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Differential Thermal Analysis Investigation of the High-Low Cristobalite Inversion Under Hydrostatic Pressure to 7 Kbar

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The high-low inversion in polycrystalline cristobalite, synthesized from quartz at 1500°C, was investigated by differential thermal analysis to 7 kbar in hydrostatic apparatus. A region of anomalous curvature ($d^2T/dp^2 > 0$) exists to ≈ 1 kbar; at higher pressure, the low \rightarrow high and high \rightarrow low transition temperatures vary linearly with pressure, with slopes of ≈ 51.1 and 53.6 deg kbar $^{-1}$, respectively. Extrapolated 1-bar intercepts are $\approx 232^\circ$ and $\approx 209^\circ\text{C}$, respectively. It is concluded that high cristobalite is less compressible than low cristobalite near the inversion. The hysteresis between the high \rightarrow low and low \rightarrow high transition temperatures decreases with increasing pressure.

I. Introduction

THE high-low inversion in cristobalite has been the subject of several quite careful investigations. Unfortunately, the lack of sufficiently large single crystals of cristobalite means that most current knowledge is based on experiments with polycrystalline material (also twinned in unknown degree), and the extent to which the various thermophysical properties are thus altered is essentially unknown. For this first-order transition, various data are available for the entropy of the transition and the volume change, so that the variation in transition temperature with pressure is presumably

predictable. A few high pressure data are already recorded^{1,2} for the transition temperature below 1 kbar. The present investigation was undertaken to obtain more extensive, accurate data on the variation with hydrostatic pressure of transition temperatures—both on heating and cooling, since appreciable hysteresis has been universally observed. Also, determination of the variation in hysteresis along the phase boundary should constrain the microscopic theory for this transition.

II. Experimental Procedure and Results

The cristobalite used had been synthesized from quartz heated 4 h at 1500°C in a Pt crucible in air.

In the first run, ≈ 12 mg of cristobalite was loaded into a Pt tube (OD 1.59 mm, wall thickness 0.13 mm) sealed at one end. For the second run, the cristobalite was mixed with an equal weight of fired BN, and ≈ 5 mg of this mixture was loaded into a similar capsule. Transitions were detected using DTA. In all runs, the measuring thermocouple, of Chromel and Alumel wires 0.13 mm in diameter, was lashed against the sample capsule with Chromel wire 0.13 mm in diameter; thermal contact was enhanced by use of silver conductive paint. The reference junction was always within ≤ 2 mm of the

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measuring junction. The arrangement of sample capsule, thermocouples, and hydrostatic pressure apparatus using Ar has been described previously.³⁻⁴

Temperature was varied at ≈ 0.3 to 1.2 deg s^{-1} and the maximum temperature difference between measuring and reference thermocouples was usually $< 1^\circ$. Sensitivities in recording temperature and differential temperature were 0.2 mV cm^{-1} and as much as $8 \mu\text{V cm}^{-1}$, respectively. The temperature corresponding to the peak of the differential signal was taken as the transition temperature. Walker *et al.*⁵ discussed the preferred identification of peak temperature with inversion temperatures. On heating and on cooling, respectively, the observed transition temperatures usually agreed to within 1° . Temperatures for the onset of the transition were obtained with less precision than peak temperatures.

In the first run, the onset temperatures were $\approx 2^\circ$ to 4° lower on heating and higher on cooling than the peak temperatures at the lower pressures and $\approx 1^\circ$ to 2° different at the higher pressures. In the second run, there was $\approx 4^\circ$ to 6° difference throughout. Near the end of the second run, the transitions were observed near 3.0 kbar with heating/cooling rates varying from ≈ 0.2 to 2.7 deg s^{-1} ; no dependence of transition temperature on rate was established within the experimental precision. From previous in situ calibrations^{1,6} of the same reels of thermocouple wire, accuracy in temperature is believed to be within 1° to 2° . Effects of pressure on thermocouple emf were considered small and no corrections were made.

