

The Use of Quartz as an Internal Pressure Standard in High-Pressure Crystallography

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(Received 8 November 1996; accepted 20 January 1997)

Abstract

The unit-cell parameters of quartz, SiO₂, have been determined by single-crystal diffraction at 22 pressures to a maximum pressure of 8.9 GPa (at room temperature) with an average precision of 1 part in 9000. Pressure was determined by the measurement of the unit-cell volume of CaF₂ fluorite included in the diamond-anvil pressure cell. The variation of quartz unit-cell parameters with pressure is described by: $a - 4.91300(11) - 0.0468(2)P + 0.00256(7)P^2 - 0.000094(6)P^3$, $c - 5.40482(17) - 0.03851(2)P + 0.00305(7)P^2 - 0.000121(6)P^3$, where P is in GPa and the cell parameters are in ångströms. The volume–pressure data of quartz are described by a Birch–Murnaghan third-order equation of state with parameters $V_0 = 112.981(2) \text{ \AA}^3$, $K_{T0} = 37.12(9) \text{ GPa}$ and $K' = 5.99(4)$. Refinement of K'' in a fourth-order equation of state yielded a value not significantly different from the value implied by the third-order equation. The use of oriented quartz single crystals is proposed as an improved internal pressure standard for high-pressure single-crystal diffraction experiments in diamond-anvil cells. A measurement precision of 1 part in 10 000 in the volume of quartz leads to a precision in pressure measurement of 0.009 GPa at 9 GPa.

1. Introduction

The determination of accurate and precise cell parameters and unit-cell volumes of crystalline materials at high pressures opens up a number of areas of research, including the precise determination of equations of state (EOSs), the evaluation of critical strain behaviour at structural phase transitions under high pressures and the more precise measurement of pressure itself. The measurement of pressure is one of the major contributions to uncertainties in high-pressure experiments. For single-crystal diffraction at high pressures in diamond-anvil

pressure cells (DACs) the common solution is to use the ruby fluorescence technique to determine pressure (e.g. Forman, Piermarini, Barnett & Block, 1972). This has the advantage that the ruby crystal used for these measurements need only be a few microns in size and thus it occupies a very small proportion of the limited sample volume in a diamond-anvil cell and it contributes very little diffracted intensity. However, although the pressure-induced wavelength shift of the ruby fluorescence spectrum can be readily measured to a precision equivalent to approximately 0.01 GPa or better in pressure, the residual data scatter in plots of crystal volumes determined by diffraction against pressures determined from the ruby fluorescence shift is significantly greater than the estimated errors. The reasons for this appear to be related to temperature variations: most ruby fluorescence measurements are, by necessity, made away from the four-circle diffractometer and temperature changes can contribute to apparent pressure differences due to the strong temperature dependence of the ruby spectrum (a 5–6 K temperature change gives the same shift as a 0.1 GPa pressure change; Wood, Welber, David & Glazer, 1980; Vos & Schouten, 1991) and to real pressure changes because of the differential thermal expansion of the components of the DAC.

These sources of uncertainty are readily overcome by the use of an internal diffraction standard to determine pressure in the DAC. Hazen & Finger (1981) reviewed the requirements for such a standard. Most importantly, it should be a high-symmetry low-unit-cell volume crystal to minimize the interference with the diffraction pattern from the sample, it must be chemically stable in both air and the pressure media used in the DAC, and it must have a well known equation of state with which to convert measured unit-cell volumes to pressures. Other considerations are that the material is readily prepared in small crystals with small mosaic spread to maximize signal-to-noise in the diffraction pattern and to produce sharp peaks whose positions can be measured precisely on the diffractometer. Hazen & Finger (1981) described the use of fluorite, CaF₂, as such an internal pressure standard, and the fluorite equation of state was further refined by Angel (1993). While fluorite is an excellent pressure standard at modest pressures, its use is restricted to pressures of less than 9.2 GPa, at which

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pressure it undergoes a phase transition (Gerward, Olsen, Marlinowski, Åsbrink & Waskowska, 1992) that destroys single crystals.

