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Crystal structure refinement of Jeremejevite ($Al_6B_5F_3O_{15}$)

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Abstract. The crystal structure of Jeremejevite, $Al_6B_5(OH, F)_3O_{15}$, has been refined from single crystal diffraction data on a natural sample from Cape Cross (Namibia). The cell dimensions are $a = 8.556(3)$, $c = 8.175(3)$ Å and the centric $P\,6_3/m$ space group has been established in the course of the structure refinement. The best convergence was achieved by assuming the absence of OH groups and the total occupancy of their positions by F atoms, its correct formula being $Al_6B_5F_3O_{15}$. The final R value was 0.030.

The mean Al–O and the Al–F distances are 1.901(1) and 1.810(1) Å respectively. The B–O bondlengths range from 1.364(1) to 1.391(1) Å and the $B(1)-O_3$ group deviates significantly from planarity. The Al–Al distance (3.200 Å) corresponding to corner-sharing octahedra and the mean B–Al distance (2.916 Å) are in accordance with the sum of the one-angle radii of O'Keeffe and Hyde (1981) (3.24 and 2.88 Å respectively).

Introduction

The crystal structure of Jeremejevite was solved by Golovastikov et al. (1955) from film-measured diffraction data. They proposed the centric space group $P6_3/m$ but the low accuracy attained does not ensure the correctness of this choice.

Moore and Araki (1976), in a study on mineral Painite, established the structural relationships of this last compound with fluoborite and jeremejevite. Based on the deviation of the $(Al_9O_{18})^{9-}$ framework from centrosymmetry, in Painite, and on a positive piezoelectric test reported by Palache et al. (1951), for jeremejevite, they suspected that a more accurate refinement of the jeremejevite structure would lead to the acentric space group $P6_3$.

Table 1. Crystal data for jeremejevite

Formula:	$Al_6B_5F_3O_{15}$	$V = 518.29(3)$ Å^3
Space group:	$P6_3/m$	$Z = 2$
$a = 8.556(3)$ Å		$D_c = 3.2872$ Mgm^{-3}
$c = 8.175(3)$ Å		$\mu(\mathrm{Mo}K\alpha) = 0.76916$ mm^{-1}

To solve this indetermination and because we are interested in the crystal chemistry of anhydrous borates, specially in the geometry of the BO_3 group, we have undertaken the present investigation.

Experimental

Single crystals were extracted from a mineral sample from Cape Cross (Namibia). They were pale blue hexagonal prisms. An irregular fragment of them was used to collect data on an automatic four-circle diffractometer, using graphite-monochromated Mo$K\alpha$ radiation. The crystal data are given in Table 1.

A total of 963 Friedel pairs were measured in the ω scan mode, leading to 868 averaged independent reflexions. 150 of them were considered as unobserved and not taken into account in the refinement. The intensities were corrected by Lorenz and polarization factors, but no absorption correction was applied ($\mu R = 0.23$). Atomic scattering factors for neutral atoms and anomalous dispersion coefficients for Al, F and O were taken from International Tables for X-ray Crystallography (1974).

Least-squares refinement on F's was started in the centric space group $P6_3/m$ from the parameters obtained by Golovastikov et al. (1955), but their x and y coordinates must be interchanged with each other to fit with our right-handed cell. In the course of refinement, the thermal parameter for O(4) (corresponding to OH in the primitive formula assumed for jeremejevite) became negative, indicating a lowering of the assumed electron density for this position. Substitution of O by F in the calculation, made the anisotropic refinement to converge rapidly and the temperature factors for F became positive, with values similar to those of the other light atoms in the structure.

Weights were applied by the program PESOS (Martínez-Ripoll and Cano, 1975) and were of the type $\omega = k/\sigma^2$, with $\sigma = a + b|F_0| + c|F_0|^2$ [1]. The final R was 0.030, $R_\omega = 0.032$. The atomic coordinates are collected in Table 2.

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[1] Additional material to this paper can be ordered referring to the no. CSD 50486, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 2. Final atomic parameters for jeremejevite, $U_{eq} = 1/3\ \Sigma(U_{ij}\cdot A_i^*\cdot A_j^*\cdot A_i\cdot A_j\cdot\cos(A_i, A_j))$. e.s.d's are given in parentheses

Atom	x	y	z	$U_{eq}(\text{Å}^2)$
Al	0.35261(5)	0.01544(5)	0.07532(5)	0.0038(2)
F	0.50014(15)	0.11314(16)	0.25000	0.0056(6)
O(1)	0.28512(13)	0.19661(12)	0.10135(12)	0.0046(4)
O(2)	0.56079(12)	0.15000(11)	−0.05455(12)	0.0045(4)
O(3)	0.30286(18)	0.18636(18)	0.75000	0.0050(7)
B(1)	0.23322(26)	0.00232(25)	0.75000	0.0048(9)
B(2)	0.66667	0.33333	−0.05402(30)	0.0047(12)

