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Compression of pyrope

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Abstract

Unit-cell parameters have been determined on a single crystal of pyrope mounted in a diamond-anvil cell at pressures from one atm to 50 kbar. From a least-squares fit of these data to a third-order Birch–Murnaghan equation of state, a value for the bulk modulus of pyrope ($K_T = 1.75$ Mbar) and its pressure derivative ($K'_T = 4.5$) were calculated. The bulk modulus is in good agreement with two other determinations using cubic-anvil and acoustic techniques but does not agree with another determination using single-crystal diamond-anvil techniques. It appears possible to obtain reasonable values and errors for K'_T with diamond-anvil techniques at low pressures (<50 kbar), even for minerals with large values of K_T, when complementary acoustic data are available.

Introduction

Pyrope-rich garnets are commonly found in rocks formed at great depth within the earth, and are thought to be an important constituent of the upper mantle. For this reason, knowledge of the elastic properties of such garnets is vital to accurate modeling of the upper mantle. There has also been much interest in their elastic properties because garnets form several solid-solution series, and thus provide material for a systematic study of how chemistry affects elasticity of crystals. Values for the elastic moduli of pyrope have been determined with acoustic techniques, static-compression techniques, and by extrapolating from data determined on non-end-member compositions. There is a great deal of scatter in the data and, in particular, the static compression values have not consistently agreed with acoustic determinations.

Four previous studies of the elastic moduli of a synthetic end-member pyrope exist (Takahashi and Liu, 1970; Sato *et al.*, 1978; Leitner and Weidner, 1978; Hazen and Finger, 1978). In the Takahashi and Liu study a powdered sample was compressed between diamond anvils with NaCl as both internal pressure standard and pressure-transmitting medium. The non-hydrostatic nature of the experiment accounts for the large value of $K_T = 1.91$ Mbar. The Sato *et al.* study used the cubic-anvil type of high-pressure apparatus. A liquid 4:1 methanol:ethanol mixture was used as the pressure-transmitting fluid during the static-compression experiment. The isothermal values of K_T, the zero-pressure bulk modulus, and K'_T, the pressure derivative of the zero-pressure bulk modulus, calculated by fitting the pressure–volume data to a third-order Birch–Murnaghan equation of state, are 1.71 Mbar and 1.8, respectively. The single-crystal elastic moduli, as well as K_S, the zero-pressure adiabatic bulk modulus, have been determined by Leitner and Weidner using the acoustic technique based on Brillouin scattering ($K_S = 1.77$ Mbar). The Hazen and Finger study was accomplished with single-crystal diamond-anvil techniques. The values of K_T and K'_T calculated by fitting their pressure–volume data to the Birch-Murnaghan equation are 1.43 Mbar and 5., respectively. The large discrepancy between this value of K_T and the other two determinations led us to repeat the diamond-anvil experiment with improved techniques. It was hoped either that the newer data would be consistent with the values determined from other techniques, or that some reason for the inconsistency could be discovered.

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Table 1. Pyrope unit-cell parameters at pressure

Pressure	a(Å)	v(Å^3)
1 atm	11.456(2)*	1503.4(5)
22.7(5) kbar	11.408(2)	1484.5(6)
30.7(5) kbar	11.392(1)	1478.3(4)
35.7(5) kbar	11.382(1)	1474.4(3)
43.2(5) kbar	11.367(1)	1468.6(3)
49.6(5) kbar	11.354(1)	1463.8(3)

*Parenthesized figures represent *esd*'s of least units cited.