A second standard material is therefore required to allow precise measurements of pressure in excess of 9.2 GPa. In addition, the choice of a material softer than fluorite would result in increased precision in pressure for the same precision in unit-cell volume measurement. Both of these requirements would be met by the use of NaCl, which remains in the B1 phase to 30 GPa, and whose room-pressure bulk modulus is 25 GPa (Decker, 1971; Birch, 1978) compared with the 81.0 GPa of fluorite (Angel, 1993). Use of NaCl would therefore, in principle, provide a factor of three improvement of precision in pressure measurement. However, although NaCl is widely used as an internal pressure calibrant in powder-diffraction experiments performed at high pressures, problems with it dissolving in popular pressure media such as alcohol and the difficulty of obtaining single crystals with small mosaic spread preclude its general use for single-crystal diffraction measurements. Therefore, we have chosen quartz as an internal pressure calibrant because it has none of the problems associated with NaCl, meets the requirements noted above and has a lower bulk modulus ($K \approx 37$ GPa; e.g. McSkimin, Andreatch & Thurston, 1965; Levien, Prewitt & Weidner, 1980) than fluorite. In addition, the hexagonal symmetry of quartz allows an internal cross-check from the unit-cell parameters a and c for the presence of anisotropic strains, and its low shear strength (McSkimin *et al.*, 1965) means that even small nonhydrostatic-pressure conditions lead to very large increases in the mosaic spread and hence the widths of diffraction peaks.

In this paper we describe the redetermination of the volume variation of quartz to a maximum pressure of 8.9 GPa with a new single-crystal diffractometer, using fluorite as an internal pressure standard. In addition to yielding significantly more precise equation-of-state parameters than were previously available for quartz, these data provide a cross-calibration of pressure measurements made with quartz and with fluorite.

2. Experimental

Gem-quality single crystals of twin-free natural quartz of approximately 5 mm linear dimensions were obtained commercially. These were sliced approximately parallel to (010) and polished to ~ 60 μm thickness. For each run a single-crystal fragment of this plate with dimensions of the order of 100 μm was mounted in the BGI design of diamond-anvil cell (Allan, Miletich & Angel, 1996) alongside a (111) plate of natural fluorite of 60–80 μm edge length and a ruby as pressure calibrants. The pressure medium was a 4:1 methanol:ethanol mixture which is reported to remain hydrostatic to pressures in

excess of 10 GPa (Piermarini, Block, Barnett & Forman, 1975). Certainly no peak broadening indicative of strain in either the fluorite or the quartz was detected in our experiments at high pressures. Gasket materials used in the seven cell loadings reported here included 750X inconel and stainless steel.

Single-crystal diffraction was performed with a Huber four-circle goniometer built from a model 511.1 χ circle with an offset φ drive mounted on two model 420 bases for ω and 2θ motions. The 2θ , ω and χ circles are driven with stepper motors with 0.001° steps, while the φ drive is geared to provide 0.002° per motor step. This last step size does not degrade resolution in diamond-anvil cell mode, as all measurements are made with $\varphi = 0$ or 180° (the so-called 'fixed- φ mode'), and φ remains stationary during all peak-profiling scans. The diffractometer is equipped with an unfiltered Mo sealed-tube X-ray source *without* monochromator to provide clean, stable and reproducible peak-profile shapes. The source-to-crystal distance is 45 cm and crystal-to-detector distance is 40 cm. The incident beam is collimated by a 0.5 mm aperture close to the source (with a larger clean-up aperture 20 cm downstream), and the detector area is defined by adjustable parallel slits. For the experiments in this paper the slits defining the divergence in the 2θ plane were kept at 6 mm width, and the perpendicular set at 2 mm. For the quartz and fluorite samples we used, this configuration results in typical FWHM at $2\theta \approx 13^\circ$ of 0.06 – 0.08° in ω .