Two or more cycles were made at each pressure and data were obtained on both increasing and decreasing pressures. Pressures were read to ± 5 bar on a 7-kbar pressure gage* and to $\pm 1/2$ bar on a similar gage of 1-kbar range. In the first run, the 7-kbar gage was used exclusively; in the second run, the 1-kbar gage was also used, simultaneously, in its range. The 1-kbar gage has recently been calibrated to within 1 bar.

Data for the transition temperatures obtained in both runs, on heating and on cooling and on increasing and decreasing pressure, are shown in Fig. 1. Beyond the initial 0.8 to 1.0 kbar, the low \rightarrow high transition data fall on a line of slope $\approx 51.1 \text{ deg kbar}^{-1}$, with 1-bar intercept $\approx 232^\circ\text{C}$. Beyond the initial ≈ 1.5 kbar, the high \rightarrow low transition data fall on a line of slope $\approx 53.6 \text{ deg kbar}^{-1}$, with 1-bar intercept $\approx 209^\circ\text{C}$. Below these indicated limits to the initial pressure ranges, both trajectories show anomalous curvature ($d^2T/dp^2 > 0$) with 1-bar intercepts $\approx 249^\circ\text{C}$ on heating and $\approx 225^\circ\text{C}$ on cooling. Agreement of the results of the two runs (Fig. 1) is within $\pm 1^\circ$.

Some of the original material was heated ≈ 24 h at $\approx 1500^\circ\text{C}$ in a covered Pt crucible in air. This annealed material, on examination in a differential scanning calorimeter, showed the same transition temperatures on heating and on cooling as did the original material and hence was not run at high pressures.

III. Discussion

Two previous studies of the high-low cristobalite inversion at high pressures have been found. Majumdar *et al.*¹ cite slopes of $5.0 \times 10^{-2} \text{ deg bar}^{-1}$ for two types of cristobalite, one with a 1-bar transition temperature of 268°C (text of Ref. 1) or 267°C (Table I of Ref. 1) and the other with a 1-bar transition temperature of 242°C (text of Ref. 1) or 225°C (Table I in Ref. 1). Majumdar, in his thesis (Fig. 7 and Table II in Ref. 7), gives data for the inversion in "cristobalite (ordered)" on heating as: $p(\pm 2 \text{ atm})$, $T(\pm 1^\circ\text{C}) = 1, 267^\circ; 340, 285^\circ; 580, 302^\circ; 1000, 317^\circ$. These data correspond to the "maximum rate of heat absorption" (pp. 21, 22 of Ref. 7), a quantity whose temperature lies between the onset and the peak of the differential signal. In Fig. 7 of Ref. 7, a linear trajectory for "cristobalite (disordered)" is drawn from $\approx 234^\circ\text{C}$ at zero pressure to $\approx 283^\circ\text{C}$ at 1 kbar; this trajectory is attributed to Roy and Hulbe, a reference which the present writers were unable to find. A linear regression fit of Majumdar's tabulated data⁷ yields a slope of $51.6 \text{ deg kbar}^{-1}$.

The DTA investigation of Berger *et al.*² to ≈ 0.45 kbar was more extensive. They found a region of anomalous curvature below ≈ 0.1 kbar, whereas, at higher pressures, both the high \rightarrow low and

