CRYSTAL STRUCTURES AT HIGH PRESSURES

HIGH-PRESSURE CRYSTAL STRUCTURES AND COMPRESSIBILITIES OF BERTRANDITE, BERYL, AND EUCLASE*

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High-pressure crystal-structure data reveal details of interatomic forces and can provide insight into the stability and physical properties of minerals. The highpressure structures of bertrandite (Be₄Si₂O₇(OH)₂), beryl (Be₃Al₂Si₆O₁₈ nH₂O), and euclase (BeAlSiO₄OH) have been determined as part of an ongoing study of structures in the system BeO-Al₂O₃-SiO₂-H₂O. The eventual objectives of this study include the correlation of physical and thermochemical properties with structure and bonding. This system, with the cations Be, Al, and Si, is

*Research supported in part by National Science Foundation grant EAR 81-15517. particularly suited to such an investigation, because of the large number of wellcrystallized, stoichiometric minerals that are available. In the present study anisotropic linear compressibilities of these minerals are related to crystal structure.

Crystals of colorless, stoichiometric bertrandite (orthorhombic, Cmm2; Z =4) from a pegmatite in Albany, Maine, were provided by the Field Museum of Natural History (No. 6969). Unit-cell parameters were measured on a crystal in air, and a reference crystal-structure refinement was performed on this crystal for comparison with high-pressure results. A second crystal was mounted in a diamond-anvil pressure cell for x-ray diffraction (Hazen and Finger, 1982), and unit-cell parameters were determined at 24 and 48 kbar (Table 19 and Fig. 58). Intensity data for a crystal-structure refinement were collected at the higher pressure. The room-temperature results are in close agreement with the previous

P, kbar		a, Å	<i>b</i> , Å	<i>c</i> , Å	β, deg	$V, Å^3$
	Bertran	randite				
0.001		8.7135(4)*	15.268(1)	4.5683(3)		607.74(8)
23.5		8.6559(4)	15.107(3)	4.5407(3)		593.74(13)
47.9		8.6021(6)	14.955(7)	4.5157(4)		580.90(27)
	Beryl					
0.001		9.2142(11)		9.1938(7)		676.0(1)
15		9.183(3)		9.159(3)		669.1(3)
30		9.163(10)		9.131(5)		663.5(11)
33		9.155(3)		9.118(2)		661.6(3)
40		9.138(10)		9.113(1)		659.2(5)
54		9.127(3)		9.064(15)		652.4(15)
	Euclase					
0.001		4.7800(3)	14.332(1)	4.6335(2)	100.310(5)	312.30(3)
18.5		4.761(1)	14.254(6)	4.610(1)	100.27(1)	307.85(15)
41.7		4.739(1)	14.158(3)	4.589(1)	100.15(1)	303.14(11)

TABLE 19. Unit-Cell Parameters of Bertrandite, Beryl, and Euclase vs. Pressure

*Figures in parentheses represent estimated standard deviations.



Fig. 58. Volume (V/V_o) and linear (d/d_o) compressibilities of bertrandite, beryl, and euclase. Linearcompressibility data include *a*- and *c*-axis compression for hexagonal beryl; *a*-, *b*-, and *c*-axis compression for orthorhombic bertrandite; and three principal axes of the compressive strain ellipsoid (Hazen and Finger, 1982) for euclase. In euclase the most compressible direction is also the unique *b* crystallographic axis.

determination of Simonov and Belov (1976).

Bertrandite compression is highly anisotropic; linear compressibility of the *b* axis ($\beta_b = \Delta b/b\Delta P = 0.00042$ kbar⁻¹) is significantly greater than compression of *a* (0.00027 kbar⁻¹) or *c* (0.00024 kbar⁻¹). Compression along *b* is the result of both bending of *T*-O-*T* angles and compression of tetrahedral Be-O bonds; compression of *a* and *c*, on the other hand, is accomplished by reduction of Be-O bond lengths alone.

Crystals of hydrated beryl (hexagonal, P6/mcc; Z = 2) were synthesized by Vacuum Ventures, Inc., and were provided by R. M. Mandle. This pale-green

synthetic beryl has approximately 0.4 wt % Cr₂O₃ (0.3 atom Cr³⁺ substituting for Al³⁺ per formula unit). Crystal-structure determination of this material under room conditions revealed electron density in the beryl channel corresponding to 0.25 H₂O per formula unit.

After unit-cell and structure determinations on a crystal in air, a crystal was mounted for high-pressure study. A striking feature of the beryl structure is an array of channels that run parallel to the hexagonal *c* axis. (See, for instance, Gibbs *et al.*, 1968.) In other channel structures, most notably zeolites (Hazen, 1982; Hazen and Finger, this Report), compressibility may differ depending on whether or not the pressure-transmitting medium interacts with the channels. The compressibility of beryl was therefore studied in both water, which presumably may enter the channels, and an organo-fluorocarbon liquid (FC-75), which has molecules that are several times larger than the beryl channels. No difference in unit-cell compression was observed between these two fluids (Table 19 and Fig. 58; $\beta_a = 0.00019$ and $\beta_c =$ 0.00023 kbar⁻¹). A high-pressure structure, determined at 33 kbar, reveals that the Be and Si tetrahedral framework is constrained both by linkages and by symmetry, so that little T-O-T bending is possible. In both fluids compression is thus controlled by changes in Be-O and Al-O bond lengths, rather than collapse of the channels.

Colorless crystals of euclase (monoclinic, $P2_1/a$; Z = 2) from Minas Gerais, Brazil, were provided by R. V. Gaines. Unit-cell parameters of this material were determined at 1 bar, 18.5 kbar, and 41.7 kbar (Table 19 and Fig. 58), and intensity data were collected under room conditions and at 41.7 kbar. An important feature of the euclase structure is a relatively rigid chain of three-member tetrahedral rings that runs approximately parallel to the a axis (Mrose and Appleman, 1962). Euclase is least compressible along this direction within the (010) plane (β_{min} = $0.00017 \text{ kbar}^{-1}$). The unique monoclinic (b) axis is the most compressible direction ($\beta_b = 0.00029$ kbar⁻¹), as a result of tetrahedral Be-O and octahedral Al-O bond compression, as well as some T-O-T bond bending.

In all three beryllium silicates tetrahedral Be-O bonds are significantly more compressible than Al-O or Si-O bonds. The distribution and linkages of Be tetrahedra, and in particular the degree to which T-O-T angles can vary, determine the bulk-compression properties of these minerals.

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Compressibility and High-Pressure Pleochroism of $CaCr^{2+}Si_4O_{10}^*$

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The rare mineral gillespite, $BaFe^{2+}$ Si₄O₁₀, and its isomorphs have been the subject of much research, owing to both an unusual square-planar coordination of the transition metal cation and a highpressure phase transition characterized by a striking red-to-blue color change (Hazen and Finger, 1983). Crystals of a new gillespite analog, CaCr²⁺Si₄O₁₀, have recently been synthesized and were described by Belsky *et al.* (1984), who kindly provided single crystals for high-pressure study.

An elongated crystal of CaCrSi₄O₁₀, approximately $130 \times 50 \times 40 \ \mu\text{m}$, was mounted in a gasketed, diamond-anvil pressure cell for optical and x-ray diffraction study (Hazen and Finger, 1982). An alcohol mixture of 4:1 methanol:ethanol was employed as the pressure-transmitting medium, and ruby chips, approximately 10 μ m in diameter, were included for pressure calibration. The crystal was mounted with the tetragonal *c* axis parallel to the diamond faces, so that both the ϵ (deep magenta under room conditions) and the ω (orange under room conditions) optical directions

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