The diffractometer was driven by the program *SINGLE* (Finger & Angel, unpublished). The determination of the setting angles of an individual peak proceeds with an initial determination of the approximate positions of 2θ , χ and ω by iteration of a sequence of relatively coarse scans of these axes coupled with parabolic fits to determine the positions of maximum intensity. Final scans of the χ and ω circles (each typically with a step size of 0.01 to 0.04° set dynamically as a function of observed peak width) are fitted with Gaussian profiles to determine peak positions with a precision better than 0.01° . The latter fit involves a constrained doublet for $K\alpha_1$ and $K\alpha_2$ to remove most of the apparent variation of wavelength with 2θ . We emphasize that no part of this centring procedure involves the use of half-slits to determine diffracted beam positions as such a procedure leads to systematic errors in 2θ if the incident radiation is not strictly monochromatic. Each peak is centred in eight positions on the diffractometer, and the setting angles are determined following the method of King & Finger (1979) to eliminate the effects of diffractometer circle zero-offsets, crystal offsets and aberrations in the diffractometer alignment. Vector least-squares fits (Ralph & Finger, 1982) are then performed to the values of all the setting angles (2θ , ω and χ) to determine unit-cell parameters unconstrained by symmetry. In all cases in which the cell parameters of quartz and fluorite differed from the

Table 1. Cell-parameter variation of quartz with pressure

Fluorite volume (\AA^3)	P (GPa)	a (\AA)	c (\AA)	V (\AA^3)	Quartz c/a
163.063 (7)	10^{-4}	4.91300 (11)	5.40482 (17)	112.981 (2)	1.10011 (6)
162.212 (13)	0.429 (9)	4.89295 (29)	5.38861 (22)	111.725 (14)	1.10130 (8)
161.512 (13)	0.794 (10)	4.87657 (12)	5.37563 (12)	110.711 (6)	1.10234 (4)
159.935 (9)	1.651 (9)	4.84201 (15)	5.34856 (14)	108.597 (7)	1.10462 (5)
159.591 (9)	1.845 (9)	4.83461 (39)	5.34284 (37)	108.150 (19)	1.10512 (12)
159.435 (10)	1.933 (9)	4.83136 (17)	5.34135 (17)	107.974 (8)	1.10556 (5)
158.246 (18)	2.628 (12)	4.80593 (16)	5.32266 (15)	106.467 (8)	1.10752 (5)
157.149 (8)	3.299 (9)	4.78306 (18)	5.30679 (16)	105.141 (9)	1.10950 (5)
156.863 (18)	3.468 (12)	4.77750 (27)	5.30341 (22)	104.831 (12)	1.11008 (8)
156.394 (16)	3.778 (12)	4.76798 (22)	5.39692 (22)	104.285 (10)	1.11094 (7)
156.013 (12)	4.026 (12)	4.75970 (27)	5.29116 (28)	103.810 (13)	1.11166 (9)
155.220 (11)	4.553 (11)	4.74411 (16)	5.28128 (14)	102.939 (7)	1.11323 (5)
154.829 (17)	4.827 (14)	4.73671 (25)	5.27699 (23)	102.534 (12)	1.11406 (8)
154.261 (10)	5.212 (11)	4.72561 (21)	5.27072 (19)	101.933 (10)	1.11535 (6)
153.973 (10)	5.416 (12)	4.71973 (17)	5.26617 (17)	101.592 (8)	1.11578 (5)
153.526 (8)	5.736 (11)	4.71137 (25)	5.26150 (21)	101.143 (11)	1.11677 (7)
152.889 (14)	6.203 (14)	4.69710 (32)	5.25385 (32)	100.385 (15)	1.11808 (8)
152.520 (14)	6.478 (13)	4.69089 (33)	5.25027 (30)	100.051 (15)	1.11925 (10)
152.160 (11)	6.751 (12)	4.68392 (18)	5.24622 (20)	99.677 (9)	1.12005 (6)
151.590 (16)	7.191 (15)	4.67228 (27)	5.23993 (21)	99.064 (12)	1.12149 (8)
150.703 (9)	7.898 (8)	4.65612 (30)	5.23058 (28)	98.204 (14)	1.1233 (9)
150.034 (13)	8.449 (15)	4.64333 (15)	5.22416 (32)	97.545 (16)	1.12509 (8)
149.494 (10)	8.905 (13)	4.63253 (38)	5.21863 (35)	96.989 (17)	1.12652 (12)

constraints imposed by the known symmetry by more than one e.s.d., the cause was identified as an experimental problem such as a moving crystal in the DAC or an insecure mounting of the DAC to the diffractometer. Such data were excluded from further consideration.

