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# The $\alpha$-$\beta$ quartz transition at high temperatures and pressures in a diamond-anvil cell by laser interferometry

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## ABSTRACT

The $\alpha$-$\beta$ quartz transition was observed using laser interferometry at simultaneous high temperatures and high pressures up to 850 °C and 1100 MPa in situ in a diamond-anvil cell. The $\alpha$ to $\beta$ transition manifested itself as an abrupt collective motion in the interference fringes produced by the laser light reflected from the top and bottom surfaces of a doubly polished quartz platelet. The $\beta$ to $\alpha$ transition was observed also as an abrupt shift of the interference fringes, but in the opposite direction. By using the method described in Shen et al. (1992a) and employing the equation of state of $H_2O$ formulated by Haar et al. (1984), we were able to calculate transition pressures accurately. The transition temperatures were fitted to a quadratic function of pressure, and the following result is obtained:

$$T\,(°\mathrm{C}) = 574.3 + 0.2559P\,(\mathrm{MPa}) - 6.406 \times 10^{-6}P^2.$$

## INTRODUCTION

The $\alpha$-$\beta$ quartz transition has been extensively studied with many different techniques since its first recognition (Le Chatelier, 1889). Early investigations were mostly measurements and observations of the changes in the optical properties, such as birefringence, refractive indices, and optical activity, as the transition occurred at atmospheric pressure. The experiments on this transition at simultaneous high temperatures and pressures were performed later by means of differential thermal analysis and differential pressure analysis methods (Bates and Phelps, 1927; Keith and Tuttle, 1952; Gibson, 1928; Coe and Paterson, 1969; Cohen and Klement, 1967; Cohen et al., 1974; Koster van Groos and Ter Heege, 1973; Mirwald and Massonne, 1980; Yoder, 1950). Sosman (1928, 1965) has provided comprehensive reviews of the experiments done before 1965.

Even though this transition has been studied extensively, there remains considerable disagreement among the published $\alpha$-$\beta$ quartz boundaries (Fig. 1, Table 1). This disagreement probably arises from the uncertainty of the effects of pressure on the measured electromotive force (emf) of the thermocouples in the high-pressure DTA apparatus and the small enthalpy change associated with the $\alpha$-$\beta$ quartz transition.

It is our intention to use the $\alpha$-$\beta$ quartz transition to determine the equations of state of various fluids (Chou et al., 1992; Shen et al., 1991, 1992b); however, discrepancies among the published $\alpha$-$\beta$ quartz boundaries are larger than the discrepancies among different equations of state for $H_2O$ at lower pressure and temperature conditions (Fig. 1). Therefore, it is possible that the equation of state for $H_2O$ can be used to refine the $\alpha$-$\beta$ quartz transition boundary.

## APPARATUS AND METHODS

The diamond-anvil cell used in this work was designed especially for hydrothermal experiments (Bassett et al., 1992) and will be described in detail in a separate paper. In this design, the diamond-anvil cell is equipped with two resistance heaters and two K-type thermocouples that are attached to each diamond to measure the temperatures at both diamond anvils simultaneously. These thermocouples are not subject to any pressure-induced emf error because they are not pressurized. Furthermore, we have carefully calibrated the thermocouples with an ASTM calibrated Hg thermometer at room temperature and with the melting temperatures of sodium nitrate (306.8 °C) and sodium chloride (800.5 °C) at room pressure. The discrepancies between the measured and the true melting temperatures of the salts are typically $<4$ °C. In addition, two variable resistors were used as shunts to the heaters to control their power; thus the temperatures at the upper and lower diamonds could be controlled to within 1 °C.

A frequency doubled Nd:YAG laser that produces green light (wavelength: 532 nm) was used as the light source to generate interference fringes so that both the optic path (distance times refractive index) between anvil faces and the abrupt change in refractive indices of quartz at the transition could be monitored. Images from two television cameras, one for direct observation of the sample

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and the other for digital temperature and time, are superimposed and recorded on a video cassette recorder so that careful analysis of transition temperatures and rate of change can be made.

