THE CRYSTAL STRUCTURE OF DUMORTIERITE

1965

SovietRxiv

Abstract

Full Text

CRYSTALLOGRAPHY

N. I. GOLOVASTIKOV

THE CRYSTAL STRUCTURE OF DUMORTIERITE

$(Al,\ Fe)_7O_3[BO_3][SiO_4]_3$

(Presented by Academician N. V. Belov, March 22, 1965)

The first X-ray studies of dumortierite were carried out by Claringbull and Hey ([1,2]). Dumortierite was assigned to the orthorhombic Fedorov group $D_{2h}^{16} = Pcmn$, with unit-cell parameters
$a = 11.79 \pm 0.01$ Å, $b = 20.209 \pm 0.002$ Å, $c = 4.701 \pm 0.001$ Å and $Z = 4$ ($d = 3.30$).

From V. N. Avtonin (Sverdlovsk Mining Institute) rather large (up to 2-3 mm) crystals of dumortierite were obtained. Most of them proved to be intergrowths of needles elongated in the direction c and turned relative to one another very often by an angle close to 120°. Laue photographs taken from the monocrystal found confirmed the orthorhombic symmetry of dumortierite; the cell parameters, determined from rotation X-ray photographs, coincided within the accuracy of our measurements with those given above. On a Weissenberg integrating goniometer (Mo radiation), layer-line rotation photographs were obtained: six hkl, $l = 0$—5; three hkl, $h = 0$—2, as well as $h0l$. These photographs also served as the experimental material for determining the structure of dumortierite. In all, about ~ 1750 symmetry-independent nonzero reflections were recorded and used in the analysis.

Systematic extinctions: $hk0$ with an odd sum $h + k$ and $h0l$ with odd l define the diffraction group $mmmP - cn$ with two Fedorov groups: $C_{2v}^9 = P2_1cn$ and $D_{2h}^{16} = Pmcn$. Measurements performed at the Department of Crystallophysics of Moscow University showed the absence of a piezoelectric effect in dumortierite. A statistical test ([3]) of the set of reflections $hk0$ and $0kl$ indicated centrosymmetry of both projections of the structure, which made it possible to choose the group $Pmcn$, given by Claringbull and Hey, but with a differently oriented cell.

The zero-layer photograph $hk0$ proved to be, to a very considerable degree, pseudohexagonal both in the geometrical arrangement of the reflections (the ratio $b : a = 1.71$ almost corresponds to the orthohexagonal $\sqrt{3}$ under centering of the cell projection due to the glide plane n) and in their intensities. In the projection of the Patterson function $P(xy)$ constructed from this photograph there appears an almost perfect hexagonal symmetry, with the peaks located at the vertices of a network filling the plane with nearly equilateral triangles.

The absence of heavy atoms in the structure, with a rather large number of medium atoms (6 Si and Al atoms in the independent part of the cell), made it difficult to interpret the Patterson projections (the projections $P(xy)$, $P(yz)$, and also the weighted $P_1(xy)$ and $P_2(xy)$ were obtained), and therefore we attempted to determine the signs of the structural factors F_{hk0} and F_{0kl} by the comparison method of I. M. Rumanova ([4]). For F_{hk0} only a trivial result was obtained: all structural factors were positive. Later this found an explanation in the fact that the peaks of the projection of the electron density $\rho(xy)$ are, in their positions, very close to the peaks of $P(xy)$. Taking into account the signs obtained for F_{0kl}, it was po-

a projection of the electron density $\rho(yz)$ was constructed; almost all of its peaks, as was subsequently found, corresponded to the actual positions of atoms. However, the heights of these peaks varied greatly, some peaks merged, and it was not possible to interpret the projection in the absence of a second "basis" projection. At the same time the signs of 114 of the 153 reflections were determined correctly, although not always with sufficient confidence.

Next, from the three-dimensional array of squares of the structure factors, a three-dimensional Patterson function $P(xyz)$ was obtained and minimized. The arrangement of the peaks in $P(xyz)$ raised some doubts about the centrosymmetry of the crystal, and therefore, for the minimization, a system of peaks $P(xyz)$ was fixed which corresponded to interatomic vectors between two independent atoms and their counterparts related to them by glide planes c and n. As a result of the minimization we arrived at a system of peaks related, in addition to the planes c and n, also by the mirror plane m.

Table 1

Coordinates of the basis atoms in the structure of dumortierite

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Si_1	0,250	0,094	0,087	O_4	0,449	0,106	0,390
Si_2	0,474	0,172	0,588	O_5	0,570	0,216	0,400
Al_1	0,250	0,249	0,392	O_6	0,250	0,047	0,388
Al_2	0,390	0,028	0,560	O_7	0,544	0,150	0,875
Al_3	0,508	0,069	0,057	O_8	0,750	0,225	0,732
Al_4	0,641	0,211	0,057	O_9	0,750	0,150	0,165
O_1	0,250	0,173	0,122	O_{10}	0,650	0,052	0,255
O_2	0,360	0,213	0,650	O_{11}	0,537	0,013	0,748
O_3	0,361	0,075	0,895	B	0,750	0,085	0,225

These peaks were identified as Si and Al atoms, and their number corresponded to the complete set of these atoms except for one (Al_1). The positions found for the heavier atoms coincided with the corresponding peaks in the projection $\rho(yz)$ obtained earlier by the direct method.