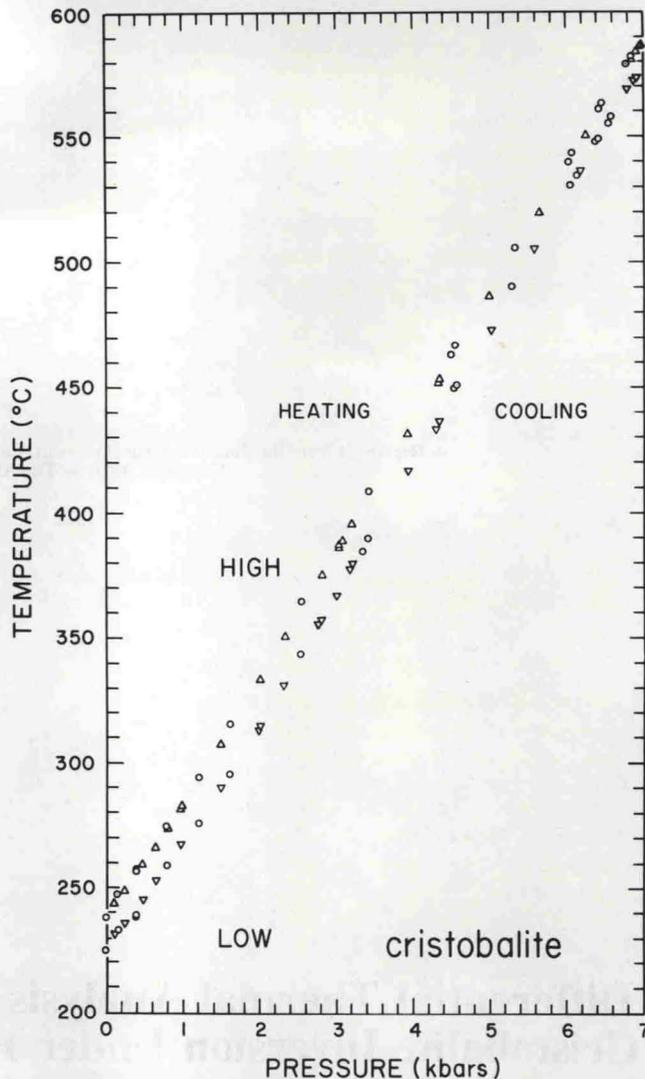


Fig. 1. Temperatures for low \rightarrow high cristobalite inversion (upper set of points, obtained on heating) and high \rightarrow low cristobalite inversion (lower set of points, obtained on cooling); data from first run (circles) and second run (triangles) were obtained on both increasing and decreasing pressures.

low \rightarrow high inversion trajectories had approximately constant slope of $\approx 50 \text{ deg kbar}^{-1}$; although the data scatter, approximately constant hysteresis is indicated.

Various values have been obtained for the discontinuities in volume and in entropy for the transition. Because sufficiently large single crystals are not available for dilatometric measurements, X-ray diffraction data seem preferable for estimating the variation of volume with temperature. Extensive X-ray diffraction investigations have been made by Johnson and Andrews,⁸ using a powder camera and samples showing the inversion near $\approx 218^\circ\text{C}$, and by Berger *et al.*⁹ using a diffractometer and samples inverting at $\approx 265^\circ$ to 270°C . Within their respective estimated accuracies, the volume of low cristobalite varies linearly with temperature up to the inversion temperature; for high cristobalite, similar results are obtained for at least some hundred degrees above the inversion. It is agreed^{8,9} that the thermal expansion coefficient is much greater below the inversion than above, but results from Ref. 9 are consistently lower than those from Ref. 8 for thermal expansion coefficients and for volumes at the same temperature. Majumdar's data⁷ tabulated for the "ordered" sample (there is a misprint for the lattice parameters given for 230°C) are consistent with data from Ref. 8 for low cristobalite (as extrapolated to higher temperatures, since there are differences between the inversion temperatures) but are higher both for volume and thermal expansion coefficient than the data from Refs. 8 and 9 for high cristobalite. Majumdar *et al.*¹ quote a volume discontinuity of $1.03 \text{ cm}^3 \text{ mol}^{-1}$ both for the

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“ordered” and “partly ordered” samples. Peacor's X-ray diffraction data¹⁰ on single-crystal cristobalite, indicating a volume discontinuity of $\approx 1.3 \text{ cm}^3 \text{ mol}^{-1}$ at 220°C , also do not agree well with the other data.^{1,8,9} The sources of these discrepancies are not known but presumably can be attributed to differences among samples.