The charge loaded into the sample chamber includes a doubly polished quartz platelet, distilled-deionized $H_2O$, and an air bubble. The sample chamber is formed by drilling a hole 500 μm in diameter in a Re foil 125 μm thick with a Q-switched Nd:YAG laser and then compressing the foil between two diamond anvils. The quartz platelet is typically about 100 × 100 × 30 μm and is oriented with the **c** axis perpendicular to the polished surfaces. Heating the sample chamber causes the liquid to expand and the air bubble to dissolve in the liquid. At the homogenization temperature, liquid and vapor become one fluid phase. Further heating of this homogenized fluid causes the pressure in the sample chamber to increase according to the $P$-$T$ path of a specific isochore, whose density can be calculated from the homogenization temperature measured.

We have conducted both interferometric and planimetric measurements in an air-filled sample chamber subjected to the same force, and the results show that the variation of the distance between the anvil faces is <0.5% and that the lateral dimensions undergo negligible change. Therefore, in the pressure and temperature region of interest, the volume of the sample chamber remains very close to a constant (within 0.5%) (Chou et al., 1992; Shen et al., 1992b). The quartz platelet in the sample chamber occupies <1.5% of the total volume; therefore, the effect on the total volume of the volume change of the quartz platelet at high temperatures and high pressures is negligible. The error due to the inclusion of an air bubble instead of an $H_2O$-vapor bubble is negligible because of the low density of the gas in the air bubble (Shen et al., 1992a).

We heated the sample until we observed the motion of interference fringes, which indicates that the α-β quartz transition has occurred. Because the refractive indices of quartz undergo an abrupt change during the α to β transition (Sosman, 1928), the interference fringes in the quartz platelet undergo an abrupt collective motion in one direction. The β to α transition manifested itself as an abrupt collective motion of the interference fringes in the reversed direction. We repeated the transition three to five times to assure the precision of the transition temperature measurements. Then we rapidly cooled the sample until the fluid was again in the two-phase region of the phase diagram. Slight reheating of the sample for a few degrees rehomogenized the two phases and yielded the homogenization temperature of this fluid. We cycled the heating and rapid cooling procedures three times for each experiment to check the reproducibility of the measured temperatures. The homogenization temperature measurement was reproducible to ±0.5 °C, and the α-β quartz transition temperature measurement was reproducible to ±1 °C.

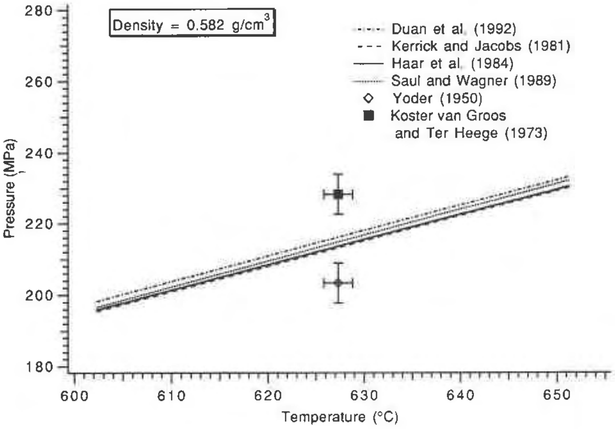

Fig. 1. A $P$-$T$ plot shows the results from one of our experiments (EOS-$H_2O$-01). This diagram includes four versions of the equation of state of $H_2O$, with the fluid density of 0.582 g/cm³, and the α-β quartz transition pressures calculated from the equations of Yoder (1950) and Koster van Groos and Ter Heege (1973) at the observed transition temperature (627.3 °C). Error bars show uncertainties in our temperature measurements and calculated pressures. It is clearly shown that, at the transition temperature, the disagreement in pressure between the two determinations of the α-β quartz boundaries is greater than the disagreement among the four versions of equation of state of $H_2O$.

