Crystal structure and compression of ruby to 46 kbar

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Crystal structures and lattice constants have been determined for ruby at hydrostatic pressures up to 46 kbar using a gasketed opposed-anvil diamond cell on a four-circle diffractometer. The measured compressibility is slightly anisotropic, having a value of $1.36 \pm 0.03 \times 10^{-4}$ kbar^{-1} parallel to c and $1.22 \pm 0.03 \times 10^{-4}$ kbar^{-1} perpendicular to c. If a Birch-Murnaghan equation of state is used and K'_0 is assumed to be 4, the isothermal bulk modulus is 2.57 ± 0.06 Mbar. Refined atomic coordinates do not change with pressure; therefore, the structure compresses in a uniform manner. This study demonstrates that crystal structures may be determined at high pressure on single crystals with a precision approaching that of room-pressure results.

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INTRODUCTION

Workers at the National Bureau of Standards[1,2] have calibrated the wavelength shift of the R_1 fluorescence line of ruby (α-Al$_2$O$_3$ doped with Cr) as a secondary pressure standard based on the Decker[3] equation of state for NaCl. This work has prompted several studies of the high-pressure response of the ruby structure. Sato and Akimoto[4] used a cubic anvil press with methanol-ethanol as the pressure-transmitting medium to determine the lattice constants at pressures up to 120 kbar. Schiferl and Jamieson[5] and d'Amour et al.[6] studied the lattice constants and crystal structure of ruby at high pressure using opposed diamond-anvil cells of differing designs. The present study reports the high-pressure crystallography and crystal structure of ruby up to 46 kbar using the miniature diamond-anvil pressure cell designed by Merrill and Bassett.[7] Refined structure parameters including anisotropic temperature factors are determined to a greater precision than in previous studies of the high-pressure structure of ruby.

EXPERIMENTAL

Four different crystals of a synthetic ruby (0.4 mol% Cr) were used in this study. The intensities of all reflections with positive Miller indices and $(\sin\theta)/\lambda < 0.7$ were measured on a crystal ($50 \times 120 \times 120 \mu$m) at 1 bar using a four-circle diffractometer system,[8] and lattice constants were refined from the diffractometer angles of 12 centered reflections. The intensities were measured by a constant-precision procedure in which the background counting time and scan rate were dynamically adjusted such that the ratio of the intensity to the standard deviation calculated from counting statistics was of the order of 100.

Data were collected at high pressure on crystals mounted in an opposed-anvil diamond cell of the type designed by Merrill and Bassett[7] and modified by Hazen and Finger[9] and Finger and King.[10] Metal gaskets of Inconel 750X (International Nickel Co.), approximately 250 μm thick with 300-μm holes, were used. The distance from the ruby crystal to the gasket wall was large enough to prevent shielding of x-rays by the gasket. In the initial experiments to 80 kbar,[11] glycerin was used as a pressure-transmitting medium; however, this liquid freezes at approximately 40 kbar, leading to

nonhydrostatic pressures. A 4 : 1 volume mixture of methanol-ethanol was used as the pressure-transmitting fluid in subsequent experiments because this liquid retains low viscosity up to pressures in excess of 100 kbar.[12] The ruby crystals were "cemented" to the face of one of the diamonds using a thin smear of the alcohol insoluble fraction of petroleum jelly. Pressures were calibrated using the R_1 fluorescence line of ruby,[1,2] with an assumed wavelength shift of 27.5 kbar/nm. The estimated precision of the pressure determination is approximately 0.5 kbar.

The first ruby to be examined at high pressure had been included as the calibration crystal in a study of garnets[13] in which the garnet was crushed. The ruby chip ($20 \times 30 \times 30$ μm) was studied at 80 kbar using glycerin as the pressure-transmitting medium. Nonhydrostatic conditions and the small size of the crystal led to large errors in the determinations of the unit-cell and structural parameters. A preliminary report on ruby compression,[11] therefore, is in error.

A second crystal ($35 \times 120 \times 135 \mu$m) used at high pressure was examined at pressures of 11, 21, and 28-kbar, but was crushed by gasket failure in an attempt to reach higher pressures, and a third crystal ($30 \times 60 \times 85 \mu$m) was studied at 35 and 46 kbar.

