

Effects of temperature and pressure on the cell dimension and X-ray temperature factors of periclase

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Abstract

The cell dimension and isotropic temperature factors of synthetic periclase, MgO, have been studied as a function of temperature and pressure, using high-temperature, low-temperature, and high-pressure X-ray diffraction apparatus. These parameters have been determined at one atmosphere at temperatures from -196°C to 1040°C, and at 23°C to pressures of 24 kb. Thermal expansion of periclase is in agreement with the previous determination of Skinner (1957). Isotropic temperature factors of magnesium and oxygen increase at similar rates with temperature, but show no significant variation with pressure. A method of correcting for X-ray absorption by the miniature single-crystal diamond cell is presented.

Introduction

The cubic NaCl-type structure of periclase was first suggested by Hull (1919), and confirmed by Davey and Hoffman (1920). An accurate lattice parameter was determined by Wyckoff (1925), and more recently by Skinner (1957). The change in periclase lattice parameter as a function of temperature from -150°C to 1200°C has been reported by several authors, including Austin (1931), White (1938), Skinner (1957), and Riano and Amoros-Portolés (1958). Linear and volume compressibilities of periclase have been studied by several researchers including the first experiments by Bridgman (1932, 1949) and, more recently, by Anderson and Schreiber (1965) and Spetzler and Anderson (1971). Data on periclase thermal expansion and compressibility have been summarized in Clark (1966). Due to the highly symmetric crystal structure of periclase, this mineral is an ideal substance for testing and improving new crystallographic techniques. The objectives of this study are: (1) to test the capabilities of recently developed high-temperature, low-temperature, and high-pressure single-crystal X-ray diffraction equipment; (2) to develop and test an X-ray absorption method for the miniature high-pressure diamond cell; and (3) to determine the effects of temperature and pressure on the thermal parameters of periclase.

Experimental

Specimen description

Fine single crystals of transparent and colorless periclase were kindly provided by Professor T. J. Shankland from material synthesized by W. and C. Spicer, Ltd., Gloucester, England. The composition of this material was determined by Spicer to be 99.94 weight percent MgO and 0.06 percent FeO, and its index of refraction is $n = 1.735 \pm 0.002$, which agrees with published values of pure magnesia (Bowen and Schairer, 1935). The material is free of visible defects. A rectangular crystal approximately $300 \times 200 \times 180 \mu\text{m}$ was selected for preliminary X-ray photographic investigation. Unit-cell parameters of periclase were determined by both back-reflection Weissenberg and single-crystal diffractometer techniques. Measurement of 65 diffractions from a back-reflection Weissenberg photograph, representing 24 $K\alpha_1$, 24 $K\alpha_2$, and 17 $K\beta$ measurements, yielded a refined cell constant of $a = 4.2121 \pm 0.0001 \text{ \AA}$, after correction for film shrinkage, specimen absorption, and camera eccentricity (Burnham, 1962). In addition, the same crystal was transferred to the four-circle diffractometer, and the locations of twelve diffraction maxima were measured at positive and negative 2θ . The unit cell edge was calculated from least-squares refinement of these measurements as $a = 4.2110 \pm 0.0012 \text{ \AA}$. The two independently determined cell constants agree within experimental error, and are consistent

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with the value of 4.2116 Å reported by Skinner (1957).

Data collection

Oriented crystals were mounted on a computer-controlled, four-circle Picker diffractometer. Unit-cell parameters of each crystal under investigation were determined by refinement of orientation data as described by Grove and Hazen (1974). Intensity data were collected by ω - 2θ scans using Nb-filtered MoK α radiation. The counting rate was not allowed to exceed ten thousand counts per second, which is below the linearity limit of the system. Data were corrected for Lorentz polarization effects as well as crystal absorption using the numerical integration program OBSTF1 (Burnham, 1966).