Fig. 1. Dumortierite. Projection of the structure onto the xy plane

Figure 1: Fig. 1. Dumortierite. Projection of the structure onto the xy plane

Fig. 2. Dumortierite. Projection of the structure onto the yz plane

Figure 2: Fig. 2. Dumortierite. Projection of the structure onto the yz plane

The fixed coordinates of the Si and Al atoms (at first these atoms were not distinguished) formed the basis for successive approximations of two projections of the electron density: first $\rho(xy)$, with a gradual increase in the number of atoms participating in the calculation of the signs F_{hk0}, and then $\rho(yz)$, where in calculating F_{0kl} it was possible to operate almost at once with all atoms, since the projection $\rho(xy)$ agreed very satisfactorily with the peaks of the projection $\rho(yz)$ obtained by the direct method.

Fig. 1. Dumortierite. Projection of the structure onto the xy plane

A slight increase in ···

the iron impurity, which isomorphously substitutes for aluminum, was not taken into account. The B atoms appeared clearly in both projections. The final discrepancy factor R for Mo reflections within the limits $\sin\theta/\lambda = 1.1$ Å^{-1}, with introduction of a temperature factor with coefficient $B = 0.45$, is 14.3% for the $hk0$ zone and 14.0% for the $0kl$ zone. In the course of the structure determination, the presence of the mirror plane m and the Fedorov group $Pmcn$ was confirmed. The atomic coordinates obtained from the final approximations of the electron-density projections are given in Table 1. The positions of the 18 basis atoms are determined by

Fig. 2. Dumortierite. Projection of the structure onto the yz plane

47 parameters. Projections of the crystal structure of dumortierite in coordination polyhedra are shown in Figs. 1 and 2.

The structural motif of dumortierite is composed of nearly strictly hexagonal (in projection) elements, repeated identically by translation a and in inverted form through half the diagonal ab of the cell by the clinoplane n. Along the pseudosixfold axis there extends a column of Al_1-octahedra connected to one another by common "basal" faces. To the vertices of the Al-octahedra, according to the law of a sixfold inversion axis 6_3, SiO_4 orthotetrahedra are attached by one O atom. The other vertices of the Si-tetrahedra simultaneously serve as vertices of other Al-octahedra, located farther from the pseudosixfold axis and connected by common edges into infinite bent chains extending along c. The described pseudohexagonal groups of polyhedra are connected to one another in such a way that, in the a direction, a chain of outer octahedra is connected with an analogous chain of another pseudohexagonal group by common faces, while in the direction of the cell diagonals two such chains are shifted relative

to one another along c so that their connection occurs through common edges. If in the a direction the chains are linked by the plane m, then in the direction of the diagonals they are linked by centers of symmetry. As a result of the pairing of chains, infinite zigzag ribbons of octahedra are formed, which project in the c direction as quadrilaterals. The ribbons are linked in pairs by common O vertices into hexagons around the Al—Si motif and into triples around pseudothreefold axes, on which, in triangles of O atoms, B atoms are placed (shown by circles in Fig. 2).

The Si—O distances calculated from the coordinates lie within the range 1.60-1.71 Å (average 1.64 Å*), and the edge lengths of the SiO_4 tetrahedra are 2.60-2.83 Å. The B—O radii are 1.35 Å, and the sides of the B triangles are 2.32-2.35 Å. The Al—O distances are 1.81-2.00 Å; the edges of Al-octahedra belonging to only one octahedron are 2.62-2.94 Å; the edges by which the Al_2- and Al_3-octahedra are joined to one another, as well as the sides of the common faces of the Al_4-octahedra, are shortened to 2.50-2.58 Å; the sides of the common faces of the Al_1-octahedra (along the pseudosixfold axis) are somewhat longer (2.60; 2.64; 2.66 Å).

* According to D. Smith and S. Bailey, this average for orthotetrahedra should be 1.63 Å [6].

The "contraindicated" connection in crystal chemistry of Al octahedra through common faces apparently accounts for the fact that, despite a hardness of 8.5 ([2]) and insolubility even in HF ([5]), dumortierite rarely forms good single crystals of appreciable size and is repeatedly twinned, with mutual rotation of the twinning components by 120° about c. In such twinning, the bonds of the Al octahedra along faces are broken and they are connected by edges. For the same reason dumortierite has cleavage along the plane (100).

The determination of dumortierite completes the structural study of an entire group of Al minerals characteristic of metamorphic rocks: corundum, topaz, and modifications of Al_2SiO_5. At least two features of dumortierite (Al octahedra joined by faces) are borrowed from the structure of corundum, whereas columns of octahedra at the vertices with centers of symmetry are represented by steps of 4 octahedra arranged according to the law of cubic packing in a motif characteristic of kyanite.

Institute of Crystallography
Academy of Sciences of the USSR

Received
1 III 1965

REFERENCES

[1] G. F. Claringbull, M. H. Hey, *Min. Abstr.*, **12**, 57 (1953).
[2] G. F. Claringbull, M. H. Hey, *Min. Mag.*, **31**, No. 242, 901 (1958).
[3] E. R. Howells, D. C. Phillips, D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

[4] I. M. Rumanova, *DAN*, **98**, No. 3, 399 (1954).
[5] A. G. Betekhtin, *Mineralogy*, 1950, p. 705.
[6] J. V. Smith, S. W. Bailey, *Acta Cryst.*, **16**, 801 (1963).

Note: Figure translations are in progress. See original paper for figures.