Lattice constants for crystals in the diamond cell were refined as described above, with one important difference. When the diamond cell is mounted on the four-circle diffractometer, it is not possible to position the crystal at the intersection of the axes of the instrument by the normal optical means. As a result, measured angles deviate from the correct values in a systematic fashion and the lattice constants are biased. To correct for these errors in crystal positioning, the method of Hamilton,[14] as modified by King and Finger,[15] is used. The apparent position of the diffracted radiation for a particular Miller plane is measured in eight different settings, four at positive 2θ and four at negative 2θ. The various types of errors may be eliminated by the appropriate linear combinations of the measured angles. The resulting data for 12 to 20 reflections, corrected for crystal centering and diffractometer alignment errors, were used in the least-squares refinement of the lattice constants at high pressure. Each set of data was refined without constraint, and the resulting "triclinic" cell was checked for agreement with the rhombo-

TABLE I. Unit-cell parameters for ruby refined without constraint.

Pressure (kbar)	a (Å)	b (Å)	c (Å)	α (degrees)	β (degrees)	γ (degrees)	V (Å³)
0.001	4.7617(9)[a]	4.7597(8)	12.9947(17)	90.02(1)	89.98(1)	120.01(1)	255.05(7)
11	4.7544(6)	4.7531(3)	12.9725(5)	89.99(1)	90.01(1)	120.01(1)	253.86(4)
21	4.7478(4)	4.7470(3)	12.9542(5)	90.000(4)	89.997(5)	120.002(4)	252.84(2)
28	4.7442(5)	4.7432(3)	12.9430(5)	90.000(4)	90.002(5)	119.998(4)	252.24(3)
35	4.7406(5)	4.7407(9)	12.9326(16)	89.99(1)	90.00(1)	120.00(1)	251.71(6)
46	4.7342(7)	4.7362(7)	12.9176(11)	90.01(1)	90.00(1)	120.00(1)	250.86(5)
80[b]	4.728(4)	4.707(6)	12.818(14)	89.43(10)	90.20(8)	120.24(6)	246.4(4)

[a] Numbers in parentheses represent one estimated standard deviation of least-significant units cited.

[b] Glycerin used as pressure medium; nonhydrostatic above 40 kbar.

hedral symmetry of ruby. The refined lattice constants in the hexagonal setting (Table I) are within 3 estimated standard deviations of the presumed symmetry. In addition, unit-cell angles are very close to the ideal values, except for the non-hydrostatic experiment at 80 kbar. It appears that observed values of unit-cell angles are a very sensitive indicator of lattice strain caused by nonhydrostatic stress in orthogonal and hexagonal crystal systems.

Intensity data were collected for all accessible reflections with $(\sin\theta)/\lambda < 0.7$ using Nb-filtered MoKα radiation and the constant-precision intensity technique described above. Two operational procedures peculiar to high-pressure intensity experiments, described in detail by Finger and King,[10] were employed. The fixed-ϕ mode of data collection was used to maximize reflection accessibility and minimize attenuation by the diamond cell, and a correction was made for x-ray absorption by the diamond and beryllium components of the pressure cell. Several methods have been proposed for determining the effects of attenuation by the beryllium and diamond parts of the pressure cell.[16-18] Because the Merrill and Bassett design has a radial axis of symmetry, the path length of the x-rays in the cell is dependent upon only two parameters, the angles between the symmetry axis and the incident and diffracted beams. Measurements of the attenuation of the direct beam by a cell without gasket or crystal were used to calculate parameters for an absorption model. The correction may be specified by a polynomial fitted to

the data[10] or, as in the present case, by stepwise series of linear functions. In either case, the correction is routinely applied as the intensity data are measured.

All intensity data were corrected for absorption by the crystal, $\mu_l = 13.2$ cm⁻¹, and a parameter required for secondary extinction calculations[19] was computed. For each data set, the average structure factor was calculated for reflections related by symmetry. No systematic deviations from the ideal symmetry or violations of the R-centered lattice were noted.

Least-squares refinement of the structural parameters was performed using a program RFINE[20] with neutral scattering factors from Cromer and Mann[21] and the anomalous scattering coefficients of Cromer and Liberman.[22] Although previous workers, including Moss and Newnham[23] and McCauley and Gibbs,[24] have suggested that the chromium atom in ruby is displaced from the position occupied by aluminum, in the present study, a common position has been assumed; however, the Cr contribution to the scattering has been included. After convergence of each data set with isotropic temperature factors and an isotropic correction for secondary extinction, the temperature factors were converted to anisotropic form and the data were refined to convergence. Table II gives the refinement conditions and refined parameters. In all data sets, the ellipsoids corresponding to the anisotropic thermal parameters were positive definite.