Experimental techniques

The synthetic end-member pyrope crystal used in this experiment was from the same sample as that of Leitner and Weidner (1978). The crystal was mounted in a modified Bassett-design single-crystal diamond-anvil cell (Merrill and Bassett, 1974). Flat beryllium disks like those described by Hazen and Finger (1977) were used in the cell. Diamonds (1/8 carat each) were cut with 1 mm anvil faces (culet). The gasket was made of 250μm-thick Inconel X750 (spring). The crystal was attached to one diamond face with the alcohol-insoluble fraction of petroleum jelly, and a 4:1 methanol:ethanol mixture was used as the pressure-transmitting medium (Finger and King, 1978; Piermarini *et al.*, 1973). A small ruby crystal (10μm; 0.5 wt.%Cr) was placed in the cell and used for pressure calibration. The calibration system, based on the shift of the fluorescence spectrum of ruby, is similar to that described in Barnett *et al.* (1973) but modified by King and Prewitt (in preparation). All pressure values reported in this paper have been calculated based on the Decker (1971) equation of state for NaCl. The diamond cell is mounted on the specially designed goniometer head (Hazen and Finger, 1977) which is, in turn, mounted on the four-circle X-ray diffractometer. Each Bragg reflection used to determine the unit cell was centered with eight different sets of diffractometer angles to remove systematic errors resulting from offsets in centering of the crystal, height of the back apertures, and zeroes of the diffractometer angles (Hamilton, 1974; King and Finger, 1979). These eight sets of angles are for one *hkl*, not symmetrically equivalent reflections. Least-squares refinement of between eight and twelve reflections with 2θ's ranging from 49° to 62° for all pressures gave unit-cell lengths within two standard deviations of being equal and angles within two standard deviations of being 90° (Table 1).

The unit-cell volumes were normalized to the room-pressure volume and then K_T, the room-pressure isothermal bulk modulus, and K_T', the pressure derivative of K_T, were determined by a least-squares fit to a third-order Birch–Murnaghan equation of state. These values are listed in Table 2, along with those of the other investigators. Bond distances were recalculated for the structural refinements of Hazen and Finger (1978), using their published fractional coordinates and unit-cell parameters calculated from our compressional data (Table 3).

Results and conclusions

In Figure 1, the normalized volumes for the three static-compression experiments are plotted as functions of pressure. The three curves drawn are the Birch–Murnaghan fits to the three data sets. The curve for Sato *et al.* (1978) and our data are in good agreement at low pressures and diverge at higher pressures. The discrepancy between the Hazen and Finger (1978) data and the other data sets begins at lower pressures and is larger in magnitude. There are two main differences between our experiments and those of Hazen and Finger. Firstly, they used a water + glycerin mixture as the pressure-transmitting medium. The hydrostatic limits of this mixture are not

Table 2. Elastic moduli of pyrope determined by several techniques

Investigator	Technique	K_T (Mbar)	K_T'
Sato *et al.* (1978)	*Cubic-anvil	1.71(3)**	1.8(7)
Leitner and Weidner (1978)	Brillouin scattering	1.75(1)	
Hazen and Finger (1978)	*Single-crystal diamond anvil	1.43(8)	5. (3.)
This work	*Single-crystal diamond anvil	1.75(1)	4.5(5)

*Values were calculated by a least squares fit of the pressure-volume data to a third-order Birch-Murnaghan equation of state:

$$P = \frac{3}{2} K_T(y^{-7/3} - y^{-5/3})[1 - \frac{3}{4} (4 - K_T')(y^{-2/3} - 1)], \qquad y = V/V_o$$

**Parenthesized figures represent *esd's* of least units cited.

Table 3. Bond distances for pyrope

M-O	1 atm	16 kbar		31 kbar		43 kbar		56 kbar	
	H&F*	H&F	LPW**	H&F	LPW	H&F	LPW	H&F	LPW
Si-O	1.634(2)†	1.626(4)	1.628	1.633(3)	1.636	1.619(4)	1.621	1.626(3)	1.630
Al-O	1.887(2)	1.875(5)	1.877	1.862(4)	1.864	1.869(5)	1.871	1.863(5)	1.867
Mg(1)-O	2.197(2)	2.188(5)	2.190	2.188(4)	2.190	2.180(5)	2.183	2.156(4)	2.161
Mg(2)-O	2.343(2)	2.341(4)	2.343	2.323(4)	2.326	2.320(4)	2.323	2.307(4)	2.312

* Values from Hazen and Finger (1978).
** Values recalculated in this work (Levien, Prewitt and Weidner).
† Parenthesized values represent *esd's* of least units cited.