All structure refinements were carried out using the full-matrix least-squares refinement program RFINE (Finger, 1969). All reflections were weighted by $w = 1/\sigma_F^2$, where σ_F is the estimated standard deviation of the observation as defined by Burnham *et al.* (1971). Observations for which integrated intensity was less than twice the estimated standard deviation of the observation were rejected from the normal equations matrix.

Liquid nitrogen temperature and high temperature

Liquid nitrogen temperature (77°K) was achieved and maintained using a Cryo-Tip refrigerator system manufactured by Air Products and Chemicals, Inc., as described by Grove and Hazen (1974). Crystal temperature was monitored continuously and found to vary no more than 2° from the minimum of -196°C.

The gas-flow heater of Smyth (1972) was employed for all experiments at high temperature. The same crystal used in the previous experiments was mounted in a silica glass capillary, which was in turn cemented to a modified goniometer head using Sauereisen Electric Heater Cement (Sauereisen Cement Company, Pittsburgh, Pennsylvania). Temperatures were measured by a platinum/platinum 90-rhodium 10 thermocouple, which was calibrated to the melting point of sodium chloride (801°C) and gold (1063°C). The thermocouple was placed around the silica capillary at the level of the crystal, and temperature was continuously monitored. The crystal was allowed to equilibrate for one hour at each temperature before unit-cell or intensity data were collected.

High pressure

A miniature diamond pressure cell (Merrill and Bassett, 1974), using Van Valkenberg's (1965) metal-

foil gasketing technique, was employed for all high-pressure diffraction experiments. Experimental procedures were identical to those used by Hazen and Burnham (1974, 1975). All accessible reflections were measured for all high-pressure data collections.

Diamond cell absorption corrections

The most significant problem associated with high-pressure single-crystal X-ray diffraction is X-ray absorption by the irregularly shaped beryllium and diamond components of the pressure cell. The high-pressure structure refinements by Merrill and Bassett (1974) and Hazen and Burnham (1974) did not take this absorption into account. *R*-values greater than 10 percent, and unusually large temperature factors were observed in these studies. Thus a method of correcting observed data for pressure-cell absorption is essential before accurate refinements can be made.

Two assumptions were made in determining an algorithm for pressure cell X-ray absorption. First, it is assumed that the absorption is radially symmetric with respect to a line perpendicular to the flat diamond faces of the pressure cell. This is reasonable since the beryllium platens are machined to be radially symmetric, and the faceted diamond crystals have approximately circular cross-sections (see Hazen and Burnham, 1974, Fig. 2). The second assumption is that the two halves of the pressure cell have identical absorption characteristics. While the diamonds may differ slightly in size and shape, these differences are small with respect to the total path-length of transmitted X-rays. Under these two assumptions, the pressure-cell absorption may be defined as a function of the angles, ψ_P and ψ_D , between the primary and diffracted X-ray beams respectively, and the line perpendicular to the pressure cell (Fig. 1). In general, ψ_P and ψ_D will not be the same. Thus pressure-cell absorption of the primary and diffracted beams will differ, and these two absorption parameters must be calculated separately. Since the two halves of the diamond cell are related by mirror symmetry, the variation of absorption with ψ will be the same for both primary and diffracted X-ray beams. Therefore, only two problems must be solved before absorption corrections may be calculated: (1) the nature of the ψ vs. absorption curve, and (2) the method for calculating ψ_P and ψ_D from crystal orientation data.

Three methods were tried to determine the ψ vs. absorption curve for the Bassett single-crystal pressure cell. The first involved measuring the dimensions