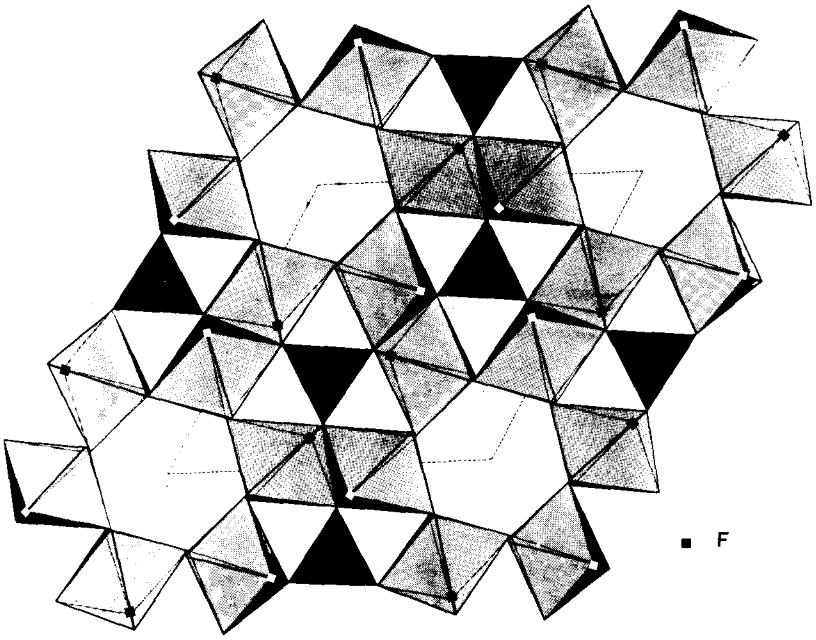

Fig. 1. Drawing of the jeremejevite structure viewed along the c axis and showing the AlO_5F octedra and the $B(2)O_3$ triangles

A final refinement was tried in the space group $P6_3$, and a high correlation was observed between parameters of splitted atoms. To minimize this correlation, two atom groups were alternatively refined during several cycles, but convergence was difficult to attain and the temperature factors for 3 atoms were always negative. This lead us to establish the centric space group $P6_3/m$ for jeremejevite.

Discussion

It is not our aim to describe again the structure, for which, the reader should be referred to the articles cited above, but to illustrate this work, a section of the structure, viewed along the *c* axis, has been drawn in Figure 1. Our drawing is inverted with respect to that published by Golovastikov et al.

All the interatomic distances and angles are collected in Table 3. The Al – O distances are similar to those expected for an AlO_6 octahedron, with an average Al – O distances of 1.901 Å, as compared with 1.91 Å from the radii values given by Shannon and Prewitt. On the other hand, the Al – F distances, $d_{Al-F} = 1.810(1)$ Å are, as expected, shorter than the Al – O distances and agree well with the values observed in other compounds as

Table 3. Interatomic distances (Å) and angles (°) for jeremejevite e.s.d's. are given in parentheses

a) Coordination polyhedron around Al.

Distances	
Al – O(1)	1.917(1)
O(2)	1.891(1)
O(2)^{v}	1.905(1)
O(3)^{xi}	1.931(1)
O(1)^{xii}	1.863(1)
F	1.810(1)
O(1) – O(2)	2.879(2)
O(1) – O(3)^{xi}	2.665(1)
O(1) – O(1)^{xii}	2.724(1)
O(1) – F	2.585(2)
O(2) – O(2)^{v}	2.407(2)
O(2) – O(1)^{xii}	2.768(1)
O(2) – F	2.530(1)
O(2)^{v} – O(3)^{xi}	2.817(2)
O(2)^{v} – O(1)^{xii}	2.702(2)
O(2)^{v} – F	2.592(2)
O(3)^{xi} – O(1)^{xii}	2.880(1)
O(3)^{xi} – F	2.407(2)

Angles	
O(1) – Al – O(2)	98.21(5)
O(1) – Al – O(3)^{xi}	87.65(5)
O(1) – Al – O(1)^{xii}	92.20(5)
O(1) – Al – F	87.79(6)
O(2) – Al – O(2)^{v}	78.72(5)
O(2) – Al – O(1)^{xii}	95.02(5)
O(2) – Al – F	86.25(5)
O(2)^{v} – Al – O(3)^{xi}	94.47(5)
O(2)^{v} – Al – O(1)^{xii}	91.61(4)
O(2)^{v} – Al – F	88.45(6)
O(3)^{xi} – Al – O(1)^{xii}	98.71(5)
O(3)^{xi} – Al – F	80.01(5)

b) Coordination around B atoms.