The body of the diamond-anvil cell limits the angles of the incident and diffracted X-ray beams to within $\sim 45^\circ$ of the cell axis. Therefore, at each pressure there are typically three each of the 111, 220 and 311 classes of reflections from the fluorite accessible, all of which were centred and used for lattice-parameter determination. With the (010) face of the quartz lying approximately parallel to the culet faces of the diamond anvils, up to 15 low-angle reflections are accessible (100, 10 $\bar{1}$, 10 $\bar{1}$, 110, 210, 012, 102, 102, 112, 112, 212, 112, 212, 212), although some of these become inaccessible at higher pressures due to either increases in 2θ values or small rotations of the crystal within the cell. A minimum of ten reflection positions were used to determine the a and c lattice parameters of quartz at each pressure.

3. Results

Unit-cell parameters are reported in Table 1. Room-pressure unit-cell determinations performed on several different crystals of fluorite and quartz (held in the DAC without pressure fluid) over a time period of approximately 9 months yield a population standard deviation of both unit-cell edges and unit-cell volumes that is less than the mean of the e.s.d.s of the individual measurements. This indicates not only the stability and reproducibility of the diffractometer configuration, but also

that the e.s.d.s in cell parameters obtained from the vector least squares are a reasonable estimate of the true precision of the measurand.

The pressure of each experiment reported in Table 1 was derived from the measured unit-cell volume of the fluorite crystal through the Murnaghan EOS of fluorite with parameters $V_0 = 163.063(7) \text{\AA}^3$, $K_{\text{TO}} = 81.0(1.2) \text{ GPa}$ and $K' = 5.2(4)$ (Angel, 1993). These EOS parameters were determined against the pressure calibration of the ruby pressure scale of Mao, Xu & Bell (1986) which is in turn tied to the Decker EOS of sodium chloride through the EOSs of copper and silver. These values used for fluorite are in excellent agreement with independent ultrasonic determinations of the elasticity of fluorite, which yield $K_{\text{TO}} = 81.7 \text{ GPa}$ and $K' = 5.0$ (Wong & Schuele, 1968), in which a manganin resistance gauge calibrated against the freezing point of mercury was employed to determine pressures. Uncertainties and fluctuations in the temperature at which the experiments were performed ($298 \pm 1 \text{ K}$ in the diffractometer enclosure) do not significantly affect the EOS parameters of fluorite because of their small temperature dependencies and because the small decrease in K_{TO} with increasing temperature is partly compensated by a corresponding increase in K' (Angel, 1993).

The precision in individual unit-cell volume determinations for fluorite range from 1 part in 8500 to 1 part in 20 000, with a mean of 1 part in 12 500. Because of the increase in magnitude of dP/dV with increasing pressure, the resulting precision in pressure measurement from fluorite also varies with the pressure. The mean precision in unit-cell volume corresponds to a precision of about 0.008 GPa at 1 GPa to 0.011 GPa at

9 GPa. The unit-cell parameters and volume of quartz are slightly inferior, with precision in volume ranging from 1 part in 5000 to 1 part in 16 000 with an average of 1 part in 9000, but, as will shortly be discussed, this leads to a greater precision in pressure determination because of the lower bulk modulus of quartz.