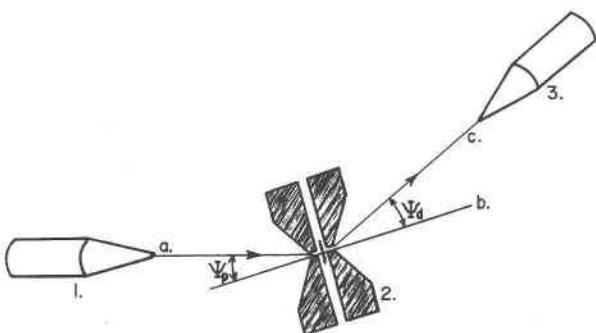


FIG. 1. Pressure cell and X-ray beam geometry for absorption corrections. (1) primary X-ray beam collimator, (2) miniature pressure cell, (3) diffracted beam collimator, (a) primary X-ray beam, (b) perpendicular to flat diamond faces, (c) diffracted X-ray beam.

of beryllium and diamond components and then computing MoK α absorption for linear paths at varying values of ψ . This technique, while theoretically sound, proved impractical due to the uncertainties in measurement of pressure-cell dimensions, and large errors in published Be and C absorption coefficients. Therefore, a second method was used in which a crystal of periclase was selected, and diffraction data were collected at room temperature in the usual way. The same crystal was then mounted in the same orientation in the diamond cell, and data were again collected at room temperature and pressure. Pressure-cell absorptions were then calculated by comparing corrected integrated intensities from the two sets of measurements. A third method was then employed in which the primary beam was passed directly through the pressure cell and measured (after attenuation by .016" of niobium foil) at 0° 2θ . The relative intensity of the direct beam was measured at various values of ψ , first for both halves of the pressure cell individually, and then for the completely assembled cell. It should be noted that the spectral composition of a niobium-filtered primary X-ray beam differs from that of a diffracted beam, and therefore absorption curves for the two cases should not be identical. However, close agreement is observed between the two independently derived absorption curves (Fig. 2), which suggests that the differences in X-ray spectra of the two techniques are not significant. An intermediate curve of ψ versus absorption was used for subsequent absorption corrections.

Before the ψ versus absorption curve can be applied it is necessary to calculate ψ for both primary and diffracted beams. On the four-circle diffractometer, a reference direction is defined with respect to the

crystal, such that the direction is parallel to the primary beam when the diffractometer angles χ , ϕ , ω and 2θ are zero. In actual practice, the pressure cell is easily oriented so that its perpendicular (Fig. 1, direction b) coincides with this reference direction at $\phi = \psi = 0^\circ$. Orientation of a crystal or pressure cell with respect to the primary and diffracted X-ray beams may be described using the direction cosines of vectors parallel to the two beams (e.g. Burnham, 1966):

$$\cos \psi_p = -\cos \theta \cos \phi - \sin \theta \cos \chi \sin \phi, \text{ and}$$

$$\cos \psi_d = \cos \theta \cos \phi - \sin \theta \cos \chi \sin \phi.$$

A computer program to calculate direction cosines for both primary and diffracted beams, and to compute resulting X-ray transmission for the Bassett-type pressure cell, has been developed as a modification of Burnham's (1966) absorption correction program GNABS.

In addition to the high absorption by the cell, there are two sources of X-ray intensity error associated with diffraction from the diamond and steel gasket components of the cell. X-ray precession photos were taken to determine the strength and position of powder rings generated by the gasket, and diffraction peaks due to the diamond anvils. Those measured