**TABLE 1.** Comparison of α-β quartz boundary

| Reference | $a$* (°C) | $b$* (°C/MPa) | $c$* (°C/MPa²) | Comments |
|---|---|---|---|---|
| This study | 574.3 | 0.2559 | $-6.406 \times 10^{-6}$ | including 1-bar datum (574 °C) |
| Gibson (1928) | 571.99 | 0.21 | $+8.6 \times 10^{-5}$ | $P$ up to 264 MPa |
| Yoder (1950) | 570.7 | 0.2871 | $-4.284 \times 10^{-5}$ | $P$ up to 1000 MPa |
| Cohen and Klement (1967) | 573–574 | 0.26 | $-4 \times 10^{-5}$ | $P$ up to 3500 MPa |
| Koster van Groos and | 572.5 | 0.155 | $+5.465 \times 10^{-4}$ | 0.1–10.65 MPa |
| Ter Heege (1973) | 567.3 | 0.265 | $-6.525 \times 10^{-6}$ | 8.8–1020 MPa |
| Coe and Paterson (1969) | 574.4 | 0.258 | $<5 \times 10^{-6}$ | $P$ up to 700 MPa |
| Cohen et al. (1974) | ** | 0.26 | no conclusion | $P$ up to 700 MPa |
| Mirwald and Massonne (1980)† | 571.194 | 0.271 084 | $-2.3607 \times 10^{-5}$ | $P$ up to 3400 MPa, including Yoder's data for $P < 1000$ MPa |

* The $a$, $b$, and $c$ are coefficients of the quadratic equation $T = a + bP + cP^2$.
** Not available.
† Formulation includes a cubic pressure term ($P^3$) with coefficient = $3.91 \times 10^{-9}$ (°C/MPa³).

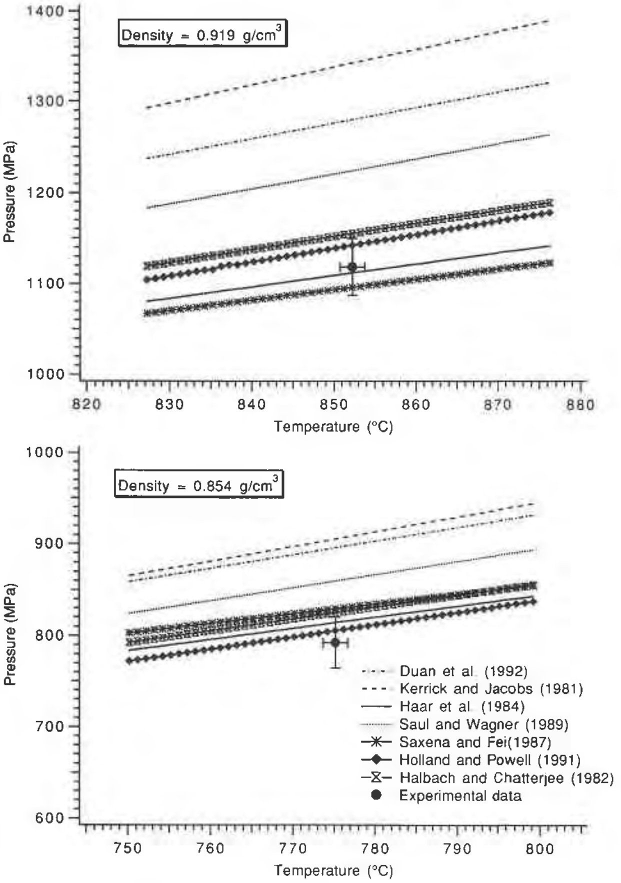

Fig. 2. Two *P-T* plots show the comparison among five versions of the equation of state of $H_2O$ at densities of 0.919 and 0.854 g/cm³ (Chou et al., 1992; Shen et al., 1991, 1992b). The $\alpha$-$\beta$ quartz transition pressures were calculated from the equation of Mirwald and Massonne (1980) at the observed transition temperatures (852.3 and 775.2 °C). Error bars show uncertainties in our temperature measurements and calculated pressures. The formulations of Haar et al. (1984), Halbach and Chatterjee (1982), Saxena and Fei (1987), and Holland and Powell (1991) all yielded transition pressures that agree with those calculated from the equation of Mirwald and Massonne (1980). However, at lower temperature-pressure conditions, the equation of state of $H_2O$ formulated by Saxena and Fei (1987) deviated slightly from the other three formulations.