At a given pressure, the volume increase for the low \rightarrow high transition is numerically less than the volume decrease for the high \rightarrow low transition. This result is derived from combining the data^{8,9} showing greater thermal expansion for low cristobalite than for high cristobalite with the experimental observation that the low \rightarrow high transition occurred at higher temperature than the high \rightarrow low.

Krisement *et al.*¹¹ obtained, by microcalorimetry, the most extensive data for heats of transition. For samples exhibiting transition temperatures of 244° to 270°C (low \rightarrow high) and 215° to 235°C (high \rightarrow low), Krisement *et al.*¹¹ found the heats of transition greater for the high \rightarrow low transition than for the low \rightarrow high. There appears to be no systematic variation of heat of transition with transition temperature but the heat (high \rightarrow low) $\leq 0.30 \text{ kcal mol}^{-1}$ and the heat (low \rightarrow high) $\geq 0.25 \text{ kcal mol}^{-1}$. Krisement *et al.*¹¹ suggest that the specific heat of high cristobalite is greater than that of low cristobalite over the temperature range of transformation.

The Clausius-Clapeyron equation,

$$dT/dp = \Delta V/\Delta S \quad (1)$$

correlates the several independently determined quantities. For the low \rightarrow high transition, dT/dp (Fig. 1) $\approx 51.1 \text{ deg kbar}^{-1}$, with an extrapolated 1-bar intercept of $\approx 232^\circ\text{C}$; for the 1-bar volume decrease at that temperature, Ref. 8 data yield $\Delta V \approx 0.95 \text{ cm}^3 \text{ mol}^{-1}$ and Ref. 9 $\approx 1.09 \text{ cm}^3 \text{ mol}^{-1}$ (with uncertainties $\approx \pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$). Peacor's data¹⁰ indicate a volume discontinuity of $\approx 1.3 \text{ cm}^3 \text{ mol}^{-1}$ at 220°C . From Eq. (1), $\Delta S \approx 0.44 \text{ cal deg}^{-1} \text{ mol}^{-1}$ (from Ref. 8 data) or 0.51 (from Ref. 9 data). Data from Ref. 11 suggest $\Delta S \leq 0.55$ to $0.58 \text{ cal deg}^{-1} \text{ mol}^{-1}$. For the high \rightarrow low transition, dT/dp (Fig. 1) $\approx 53.6 \text{ deg kbar}^{-1}$, with an extrapolated 1-bar intercept of $\approx 209^\circ\text{C}$; for the 1-bar volume increase at that temperature, Ref. 8 data suggest $\approx 0.99 \text{ cm}^3 \text{ mol}^{-1}$ and Ref. 9, ≈ 1.13 (both $\approx \pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$). From Eq. (1), $\Delta S \approx 0.44 \text{ cal deg}^{-1} \text{ mol}^{-1}$ (Ref. 8) or 0.50 (from Ref. 9). Ref. 11 data suggest $\Delta S \geq 0.49$ to $0.51 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The consistency of these data is fairly good, with those of Ref. 11 and Ref. 9 resulting in the greatest consonancy. The conclusion most clearly demonstrated here is that the somewhat steeper initial slope of the high \rightarrow low transition (as compared to the low \rightarrow high) can be quantitatively correlated with the greatly different thermal expansion coefficients of low and high cristobalite and the appreciable hysteresis in the transition.

It is expected that, at pressures higher than obtained here, the trajectories of the low \rightarrow high and high \rightarrow low transitions will be essentially parallel, i.e. with constant hysteresis. Within the precision of the present data (Fig. 1), no curvature is apparent in either phase boundary beyond the low-pressure region, and there is no prediction as to where the trajectories become essentially parallel. Linear extrapolations of the present data suggest an intersection at $\approx 9 \text{ kbar}$, which is impossible but perhaps indicative of the rapidity with which the trajectories are converging with increasing pressure. It is clearly seen (Fig. 1) that the hysteresis in the inversion, whatever its origin, varies with pressure and cannot be considered as constant.