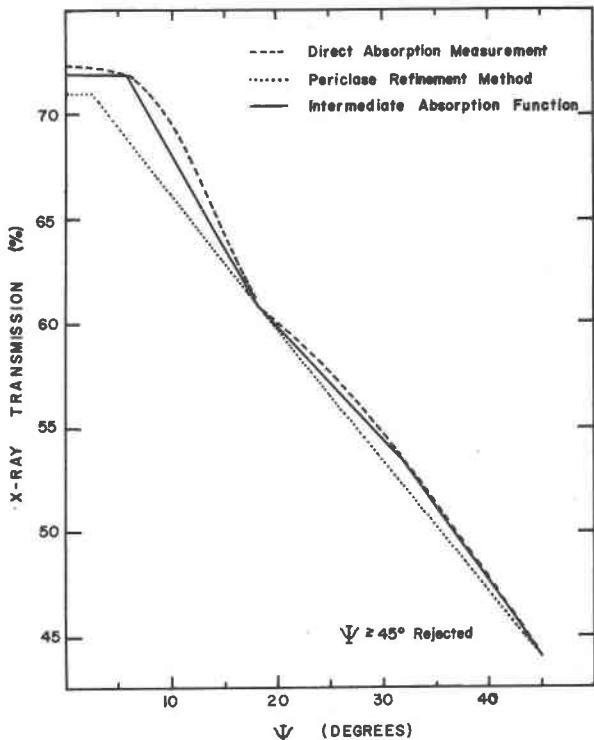


FIG. 2. X-ray absorption curves for the miniature pressure cell: ψ versus absorption.

diffraction maxima which were seriously affected were rejected.

Results

Room temperature and pressure

A reference structure refinement at room temperature and pressure was made with 29 observed reflections representing the average of 395 hkl 's in one hemisphere of reciprocal space from 10° to $90^\circ 2\theta$. In addition, reflection 200 was rejected due to large negative ($F_{\text{obs}} - |F_{\text{calc}}|$), interpreted as due to secondary extinction. The data were corrected for crystal absorption using a linear absorption coefficient of $\mu = 10.734 \text{ cm}^{-1}$, and transmission varied from 78 percent to 87 percent. In periclase both magnesium and oxygen lie on fixed special positions, with site symmetry $4/m\bar{3}2/m$. Therefore, only three variables, a scale factor, and the magnesium and oxygen isotropic temperature factors, need be refined in the least-squares procedure. Values of $B_{\text{Mg}} = 0.34 \pm 0.01$, and $B_0 = 0.37 \pm 0.02$, with a weighted R of 4.2 percent (4.8

percent unweighted) resulted from this refinement. The isotropic temperature factor of oxygen is somewhat lower than that of many oxide minerals (Burnham, 1965). This may be due in part to the relatively large six-coordination of oxygen by magnesium. It should also be noted, however, that the values of calculated periclase temperature factors are strongly dependent on the magnesium and oxygen form factor employed (Raccah and Arnott, 1966). The values for B_{Mg} and B_0 obtained in the present study (using Mg^{2+} and O^{2-} form factors of Cromer and Mann, 1968) agree well with the best values of Raccah and Arnott ($B_{\text{Mg}} = 0.45$, $B_0 = 0.35$).

Effects of temperature from -196° to 1042°C

Periclase unit-cell parameters and isotropic temperature factors have been determined at several temperatures from -196° to 605°C . The same crystal used in room-temperature studies was mounted in a silica capillary for high-temperature data collection. Unit-cell dimensions and diffraction intensities were measured at room temperature (23°C) and then at 150 , 300 , 450 , and 605°C . Unit-cell dimensions were

TABLE 1. Periclase structure parameters and refinement conditions

P	T	Conditions	a(Å)	$B_{\text{Mg}}(\text{\AA}^2)$	$B_0(\text{\AA}^2)$	wR(%) ^a	R(%) ^b	No. of reflections used
1 atm	23	Standard mount	4.2110(12)	0.34(1)	0.37(2)	4.2	4.8	29
"	23	Silica capillary	4.211(1)	0.39(3)	0.39(4)	4.4	5.3	29
"	150	"	4.217(1)	0.54(4)	0.50(5)	5.0	5.9	29
"	300	"	4.225(1)	0.91(5)	0.78(7)	5.8	7.0	29
"	450	"	4.233(1)	1.09(5)	0.93(7)	5.8	6.6	29
"	605	"	4.241(2)	1.33(9)	1.12(9)	8.8	8.8	29
"	753	"	4.249(1)					
"	915	"	4.257(1)					
"	1042	"	4.264(2)					
"	23	Cryo-Tip with Be shroud	4.208(5)	0.25(3)	0.26(4)	4.4	5.1	29
"	-196	"	4.203(5)	0.10(2)	0.16(3)	2.9	3.4	29
"	23	Pressure cell absorption curve 1 ^d	4.212(1)	0.43(4)	0.56(6)	3.5	4.3	9
"	"	Pressure cell absorption curve 2 ^d	4.212(1)	0.43(4)	0.55(6)	3.5	4.2	9
17 kb	"	Pressure cell	4.198(1)	0.3(2)	0.5(3)	8.5	10.9	9
24 kb	"	"	4.193(1)	0.4(1)	0.7(1)	5.5	6.8	9
1 atm	"	Pressure cell after high pressure	4.212(5)					