Equation-of-state parameters of quartz were determined by a least-squares fit of third- and fourth-order Birch–Murnaghan EOSs (Birch, 1947) to the volume data with pressures determined with the fluorite. Fits were performed with pressure as the dependent variable, and weights assigned to each data point as $w = [\sigma^2(V') + \sigma^2(P)]^{-1}$, where $\sigma(V')$ is the uncertainty in pressure corresponding to the e.s.d. of the unit-cell volume of quartz $\sigma(V)$. The value of $\sigma(V)$ at room pressure was taken as the population standard deviation of the five room-pressure cell determinations, and $\sigma(P)$ at room pressure was assigned the value of 10^{-6} GPa (= 0.01 bar). The value of $\sigma(P)$ at elevated pressures was obtained by propagation of the experimental e.s.d. of the unit-cell volume of fluorite at pressure and the e.s.d. of the same volume determined at room pressure (0.007 \AA^3 , Table 1) through the EOS of fluorite. The uncertainties in K_{T0} and K' of fluorite were not included in this propagation as they do not contribute to the estimated precision of the EOS determined for quartz. Despite high correlations between some variables (>90%), all least-squares refinements of the EOS parameters converged to a stable global minimum. For a third-order Birch–Murnaghan EOS we obtain $V_0 = 112.981(2) \text{ \AA}^3$, $K_{T0} = 37.12(9) \text{ GPa}$ and $K' = 5.99(4)$. A refinement of a fourth-order Birch–Murnaghan EOS yields $V_0 = 112.981(3) \text{ \AA}^3$, $K_{T0} = 36.9(2) \text{ GPa}$, $K' = 6.3(2)$ and $K'' = -0.46(12) \text{ GPa}^{-1}$. This value of K'' differs by only slightly more than one combined e.s.d. from the value of $-0.27(10) \text{ GPa}^{-1}$ implied by the values of K_{T0} and K' in the third-order EOS, and its inclusion does not reduce the χ_w^2 of the fit. We therefore conclude that the third-order equation of state with $\chi_w^2 = 0.95$ from three parameters and 22 data represents an adequate representation of the volume–pressure data of quartz. This EOS has a maximum residual $|P_{\text{obs}} - P_{\text{calc}}|$ of 0.025 GPa (Fig. 1). The closeness of the value of χ_w^2 to unity indicates that the e.s.d.'s in unit-cell volumes derived from the least-squares fit to the diffractometer angles represent a realistic estimate of the true precision of the experimental technique.

The variation with pressure of the unit-cell parameters of quartz can be described by the polynomial equations

$$a - 4.91300(11) = -0.0468(2)P + 0.00256(7)P^2 \\ - 0.000094(6)P^3$$

$$c - 5.40482(17) = -0.03851(2)P + 0.00305(7)P^2 \\ - 0.000121(6)P^3,$$

where P is in GPa and the cell parameters are in ångströms. The strong initial anisotropy in the quartz compression, with c 50% stiffer than a , leads to a rapid increase in the c/a ratio with pressure (Fig. 2) described by

$$c/a = 1.10006(4) + 0.00280(3)P + 0.000022(3)P^2,$$

where P is in GPa. The positive coefficient for the P^2 term indicates that the elastic anisotropy of quartz increases with pressure over the pressure range in which we have made our measurements. We caution that these polynomials should not be used for predicting the behaviour of the individual lattice parameters of quartz at pressures significantly higher than the limit of our experimental data.

4. Discussion

The accuracy of the equation of state that we have measured for quartz can be assessed through a comparison with independent determinations of the elastic constants of quartz at high pressure. The most precise data available are that of McSkimin *et al.* (1965) who determined the elastic constants of single crystals of quartz to pressures of 30 000 p.s.i. (approximately 0.21 GPa) by ultrasonic techniques coupled with a dead-weight tester for pressure measurement. From their data they obtained $K_{T0} = 37.12(6) \text{ GPa}$ in fortuitously perfect agreement with our value. Their value of $K' = 6.3$ is also in agreement with our determination within the uncertainty of ± 0.3 of their measurement (estimated by Levien *et al.*, 1980). However, use of $K' = 6.3$ in a Birch–Murnaghan third-order EOS results in an over-

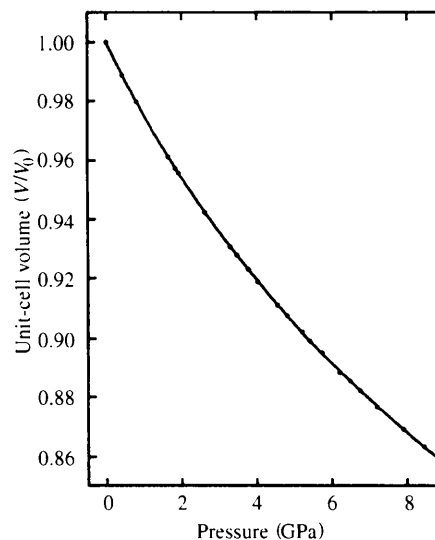


Fig. 1. The volume variation of quartz with pressure. Symbols are approximately ten e.s.d.'s in size and represent the experimental data. The line is the fitted third-order Birch–Murnaghan equation of state.

