cell)

Attempts to construct projections of the electron density, treating P as the "heavy" atom, were unsuccessful. An attempt to use direct methods for determining the signs of the structure factors likewise did not give the expected result. The signs of the structure factors F_{h0l} could not be determined, while for the structure factors F_{0kl} several variants of signs were obtained. In electron-density projections constructed according to different variants, peaks corresponding to the positions of the P atoms were present, but they had different heights. As became clear later, some of the peaks in the projections corresponded to the positions of certain other atoms, but it was not possible to distinguish them from the large number of false peaks. In the work with direct methods, in addition to reflections obtained with copper radiation, the reflections $h0l$ and $0kl$, obtained with molybdenum radiation, were used.

Next, the three-dimensional function of interatomic vectors $P(xyz)$ was constructed (13 sections of half the cell). From analysis of this function it became clear that the Na atoms are located at the centers of hexagons formed by P atoms (in the XZ projection), at heights close to 0 and $\frac{1}{2}$. The general picture of the structure in Fig. 4 became evident; however, it was not possible to determine the coordinates of every O atom, nor the vertical coordinates of individual Na atoms, because of overlap of the corresponding peaks in $P(xyz)$.

Eleven successive approximations of the electron-density projections $\rho(xz)$ and $\rho(yz)$ were carried out. For the first approximation of the projection $\rho(xz)$, the

Fig. 3. Projection of the electron density $\rho(yz)$

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signs of the structure factors were calculated from the approximate coordinates of all P and Na atoms, as well as 9 (of 12) O atoms; subsequently all the remaining atoms were also included in the calculation. In calculating the first approximations, a small number (about 60 for each projection) of close reflections was used, since the absence of sufficiently accurate coordinates for a considerable number of atoms would have given incorrect signs for more distant reflections. At the next stages the number of reflections in the syntheses was doubled, and then all reflections obtained with Mo radiation were included (337 nonzero $h0l$ reflections and 253 $0kl$ reflections).

Fig. 3. Projection of the electron density $\rho(yz)$

The final projections of the electron density $\rho(xz)$ and $\rho(yz)$ are shown in Figs. 2 and 3. Figure 2 gives one half of the reduced cell, which may be chosen for the XZ projection if the pseudonode at the center of the projection, produced by the clinoplane, is taken as the actual lattice node. Figure 3 shows 1/4 of the projection of the full cell onto the YZ plane. The atomic coordinates obtained from these projections are given in Table 1. The structure is determined by 63 parameters with 84 atoms in the unit cell. The Be atoms are resolved only in the YZ projection; in the XZ projection they are overlapped by P atoms. Therefore their x coordinates were obtained from elementary geometrical considerations. The x coordinates of the Na atoms should be regarded as approximate, since in the XZ projection pairs of Na atoms merge. A number of peaks also merged in the YZ projection, which affected the accuracy of determining the y coordinate of some atoms.

Table 1

Coordinates of atoms in the crystal structure of beryllonite (in angstroms)

Atom	x	y	z	Atom	x	y	z
P_1	0.921	0.788	0.238	O_6	0.552	0.252	0.016
P_2	0.106	0.291	0.081	O_7	0.949	0.664	0.155
P_3	0.432	0.790	0.092	O_8	0.239	0.171	0.053
Na_1	0.248	0.004	0.248	O_9	0.535	0.664	0.148
Na_2	0.747	0.472	0.084	O_{10}	0.923	0.964	0.198
Na_3	0.763	0.031	0.069	O_{11}	0.164	0.473	0.062
O_1	0.435	0.266	0.192	O_{12}	0.495	0.971	0.110
O_2	0.066	0.268	0.188	Be_1	0.917	0.161	0.239
O_3	0.252	0.774	0.123	Be_2	0.103	0.662	0.082
O_4	0.739	0.253	0.214	Be_3	0.431	0.165	0.090
O_5	0.948	0.253	0.022				

Fig. 4. Projection of the crystal structure of beryllonite onto XZ

Figure 4: Fig. 4. Projection of the crystal structure of beryllonite onto XZ

Figure 4 shows the projection of the structure onto the XZ plane. Around halves of the 2_1 axes there are arranged 6 PO_4 tetrahedra and 6 BeO_4 tetrahedra, which are joined in the direction of the b axis into pairs by common vertices. Such pairs are located at different levels according to the law of a sixfold three-start axis 6_3 and are connected with one another by the vertices of the bases of their tetrahedra. The resulting sixfold "tubes" are linked to one another in the direction

the a axes by screw axes 2_1, and in the direction of the diagonals of the projection by centers of symmetry; in both cases they are joined by common vertices of tetrahedra. In the intervals between the described "tubes" there are channels of less regular shape, but in projection they are likewise surrounded by six pairs of tetrahedra. The structure is characterized by a continuous framework of tetrahedra, in which each P-tetrahedron is surrounded by four Be-tetrahedra and vice versa. The Na atoms are located in the channels of this framework. The Na_1 atoms are situated very close to the 2_1 axes—pseudo-axes 6_3; each of them is surrounded by nine O atoms, and the nine-vertex polyhedra formed by the latter touch one another

Fig. 4. Projection of the crystal structure of beryllonite onto XZ

by other common faces, forming infinite columns. The Na_2 and Na_3 atoms are located in irregular octahedra joined by common faces in pairs. Between such pairs in the direction of the b axis there are gaps—voids occupied by nothing. It may be considered that the Na-polyhedra, having common faces, are the main reason for the perfect cleavage of beryllonite along the plane perpendicular to the b axis.

The P—O distances lie within the range from 1.48 to 1.56 Å, and the edges of the PO_4-tetrahedra have lengths from 2.42 to 2.54 Å. The Be—O distances vary from 1.58 to 1.66 Å, and the edges of the corresponding tetrahedra from 2.58 to 2.76 Å. The Na and O atoms are separated by distances from 2.22 to 2.82 Å. The short Na—O distances (2.22-2.46 Å) are due to the fact that the Na_2 and Na_3 atoms, being in a pair of octahedra having a common face, repel one another and thereby approach the outer O atoms of the pair.

The final discrepancy factor for the XZ projection, calculated from the structure factors F_{hol}, taken up to $\sin\theta/\lambda = 1.1$ (without experimental zeros), is 19.8%. The experimental material was obtained from a rather large beryllonite specimen (0.4-0.5 mm), and therefore absorption played a significant role. If the differences in the magnitudes of the calculated and experimental amplitudes of the six strongest near reflections are discarded, the discrepancy factor improves to 17%. The discrepancy factor for the YZ projection under the same conditions is 19%, and, upon excluding the three strongest near reflections, 15%. In calculating the discrepancy factor, a correction for the temperature factor with coefficient $B = 0.6$ was introduced.

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