$$a) wR = \left[\frac{\sum w(F_{\text{obs}} - |F_{\text{calc}}|)^2}{\sum w F_{\text{obs}}^2} \right]^{\frac{1}{2}} \times 100$$

$$b) R = \frac{\sum |F_{\text{obs}} - |F_{\text{calc}}||}{\sum F_{\text{obs}}} \times 100$$

c) Parenthesized figures refer to the esd of least units cited.

d) See Fig. 2.

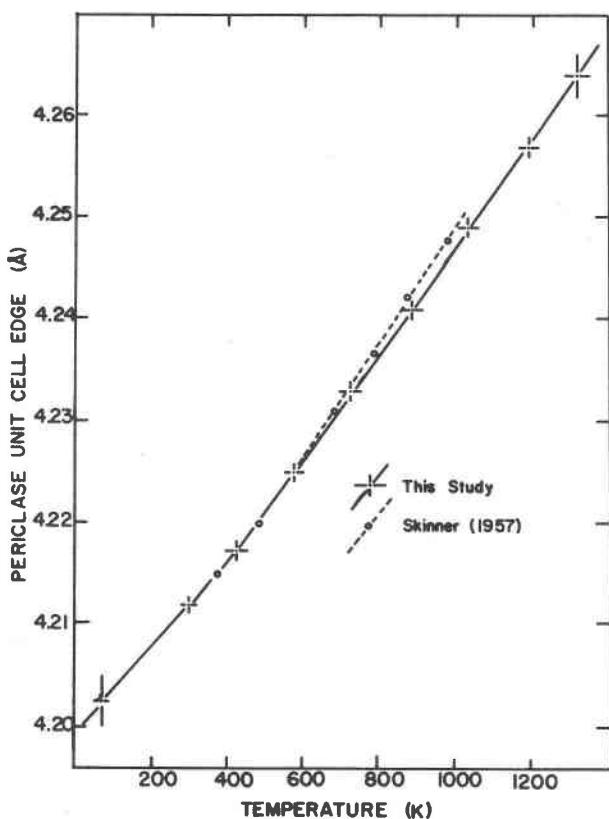


FIG. 3. Periclase cell dimension versus temperature.

then measured at 753, 915, and 1040°C, but an attempt to collect intensity data at approximately 900°C failed due to fracture of the silica capillary and subsequent loss of the crystal. However, the data already collected were considered sufficient to characterize the behavior of periclase at high temperature, and no further heating experiments were performed.

A second crystal approximately 240 × 200 × 130 μm was mounted for low-temperature study. Cell dimensions and intensity data for this crystal were first measured at room temperature without the beryllium vacuum shroud. A second 23°C data collection was made with the shroud to confirm that corrections for beryllium absorption were not required. Finally data were collected at liquid nitrogen temperature in the usual way. Unit-cell and structure refinement data are presented in Table 1.

Expansion data of periclase from -196°C to 1040°C are illustrated in Figure 3, together with previous data of Skinner (1957). This study agrees with Skinner within experimental error at all values of temperature examined. As the temperature approaches absolute zero, the coefficient of thermal ex-

pansion is observed to decrease, and the absolute zero cell edge of Spicer periclase appears to be $a = 4.199 \pm 0.002$ Å.

