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Notes

Buetschliite Derivative $K_2Zr(BO_3)_2$

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Introduction

The minerals eitelite, $Na_2Mg(CO_3)_2$, and buetschliite, $K_2Ca(CO_3)_2$, have been known since the early 1970's when synthetic forms were prepared and their structures determined by Pabst.[1,2] Each structure contains cations dispersed between sheets of planar CO_3 groups. Buetschliite is related to the parent eitelite by rotation of the CO_3 groups about the C_3 axis.

From a phase study of the K–Zr borate system, we have identified the new compound $K_2Zr(BO_3)_2$, which is isoelectronic and isostructural to buetschliite. Because such layered compounds can exhibit significant birefringence, we have determined the structure of the material and measured its refractive indices.

Experimental Section

Synthesis. A powder sample of $K_2Zr(BO_3)_2$ was prepared from the molar ratio of 1 $ZrOCl_2 \cdot 8H_2O$ (Aesar, 99.9%), 2 B_2O_3 (Alfa, 99.98%), and 4 KF (aesar, 99.9%). The mixture of oxide chloride and B_2O_3 was heated at 873 K for $^1/_2$ h followed by addition of KF; then the sample was ground and heated at 1000 K for 12 h. Residual K compounds were removed by washing the sample in H_2O. Crystals were grown for X-ray structure analysis by melting the sample in excess KF flux in a Pt crucible at 1073 K, slowly cooling at 6 K/h to 500 K, and rapidly cooling at 50 K/h to room temperature. The KF flux was dissolved in hot water, providing crystals of hexagonal morphology.

Crystallographic Study. A colorless, transparent crystal of dimensions $0.12 \times 0.15 \times 0.08$ mm was selected and mounted on a glass fiber with epoxy for structure determination. All measurements were made on a Rigaku AFC6R single-crystal diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement with 19 automatically-centered reflections in the range $30 \le 2\theta \le 36°$. The cell constants correspond to a hexagonal cell; Laue symemtry $\bar{3}m$ was determined on the diffractometer. Intensity data were collected over the range of indices $-8 \le h \le 8$, $0 \le k \le 8$, $-28 \le l \le 28$ by using the ω scan technique to a maximum 2θ value of 70°, and from 1395 measured reflections a total of 1305 were observed $[F_o^2 > 3\sigma(F^2)]$. The intensities of three representative reflections measured after every block of 200 data varied by an average of 2% during the collection.

The structure was solved by using the TEXSAN software package.[3] The crystal was found to form in the centerosymmetric space group $R\bar{3}m(h)$. The positions of the K and Zr atoms were derived from the direct methods program SHELXS, while the remaining atoms O and B were located from difference electron density maps.[4] After a full-matrix isotropic refinement of the model an absorption correction was applied (transmission factors 0.79–1.14) by using the program DIFABS.[5] The data were averaged ($R_{int} = 0.112$), and the model was refined with anisotropic thermal displacement coefficients on each atom. Final least-squares refinement resulted in the residuals $R = 0.022$ and $R_w = 0.028$. The largest peak in the final difference electron density map corresponds to 0.36% of the Zr atom. Crystal data are outlined in Table 1, and atomic positional and thermal parameters are listed in Table 2.

Table 1. Crystallographic Data for $K_2Zr(BO_3)_2$

chem formula $K_2Zr(BO_3)_2$
$a = 5.283(8)$ Å
$c = 17.518(2)$ Å
$V = 423.35(1)$ Å^3
$Z = 3$
$\mu = 33.57$ cm^{-1}
fw 287.03 u
space group $R\bar{3}m$ (No. 166)
$T = 23$ °C
$\lambda = 0.710\,69$ Å
$\rho_{calcd} = 3.377$ g cm^{-3}
$R(F_o)^a = 0.022$
$R_w(F_o)^a = 0.028$

^{a} $R = \sum||F_o - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

Table 2. Positional and Thermal Parameters (B_{eq}'s) for $K_2Zr(BO_3)_2$

	site sym	x	y	z	B_{eq} (Å^2)^a
K	D_{3d}	0	0	0	0.70(1)
Zr	C_{3v}	0	0	0.209 63(4)	1.21(1)
O	C_s	0.1827(1)	0.3654	0.070 89(7)	1.10(1)
B	C_{3v}	$^1/_3$	$^2/_3$	0.070 0(2)	0.75(5)