TABLE II. Refinement conditions and refined parameters for ruby.

	1 bar	11 kbar	21 kbar	28 kbar	35 kbar	46 kbar	80 kbar[a]
Crystal number	1	2	2	2	3	3	4
Weighted R[b](%)	3.5	2.8	2.3	2.4	2.5	2.8	3.7
R[c](%)	3.0	3.1	2.9	3.5	3.5	2.9	5.5
No. of observations[d]	86	64	65	64	53	49	80
Z_m	0.35216(8)	0.3520(1)	0.35201(8)	0.3519(1)	0.3520(1)	0.3522(1)	0.3514(2)
X_0	0.3061(5)	0.3060(6)	0.3057(5)	0.3071(7)	0.3074(7)	0.3065(8)	0.3054(12)
B_m[e] (Å²)	0.31(4)	0.26(4)	0.31(4)	0.20(4)	0.26(4)	0.28(4)	0.24(5)
B_0 (Å²)	0.33(5)	0.48(6)	0.59(5)	0.44(6)	0.76(8)	0.63(9)	0.74(9)
r* (×10⁵)	0.6(3)	1.1(4)	1.0(3)	0.4(3)	1.6(5)	2.2(6)	...

[a] Data collected on crystal in glycerin; conditions are nonhydrostatic.
[b] Weighted $R = [\Sigma w(F_0 - F_c)^2/\Sigma w F_0^2]^{1/2}$.
[c] $R = \Sigma |F_0 - F_c|/\Sigma |F_0|$.

[d] $I > 2\sigma$. Number of nonequivalent reflections, except for 80 kbar.
[e] Isotropic temperature factor equivalent to the anisotropic values.

TABLE III. Selected interatomic distances (Å), angles (degrees), octahedral volumes, and distortion indices for ruby.

	1 bar	11 kbar	21 kbar	28 kbar	35 kbar	46 kbar	80 kbar[a]
$M-O_1$ (3)[b]	1.971(2)	1.967(2)	1.963(2)	1.965(2)	1.966(3)	1.961(3)	1.941(5)
$M-O_5$ (3)	1.856(1)	1.854(2)	1.852(1)	1.848(2)	1.845(2)	1.844(2)	1.843(3)
O_1-O_2 (2)	2.524(4)	2.519(5)	2.514(4)	2.523(5)	2.524(6)	2.513(7)	2.496(10)
O_1-O_3 (4)	2.868(2)	2.864(3)	2.861(2)	2.853(3)	2.849(3)	2.850(4)	2.845(6)
O_1-O_4 (2)	2.620(1)	2.615(1)	2.611(1)	2.612(1)	2.611(1)	2.605(2)	2.587(3)
O_1-O_5 (4)	2.726(1)	2.722(1)	2.719(1)	2.714(1)	2.712(1)	2.709(1)	2.695(3)
M-M, shared edge (3)	2.792(1)	2.787(1)	2.783(1)	2.781(1)	2.779(1)	2.777(1)	2.763(2)
M-M, shared face (1)	2.655(2)	2.648(3)	2.643(2)	2.639(3)	2.639(3)	2.639(4)	2.600(6)
O_1-M-O_2 (3)	79.6(1)	79.6(1)	79.6(1)	79.9(1)	79.9(1)	79.7(1)	80.0(2)
O_1-M-O_5 (6)	86.4(1)	86.4(1)	86.3(1)	86.4(1)	86.4(1)	86.3(1)	86.2(1)
O_1-M-O_6 (3)	101.2(1)	101.1(1)	101.1(1)	101.0(1)	101.1(1)	101.2(1)	101.0(1)
O_1-M-O_6 (3)	164.2(1)	164.2(1)	164.2(1)	164.5(1)	164.5(1)	164.2(2)	164.6(2)
Al octahedral volume (Å³)	9.08	9.03	8.99	8.99	8.97	8.93	8.78
Quadratic elongation	1.02	1.02	1.02	1.02	1.02	1.02	1.02
Angle variance	67.3	66.8	66.9	65.0	64.9	67.0	64.3

[a]Data collected on crystal in glycerin; conditions are nonhydrostatic.   [b]Multiplicity of bond or angle.