**Table 2.** Experimental results

| Expt. | $T_h$ (°C)* | $\rho$ (g/cm³)** | $T_{tr}$ (°C)* | $P_{tr}$ (MPa)** |
|---|---|---|---|---|
| EOS-$H_2O$-04 | 147.5 | 0.919 | 852.3 | 1111.7(±7.5) |
| EOS-$H_2O$-03 | 208.7 | 0.854 | 775.2 | 814.2(±6.5) |
| EOS-$H_2O$-07 | 306.9 | 0.698 | 672.8 | 376.6(±5.5) |
| EOS-$H_2O$-01 | 348.1 | 0.582 | 627.3 | 213.6(±3.8) |
| EOS-$H_2O$-13 | 367.0 | 0.482 | 612.6 | 144.0(±3.4) |

*Note:* Symbols used: $T_h$ = measured homogenization temperatures of the two-phase fluid of $H_2O$; $T_{tr}$ = measured $\alpha$ to $\beta$ quartz transition temperatures; $P_{tr}$ = calculated $\alpha$ to $\beta$ quartz transition pressures; $\rho$ = density. EOS = equation of state.

* Temperatures after correction.

** Calculated from the NBS/NRC Steam Table (Haar et al., 1984).

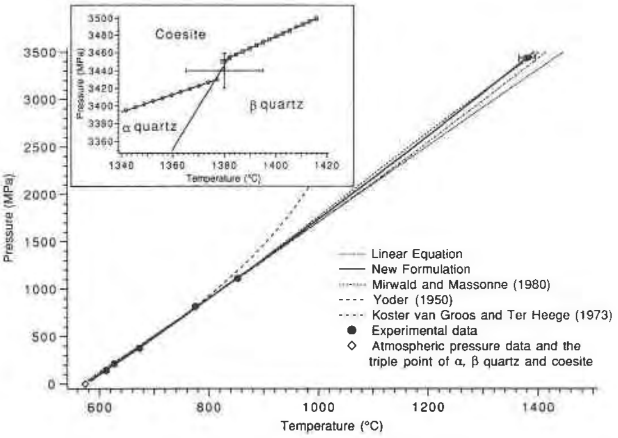

Fig. 3. A *P-T* plot compares our new formulation for the $\alpha$-$\beta$ quartz boundary with other formulations. The linear equation is obtained by fitting our data to a function $T = a + bP$. Above 1000 MPa, Yoder's equation (Yoder, 1950) starts to deviate from other formulations and approaches 1050 °C asymptotically. The curve based on Yoder's equation does not go through the $\alpha$-quartz, $\beta$-quartz, and coesite triple point at 3440 ± 20 MPa and 1380 ± 15 °C (Mirwald and Massonne, 1980). On the other hand, Yoder's data do not exceed 1000 MPa. The new formulation is in excellent agreement with the triple point; however, the linear extrapolation does not agree with the triple point within the uncertainty limit. The insert shows an enlargement of the *P-T* region near the $\alpha$-quartz, $\beta$-quartz, and coesite triple point. The error bars show uncertainties reported in Mirwald and Massonne (1980). The coesite and $\alpha$-quartz boundary (open circles) and the coesite and $\beta$-quartz boundary (open squares) are from Mirwald and Massonne (1980).