Magnesium and oxygen isotropic temperature factors of periclase are plotted versus temperature in Figure 4. Below 450 K, isotropic temperature factors of magnesium and oxygen are the same within their estimated standard deviations, and both approach zero at absolute zero. However, above 500 K magnesium vibrations have a slightly larger amplitude than those of oxygen.

Effects of pressure from 1 atm to 24 kb

Compressibility of MgO has been well-established by Bridgman (1949) and Anderson and Schreiber (1965), and thus changes in periclase cell volume were used to calibrate pressure. The same crystal used in low-temperature studies was mounted in the diamond cell, and data were collected at room pressure to test the pressure-cell absorption model. The one atmosphere data were corrected first using absorption curve 1 and then absorption curve 2, illustrated

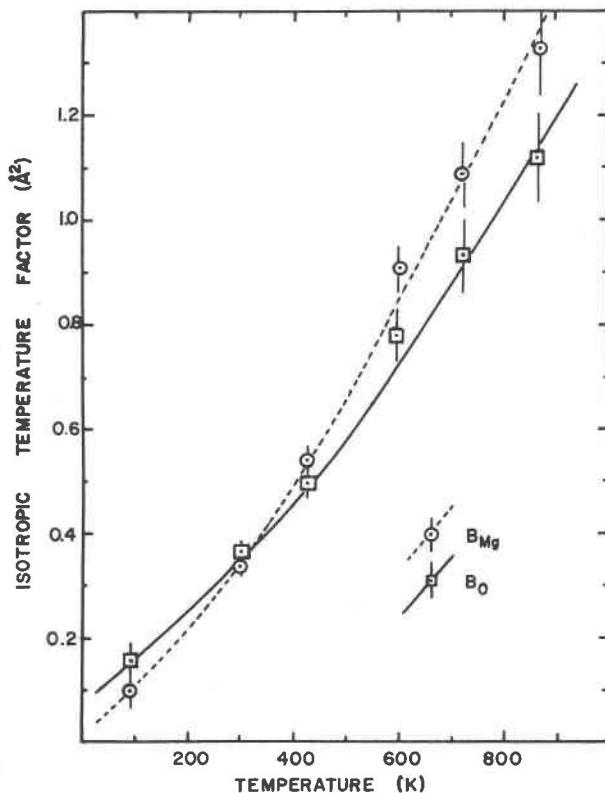


FIG. 4. Periclase isotropic temperature factors versus temperature.

in Figure 2: these two data sets yielded essentially identical results, as indicated in Table 1.

The pressure cell was tightened and the unit-cell edge was determined to be $a = 4.198 \pm 0.001 \text{ \AA}$, corresponding to a pressure of $17 \pm 1 \text{ kb}$. Diffraction data were collected in the usual way. The cell was tightened further, giving a cell edge of $a = 4.193 \pm 0.001 \text{ \AA}$, equivalent to $P = 24 \pm 1 \text{ kb}$. The data collection process was repeated, and a third attempt to raise the pressure was made. However, numerous fractures appeared in the periclase crystal, and diffraction peaks became broad and diffuse, implying a partial crushing of the crystal at a pressure above 24 kilobars. The pressure cell was loosened, and a rough room-pressure unit-cell constant measurement from these diffuse peaks yielded $a = 4.211 \pm 0.005 \text{ \AA}$. While the crystal did suffer mechanical damage, no alteration of the crystal structure had occurred. Unit-cell and structure refinement data from these experiments are also presented in Table 1.

Values of isotropic temperature factors at elevated pressures have not been previously reported for periclase. The absorption of X-rays by the pressure cell, as well as the high level of background scattered X-radiation from the cell, resulted in over 60 percent of the diffractions being unobserved. Since a very limited volume of reciprocal space was accessible, only nine independent hkl 's were observed. Nevertheless, reasonable values for magnesium and oxygen isotropic temperature factors were obtained from all diamond-cell refinements. Furthermore, the temperature factors do not appear to change from 1 atm to 24 kb within the experimental uncertainty of the measurement.

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