Distances	
B(1) – O(1)^{xi}	1.391(1)
O(1)^{xxiv}	1.391(1)
O(3)	1.377(3)
B(2) – O(2)	1.364(1)
O(2)^{vii}	1.364(1)
O(2)^{xiv}	1.364(1)

Angles	
O(1)^{xi} – B(1) – O(1)^{xxiv}	121.73(15)
O(1)^{xi} – B(1) – O(3)	119.12(8)
O(1)^{xxiv} – B(1) – O(3)	119.12(8)
O(2) – B(2) – O(2)^{vii}	120.00(5)
O(2) – B(2) – O(2)^{xiv}	120.00(6)
O(2)^{vii} – B(2) – O(2)^{xiv}	120.00(3)

Table 3. (Continued)

c) Coordination around O and F atoms.

Distances		Angles	
O(1) – Al	1.917(1)	Al – O(1) – B(1)^{xvii}	123.24(11)
Al^{xviii}	1.863(1)	Al – O(1) – Al^{xviii}	115.62(6)
B(1)^{xvii}	1.391(1)	B(1)^{xvii} – O(1) – Al^{xviii}	120.19(12)
O(2) – Al	1.891(1)	Al – O(2) – B(2)	125.48(10)
Al^{v}	1.905(1)	Al – O(2) – Al^{v}	101.28(5)
B(2)	1.364(1)	B(2) – O(2) – Al^{v}	124.98(7)
O(3) – Al^{xvii}	1.931(1)	Al^{xvii} – O(3) – Al^{xxviii}	95.33(8)
Al^{xxviii}	1.931(1)	B(1) – O(3) – Al^{xxviii}	131.43(4)
B(1)	1.377(3)	B(1) – O(3) – Al^{xvii}	131.43(4)
F – Al	1.810(1)	Al – F – Al^{xxii}	104.17(6)
Al^{xxii}	1.810(1)		

Symmetry code:

I:	$x, y, 1+z$	XV:	$1-x+y, 1-x, z-1$
IV:	$1-x, -y, 1-z$	XVII:	$x-y, x, 1-z$
V:	$1-x, -y, -z$	XVIII:	$x-y, x, -z$
VII:	$1-x+y, 1-x, z$	XXI:	$1-x, -y, 1/2+z$
VIII:	$1-y, x-y, 1-z$	XXII:	$x, y, 1/2-z$
XI:	$y, -x+y, 1-z$	XXIV:	$y, -x, 1/2+z$
XII:	$y, -x+y, -z$	XXVIII:	$x-y, x, 1/2+z$
XIV:	$1-y, x-y, z$		

Table 4. Cation – cation distances (Å) for jeremejevite. The e.s.d's are 0.001 Å. The symmetry code is the same as in Table 3

B(1) – Al^{i}	2.831	B(2) – Al	2.903
Al^{xviii}	2.831	Al^{xi}	2.903
Al^{ix}	2.922	Al^{v}	2.903
Al^{xx}	2.922	Al^{iv}	2.910
Al^{xiv}	3.024	Al^{viii}	2.910
Al^{xxi}	3.024	Al^{xv}	2.910
Mean value	2.926	Mean value	2.907
	Al – Al^{x}	3.200	

$AlF_3 \cdot H_2O$ ($d_{Al-F} = 1.805$ Å) (Chandross, 1964) and AlF_3($d_{Al-F} = 1.79$ Å) (Hanic et al., 1962). This fact also supported the substitution of O by F during the least-squares refinement.

The two crystallographycally independent BO_3 triangles show differences in their geometry. The $B(2)O_3$ group, situated in the three-fold axis (see

Fig. 1), is completely planar as can be seen from the z coordinates of B(2) and O(2) in Table 2, with a relatively short B−O distance of 1.364(3) Å. The $B(1)O_3$ triangle, on the contrary, is significantly non planar. B(1), lying on the mirror planes at $z = 1/4$, deviates 0.013(2) Å from the plane defined by the three oxygens. It exhibits two rather lang B—O bond lengths of 1.391(3) Å and the third one of 1.377(3) Å, as expected (1.380 Å) from the ionic radii of Shannon and Prewitt (1969).

Finally we have calculated the Al−Al and B−Al distances to check the constancy of the one-angle radii of O'Keeffe and Hyde (1981). This can be applied to the B(1) and B(2) triangles, for which each O atom is common to two edge-sharing Al octahedra, and also to the corner-sharing $Al(O,F)_6$ octahedra. These distances are collected in Table 4.

These radii are 1.62 Å for Al and 1.26 Å for B, and their sum (3.24 Å for Al−Al and 2.88 Å for B−Al) compare well, within 1−2 %, with the mean values expressed in Table 4, although significant deviations from the mean are observed for individual values in the case of the B(1)−Al distances.

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