estimate of the volume at a given pressure, reaching as much as 0.3% at 8.9 GPa, or more than 20 times our uncertainties in volume measurements. Given that our value of K_{T0} agrees with that of McSkimin *et al.* (1965), and that the fluorite equation of state from which we have derived pressures is indistinguishable from that determined ultrasonically (Wong & Schuele, 1968; Angel, 1993), we believe that our value of K' is the more accurate one. Finally, we would note that other static compression data (see review by Levien *et al.*, 1980) generally are, within their larger uncertainties, also in agreement with our determination. The only significant exception is the data of McWhan (1967) which come from experiments in a nonhydrostatic pressure medium and which yield a significantly higher value of the bulk modulus of 44.5 (2) GPa.

Further assessments of the accuracy of our data are provided by the pressure variation of the cell parameters, from which the isothermal linear moduli at room pressure of $-a_0 dP/da|_{P=0} = 105.0(5)$ GPa and $c_0 dP/dc|_{P=0} = 142.6(1.0)$ GPa can be obtained. These values are in reasonable agreement with the values of 101.9 and 136.9 GPa, respectively (with uncertainties of the order of ± 2 GPa) that can be derived from the measurements of McSkimin *et al.* (1965) through the relationship between elastic compliances and linear compressibilities (*e.g.* Nye, 1957). The ratio of these linear moduli actually increases with pressure from a value of 1.36 at room pressure to 2.1 at 9 GPa, at which pressure we obtain moduli of 197 GPa for a and 410 GPa for c . Both this highly anisotropic behaviour and the extreme curvature in the variation of cell parameters with pressure are related to the connectivity of the structure and the approach of the Si–O–Si angles to 120°

(Levien *et al.*, 1980; Sowa, 1988; Hazen, Finger, Henley & Mao, 1989; Glinnemann *et al.*, 1992).

The new equation of state for quartz provides a precise internal pressure standard for single-crystal high-pressure diffraction experiments. If the unit-cell volumes of quartz can be determined to a precision of 0.0001 (1 part in 10 000) then the resulting precisions in pressure will be 0.004 GPa at 1.0 GPa, 0.006 GPa at 5 GPa and 0.009 GPa at 9 GPa ($= 0.1\%$), compared with precisions from fluorite of 0.009, 0.010 and 0.013, respectively. Because the value of K' of quartz is larger than that of fluorite, the relative advantage of quartz as an internal pressure standard over fluorite decreases with increasing pressure by a factor of approximately two over this pressure range. The other factor to consider in the choice between the use of quartz and fluorite is the actual precision with which the unit-cell volumes can be measured. For the same volume of crystal the signal level from quartz is lower than that from fluorite, leading to a lower precision in the final unit-cell volumes. Our *average* precisions in volume for the two materials (1 part in 12 500 for fluorite, 1 part in 9000 for quartz) yield much closer precisions in pressure, with quartz being marginally better for pressure determination at lower pressures and marginally worse than fluorite at 9 GPa. Thus, quartz is more suited to pressure measurement at low pressures and, of course, can be used at pressures in excess of the limit of 9.2 GPa at which fluorite undergoes a phase transition which is destructive of single crystals (Gerward *et al.*, 1992).

The support of the Alexander-von-Humboldt foundation in the form of a Humboldt Preis to LWF and a Humboldt Fellowship to RM is gratefully acknowledged.

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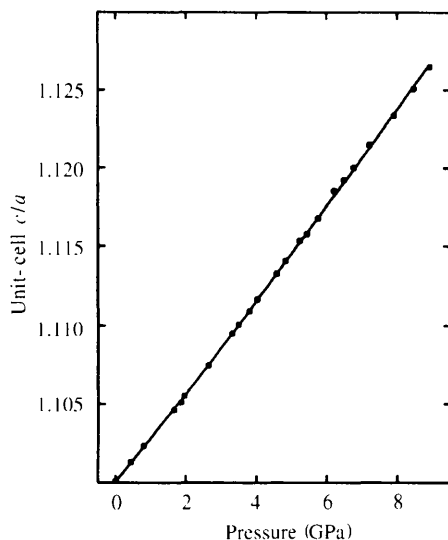


Fig. 2. The variation of the c/a ratio of quartz with pressure. The line is a quadratic fit to the data.

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