Ignoring the small differences in various quantities for the inversion on heating and on cooling, the equation

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta S} \left[\left(\frac{\partial \Delta V}{\partial p} \right)_T + 2 \left(\frac{dT}{dp} \right) \left(\frac{\partial \Delta V}{\partial T} \right)_p - \left(\frac{dT}{dp} \right)^2 \left(\frac{\partial \Delta S}{\partial T} \right)_p \right] \quad (2)$$

may be examined under two assumptions for d^2T/dp^2 . For $(\partial \Delta V/\partial T)_p \approx -1.6 \times 10^{-3} \text{ cm}^3 \text{ deg}^{-1} \text{ mol}^{-1}$ ^{8,9} and $(\partial \Delta S/\partial T)_p \approx (50 \text{ cal mol}^{-1}) (30 \text{ deg})^{-1} (500 \text{ deg})^{-1}$ (from Ref. 11 results) and $d^2T/dp^2 \approx 0$, $(\partial \Delta V/\partial p)_T \approx 0.55 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$. If $|d^2T/dp^2| \leq 0.1 \text{ deg kbar}^{-2}$ (as a possible upper limit obtained from the

present experiments), the above value for $(\partial \Delta V/\partial p)_T$ is scarcely altered. Therefore, it is concluded that $(\partial \Delta V/\partial p)_T > 0$, and this is not usual since, for most transitions, the high-temperature phase is more compressible than the low-temperature phase.

The initial fractional rate of change of transition entropy with pressure may be calculated since

$$\frac{d\Delta S}{dp} = \left(\frac{\partial \Delta S}{\partial p} \right)_T + \frac{dT}{dp} \left(\frac{\partial \Delta S}{\partial T} \right)_p \quad (3)$$

and $(\partial \Delta S/\partial p)_T = -(\partial \Delta V/\partial T)_p$. Rearrangement of Eq. (3) and use of values given above suggest that $(1/\Delta S)(d\Delta S/dp) \approx +0.08 \text{ kbar}^{-1}$. For the slope to remain nearly constant, as observed, the volume change for the transition must increase accordingly and the greater compressibility of low cristobalite, compared to high cristobalite, contributes to this effect.

The anomalous curvature found at the lowest pressures (Fig. 1) is not understood but is possibly related to the polycrystallinity. Bogardus and Roy¹² reported that grinding increases the high-low inversion temperatures somewhat in both cristobalite and quartz, both showing increases in transition temperature with hydrostatic pressure; on the other hand, they¹² also showed that grinding lowers the transition temperature in BaTiO_3 , for which dT/dp is also positive. The role of residual stresses, probably of importance in these refractory materials, is yet to be clarified for these transitions.

From the decrease in transition temperature in cristobalite and quartz under neutron bombardment, Roy and Buhsmer¹³ suggested the effect of the neutrons was akin to that of negative hydrostatic pressure. The more extensive investigation by Schenk¹⁴ on the effects of neutron irradiation on the high-low cristobalite inversion does not corroborate the Roy and Buhsmer data,¹³ which nevertheless may be looked at anew. Plotting high-low quartz inversion temperatures vs high-low cristobalite inversion temperatures for the same neutron dose gives an approximately straight line; thus these data¹³ suggest that a given dose of neutrons lowers the cristobalite inversion temperature $\approx 9 \pm 2$ times as much as the quartz inversion temperature. By comparison, application of hydrostatic pressure raises the cristobalite inversion temperature nearly twice as much as the quartz inversion temperature.⁴ Thus the correlation between hydrostatic pressures and neutron bombardment, if any, is difficult to quantify. The absence of any compressibility data for cristobalite continues to hamper such theory.

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