known and, therefore, some of their data may have been collected under non-hydrostatic conditions. In fact, Hazen and Finger (personal communication) have indicated that this is true of their 56 kbar data. The second difference in our experiments was the manner in which the reflections used to calculate the unit cell were collected. As mentioned earlier, we measured each reflection used to determine the unit cell with eight different diffractometer settings to eliminate potential systematic errors. From the angles of the eight reflections measured with this technique, the offset of the crystal from the physical center of the diffractometer can be calculated, and translation devices on the specially-designed goniometer head can then be used to correct the crystal centering. Unfortunately this centering procedure is only good to about 30μm, at best (King and Finger, 1979). Although Hazen and Finger used this technique to physically center their crystal, they did not use it to collect the reflections which were used to determine their unit cells. This may have resulted in systematic errors in their unit-cell parameters, as the crystal could still have been 30μm or more off-center. The bond distances of the structural refinements for pyrope, based on these small unit cells, have also been slightly influenced (Table 3). Although the bond distances reported by Hazen and Finger are systematically smaller than our recalculated distances, the differences are only significant in the 56 kbar experiment.

There have been two ultrasonic measurements of K'_T for different garnet compositions, grossular (K'_T = 4.25) (Halleck, 1973) and an almandine–pyrope solid solution (K'_T = 5.45) (Soga, 1967), which can be compared to the isothermal values discussed in this study. We feel that the value for K'_T calculated from our data (K'_T = 4.5) reflects the best of the three isothermal determinations for pyrope. Hazen and Finger's (1978) value for K'_T (5.) has a 60% error, which encompasses essentially the entire range of realistic values for K'_T. The Sato *et al.* (1978) value for K'_T (1.8) is very low and out of the range in which most values of the pressure derivative for silicates fall. The good agreement of our K'_T value with those determined ultrasonically gives us additional confidence in the accuracy of our diamond-anvil experiment, and shows that it is possible to obtain reasonable values for K'_T at low pressures (<50 kbar), even for minerals which have very large bulk moduli. Pyrope may be unique as it has high-intensity Bragg reflections at large 2θ values, which allowed us to obtain a precision of one part in ten thousand in our unit-cell parameters.

The uncertainties reported in Table 2 for K_T and K'_T reflect the statistical scatter or dispersion of the individual data points from the analytical Birch–Murnaghan curve, based on the assumption that the average scatter accurately reflects the experimental uncertainty in the data. As Bass *et al.* (1979) have demonstrated, this approach leads to an underestimate of the uncertainties in K_T and K'_T if this dispersion is fortuitously small when compared to the errors in pressure and volume (Table 1). If these larger errors are incorporated into the least-squares

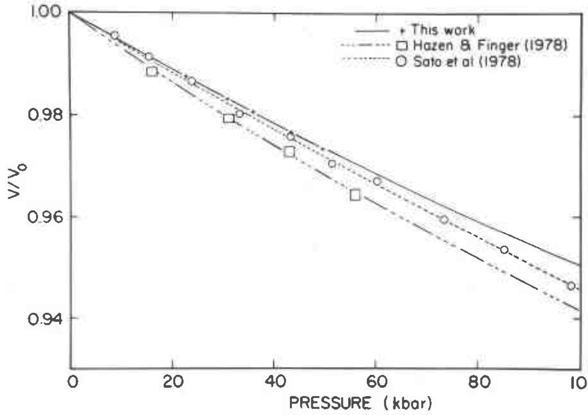

Fig. 1. V/V_0 *vs.* pressure for pyrope. Curves represent third-order Birch–Murnaghan equation of state for each of the sets of data.

analysis, K_T and K_T' appear to be very poorly determined, especially when the number of data points is small. To improve this resolution, Bass *et al.* have suggested that the zero-pressure bulk modulus, K_T, be constrained to be equal to the value determined acoustically, and the compression data be used to determine only one parameter, K_T'; using this approach and the Leitner and Weidner (1978) determination of $K_T = 1.75 \pm 0.01$ Mbar for pyrope, they obtain a $K_T' = 4.5 \pm 1.0$ from our pyrope compression data. Thus volume–compression data obtained with single-crystal diamond-anvil techniques are sufficiently precise to extract significant values of K_T' when complementary acoustic data are available.

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