RESULTS

Linear compressibilities of ruby

Compressibilities of a and c axes, based on only the hydrostatic 1-bar and 11-, 21-, 28-, 35-, and 45-kbar unit-cell data, are 1.22(3) and 1.36(3)$\times 10^{-4}$ kbar^{-1}, respectively. Ruby, therefore, deviates only slightly from istropic compression, c being approximately 10% more compressible than a. The bulk modulus of ruby is $K_0 = 2.57(6)$ Mbar, if K'_0 is assumed to be 4, using either a second-order Murnaghan or Birch-Murnaghan fit of the volume data.

Crystal structure at high pressure

The corundum structure has space group $D_{3d}^6 (R3c)$ with (Al, Cr) at $(0, 0, z)$ and oxygen at $(x, 0, \frac{1}{4})$ if the R-centered cell is used. Both variable positional parameters remain essentially constant with increasing pressure ($z_{Al} = 0.3521$ within ± 0.0002; $x_0 = 0.3065$ within ± 0.0008) on the basis of the six refinements to 46 kbar (Table II). Note, however, that the nonhydrostatic 80-kbar data do not fit this pattern. To a close approximation, the compression of ruby may be represented by a simple scaling of the room-pressure structure, with all distances compressing equally and all interatomic angles unchanged. Selected interatomic distances and angles of ruby at several pressures are listed in Table III along with the aluminum octahedral volume and distortion parameters. Note that, because of the scaling of the structure at high pressure, octahedral distortion indices such as bond-angle variance and quadratic elongation[25] do not change with pressure.

The atomic positions determined by Schiferl and Jamieson[5] and d'Amour et al.[6] range between 0.3515 and 0.3523 for the z position of the metal cation with a stated uncertainty of approximately 0.0004. Their results are similar to those of the present study; however, our uncertainties in the parameters are reduced by a factor of 3–4.

Ruby temperature factors do not deviate significantly from isotropic, although they were refined using an anisotropic model to test the absorption correction procedures. Temperature factors, as well as the extinction factor, are sensitive to systematic errors in absorption corrections of the type that may occur in diamond-cell experiments owing to beryllium, diamond, and gasket components of the cell. It is significant, therefore, that all temperature parameters and the extinction parameter in the 1-bar–46-kbar experiments show little variation, in spite of the fact that three different crystals were used, each in a different orientation and in two different diamond cells. The equivalent aluminum isotropic temperature factor is essentially constant at 0.26 Å²; the oxygen temperature factor displays more variation and may increase slightly with pressure, although a range of 0.33 to 0.76 Å² encompasses all observed values.

SUMMARY

This study of ruby at high pressure demonstrates that crystal structures of materials may be determined at high pressure on single crystals with a precision approaching that of room-pressure results; thus, an understanding of the relationships between compression and interatomic variations may be obtained. Significant reductions of interatomic distances may be measured even on relatively incompressible materials such as ruby. It is critical, however, that several steps be taken in collecting and refining the data on crystals at high pressure. The single crystal *must* be in a hydrostatic environment, and unit-cell parameters should be measured so as not to presuppose the constraints of a given crystal system. The crystal must be centered in the gasketed area to prevent gasket shadowing of the x-rays in specific orientations, and the x-ray data must be corrected for absorption by the diamonds and beryllium components of the pressure cell, as well as absorption by the single crystal under investigation. Finally, in experiments on gem-quality single crystals

such as the ruby described in this study, a correction for secondary x-ray extinction must also be included.

This study demonstrates both the advantages and the disadvantages of the Merrill and Bassett[7] design of the diamond pressure cell. The simplicity of the cell results in a very inexpensive pressure device with relatively simple absorption geometry and operating procedures. The cell is ideal for most single-crystal x-ray experiments to 50 kbar.

The Merrill and Bassett pressure cell has not yet proved satisfactory for routine operation above 50 kbar, owing in part to the lack of features for alignment of diamond anvil faces and the weakness of the beryllium seats for the diamonds. Pressures approaching 100 kbar have been attained using glycerin as the pressure-transmitting medium (glycerin is much less compressible than methanol : ethanol and results in less deformation of the gasket to achieve a given pressure), but these experiments result in a nonhydrostatic environment. Experiments using stronger beryllium diamond supports and preindented gaskets are now under way to determine the pressure limits of the Merrill and Bassett cell. In the meantime, other designs, such as those of Keller, Dietrick, and Holzapfel[26] and Schiferl, Jamieson, and Lenko,[16] may be superior for experiments above 50 kbar.

ACKNOWLEDGMENTS

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