## RESULTS AND DISCUSSION

The results of our experiments are summarized in Table 2. The density of fluid, $\rho$, for each experiment is calculated from the measured homogenization temperature, $T_h$. The $\alpha$-$\beta$ quartz transition pressure, $P_{tr}$, is calculated from the measured transition temperature, $T_{tr}$, by using the equation of state for $H_2O$ formulated by Haar et al. (1984). We chose this equation of state for $H_2O$ as a result of a comparison of five equations of state for $H_2O$ in an earlier study (Chou et al., 1992; Shen et al., 1991, 1992b). Figure 2 shows the results of two high-pressure experiments from this study (density equals 0.919 and 0.854 g/cm³, respectively). The equation of state for $H_2O$ formulated by Haar et al. (1984) yields transition pressures consistent with those interpolated from the experimental results given by Mirwald and Massonne (1980). When we compared our results with the equation of state for $H_2O$ formulated by Halbach and Chatterjee (1982), Saxena and Fei (1987), and Holland and Powell (1991), all three formulations were very close to or within our experimental uncertainties at high pressures and temperatures, but, at low pressure-temperature conditions, Saxena and Fei (1987) showed deviation from Haar et al. (1984), Halbach and Chatterjee (1982), and Holland and Powell (1991). Therefore, for the pressure-temperature conditions covered by this study, using the formulations of the equation of state for $H_2O$ by Haar et al. (1984), Halbach and Chatterjee (1982), and Holland and Powell (1991) should yield a very similar result. We fitted our data and the atmospheric pressure point of the $\alpha$-$\beta$ quartz transition (574 °C) to the following quadratic equation by a least-squares method: $T_{tr}$ (°C) = 574.3 + 0.2559$P_{tr}$ (MPa) − 6.406 × $10^{-6}P_{tr}^2$.

Furthermore, when the $\alpha$-quartz and coesite boundary and $\beta$-quartz and coesite boundary from Mirwald and Massonne (1980) were employed, our equation was found to intersect the $\alpha$-quartz and coesite boundary at 1376 °C and 3429 MPa, and to intersect the $\beta$-quartz and coesite boundary at 1381 °C and 3454 MPa. These results are within the uncertainties of the temperature and pressure of the $\alpha$ quartz, $\beta$ quartz, and coesite triple point at 1380 ± 15 °C and 3440 ± 20 MPa reported by Mirwald and Massonne (1980) (see insert of Fig. 3).

The accuracy of our transition pressure determination depends on the accuracies of the temperature measurements and the equation of state for $H_2O$. The accuracy of our homogenization temperature measurements is believed to be within ±0.5 °C, which corresponds to a maximum density uncertainty of ±0.004 (g/cm³). Combining this uncertainty with those of the density determination of the formulation (Fig. A.39 of Haar et al., 1984), we expect the maximum density uncertainty to be ±0.0041 (g/cm³). The accuracy of the transition temperature measurements is believed to be within ±1.5 °C. Uncertainties of the transition pressures given in Table 2 include those for the density and the transition temperature measurement. Another source of error in our pressure determination may derive from our assumption that the effect of dissolved silica on the equation of state for $H_2O$ is negligible. The solubility of quartz at low pressures and moderate temperatures is known to be very small (a few parts per million); however, at higher pressure and temperature conditions, it is not well understood. Accurate determination of the refractive index or sound velocity in the fluid may provide this important information.

In comparison with the previous results (Table 1, Fig. 3), our initial slope is in agreement with the results from Coe and Paterson (1969) and Cohen et al. (1974), yet our curvature is smaller than most of those obtained in the previous studies. It is clearly shown in Figure 3, however, that a straight line does not describe the $\alpha$-$\beta$ quartz boundary and that a negative curvature is necessary. A thermodynamic interpretation of this curvature cannot be derived from our data, as the pressure dependence of the volume change or entropy change along the phase boundary cannot be determined. It is reasonable to assume that the variation of the entropy change along the phase boundary is responsible for the curvature.

## CONCLUSIONS

Laser interferometry was used to observe the $\alpha$-$\beta$ quartz transition at high pressures and high temperatures in a sample chamber of a diamond-anvil cell with a fluid medium. This transition manifested itself as a swift motion of interference fringes caused by the abrupt change in refractive indices as the transition occurred. Temperatures in our new diamond-anvil cell, calibrated with the ASTM Hg thermometer and the melting points of sodium nitrate and sodium chloride, are believed to be accurate to ±1.5 °C. Pressure along the isochore, calculated from the density and temperature, is believed to be accurate to ±1%. With this technique, we expect to be able to determine or refine the phase boundaries of other materials in which transitions manifest themselves by observable changes in optical properties. These transition boundaries, in turn, can serve as independent and accurate pressure calibrants for fluids having less well known equations of state at high pressures and high temperatures. Another potential application of our new technique is to investigate the stability field of the incommensurate phase existing over a range of 1.4 K between the $\alpha$-quartz and $\beta$-quartz stability fields (Bachheimer, 1980; Dolino et al., 1983).

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