^{a} $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

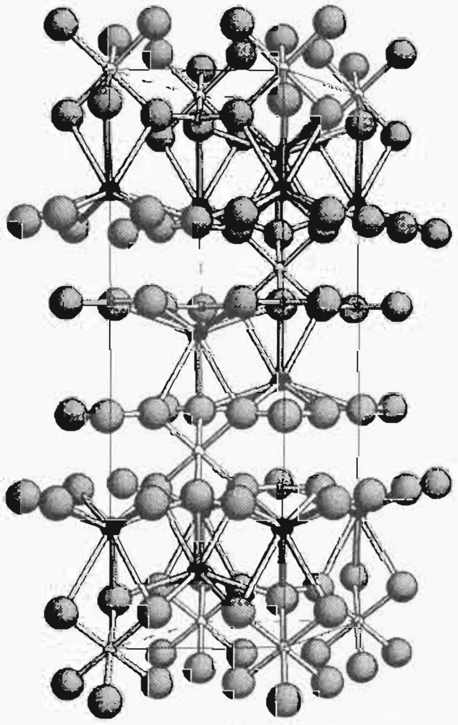

Figure 1. Sketch of the unit cell of $K_2Zr(BO_3)_2$ as viewed orthogonal to the c axis. The large shaded circles represent O atoms, the dark circles represent the K atoms, and the small gray circles represent the Zr atoms.

Results and Discussion

The structure of the title compound is that of the mineral buetschliite. Layers of flat orthoborate groups extend orthogonal to the crystallographic c axis (Figure 1), a standard feature of simple borate structures. Interleaved between these layers are double sheets of K atoms and single sheets of Zr atoms.

The chemically and crystallographically distinct K atom is nine coordinate, providing a prototypical example of a hexagonal base–trigonal base environment (Figure 2) that we have found to be a common feature of borate structures containing large alkaline-earth metals.[6,7] The average K–O bond length is 2.85(7)

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(1) Pabst, A. *Am. Mineral.* **1973**, *58*, 211–217.
(2) Pabst, A. *Am. Mineral.* **1974**, *59*, 353–358.
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(5) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.
(6) Alekel, T. Ph.D. Dissertation, Oregon State University, 1993.

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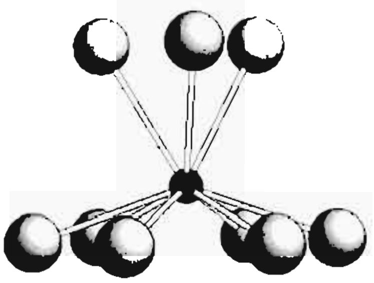

Figure 2. Sketch of the coordination environment about the K atom. The small dark circle represents the K atom, and the larger circles represent O atoms.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $K_2Zr(BO_3)_2$

Zr–O (×6)	2.083(1)	O–Zr–O	88.09(5)
K–O (×3)	2.950(1)	O–K–O	79.14(4)
K–O (×6)	2.8025(6)		58.79(4)
			107.56(3)
			78.14(4)
			136.03(2)
			62.21(5)
			50.41(5)
			109.67(3)
			140.95(5)
B–O	1.378(1)	O–B–O	119.99(1)

Å; the six O atoms lying on the distorted hexagonal plane are bonded to the K atom at a distance of 2.8025(6) Å, and the three O atoms lying on the trigonal base are located at a distance of 2.950(6) Å (Table 3). Adjacent K atoms are linked via triangular O faces of the 9-vertex polyhedra. The polyhedron also shares its smallest trigonal face with the Zr-centered octahedron.

The six O atoms around the Zr atom distort slightly from an ideal octaheddron; O–Zr–O angles deviate from orthogonality by less than 2°, and the Zr–O distance is normal. The Zr atoms within the same plane are bridged by BO_3 groups; as a result, there are no common O vertices shared between the Zr-centered octahedra. The distances and angles in the BO_3 trigonal planes are unexceptional.

Crystalline $K_2Zr(BO_3)_2$ exhibits uniaxial negative birefringence. The refractive indices of the crystals as determined by the oil-dispersion technique ($\lambda = 5893$ Å) are $\omega = 1.773(1)$ and $\epsilon = 1.747(3)$, and the birefringence $\omega - \epsilon = 0.026$.[8] These values may be compared with those of buetschliite, $\omega = 1.600$, $\epsilon = 1.462$, and $\omega - \epsilon = 0.138$. By using the Gladstone–Dale relationship, $(n - 1)/\rho = K$, the X-ray results, and tabulated values of specific refractivities (k),[9] average refractive indices $[n = (2\omega + \epsilon)/3]$ may be computed. For $K_2Zr(BO_3)_2$ $n_{\text{obsd}} = 1.76$ and $n_{\text{calcd}} = 1.70$, while for buetschlitte $n_{\text{obsd}} = 1.53$ and $n_{\text{calcd}} = 1.55$. The larger index for the Zr compound arises primarily from the presence of the Zr atom and a density that is 30% greater than that of buetschliite. Presumably, in making a contribution of nearly 45% to the refractive energy that is largely isotropic, the ZrO_2 component also leads to the reduced birefringence.

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Supplementary Material Available: Tables listing complete crystallographic and data collection information and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.

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(7) Cox, J. A.; Keszler, D. A. Unpublished results.

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