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Direct observations of a double phase transition during the low to high transformation in quartz single crystals to 700 °C and 0.6 GPa

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Abstract

Isobaric thermal analysis (TA), differential thermal analysis (DTA), and isothermal pressure analysis (PA) were used in an investigation of the low (α) to high (β) transition in quartz. Peaks for a double phase transition (at 573 and 574.5 °C at 1 atmosphere) were observed, and the presence of an intermediate phase over this 1.5 degree interval is indicated. The findings are consistent with recent observations on the incommensurate structure of the intermediate phase, 3q, between low (α) and high (β) quartz.

Keywords: low (α) quartz, high (β) quartz, incommensurate, phase transition, DTA.

1. Introduction

There have been many direct observations of the low (α) to high (β) transition in quartz made by a variety of methods (see Fig. 1; Table 1) at elevated temperatures at one bar and higher pressures. Recent work by Shen et al., (1993) has determined the location of the α–β quartz transition temperature by laser interferometry in a diamond anvil cell and obtained the relation:

$$Tc = 574.3 + 25.9P - 6.406 \times 10^{-5} P^2$$
(with dT/dP = approx. 25.6 °C/kbar)

There have been several experimental observations for the occurrence of at least one intermediate phase between low- and high-quartz. Bachheimer (1980) found a first-order transition from α-quartz to an intermediate form at 574 °C (Tc), and a second-order transition to β-quartz at 574.3 °C (Ti). These observations have been verified by Differential Scanning Calorimetry (Zeyen et al., 1983; Drebushchak and Dement'ev, 1993) by AC-Calorimetry (Hatta et al., 1985), and by Differential Thermal Analysis (Raz, 1983; see review by Heaney, 1994, p. 17).

The apparatus described by Raz et al. (2002) allows both pressure and temperature scans to be made in the P–T range 0.6 GPa at 500 °C and 0.05 GPa at 900 °C; i.e. compressibility with increasing temperature and thermal expansion with increasing pressure may be measured directly. The scan range for pressure and temperature may be chosen in either direction (up or down P and T). This feature proved to be extremely helpful for the volumetric and kinetic study of selected phase transitions. Here we present some results across the α–β transition in quartz which will serve to illustrate the capabilities of the technique. We show that two phase transitions are observed for two natural quartz samples (vein quartz, smoky quartz) but not for a synthetic single quartz sample.

2. Measurement procedures for PA, TA and DTA

Pressure analysis (PA) was conducted on the same apparatus as described for measurements of length changes on quartz single crystals by Raz et al. (2002). The individual parts of the assembly were optimized in their dimension so as to minimize the resulting dead volume to increase the sensitivity for pressure analysis. In theory the sensitivity of pressure analysis may be increased towards infinity by approaching a zero dead volume.

Thermal analysis (TA) was carried out both isobarically and polybarically with a single thermocouple technique. This is different to differential thermal analysis (DTA) which uses two individual thermocouples, one each for the reference

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Table 1 Reported α to β transition temperatures in quartz at 1 bar. Note the difference between the natural smoky quartz and the synthetic quartz of approximately 1.5 K.

Author	$T_{heating}$ [K]	$T_{cooling}$ [K]	Method
Sinelnikov (1953)	847.1		Adiab. Calorimetry
Moser (1936)	847 +/–1		Adiab. Calorimetry
Keith and Tuttle (1952)	846.1 +/–0.5		DTA
Klement and Cohen (1968)	847		DTA (P)
Ghiorso et al. (1979)	848.3 +/–0.1		DSC
Coe and Paterson (1969)	846.7 +/–1		Strain (P)
Mayer (1960)	847.1		Strain
Banda et al. (1975)	846.5	844	Strain
Bachheimer and Dolino (1974)	846.3	844.8	SHG
Shapiro and Cummins (1968)	846.5	845.5	Raman
Shapiro and Cummins (1968)	847.4	846.1	IR
This study (synthetic Qz)		844.9 +/–0.6	TA/DTA (P)
This study (smoky Qz)		846.3 +/–0.3	TA/DTA (P)

DTA = Differential Thermal Analysis
DSC = Differential Scanning Calorimetry
SHG = Second Harmonic Generation (of Light)
TA = Thermal Analysis
IR = Infrared Spectroscopy
(P) = also at pressures above ambient

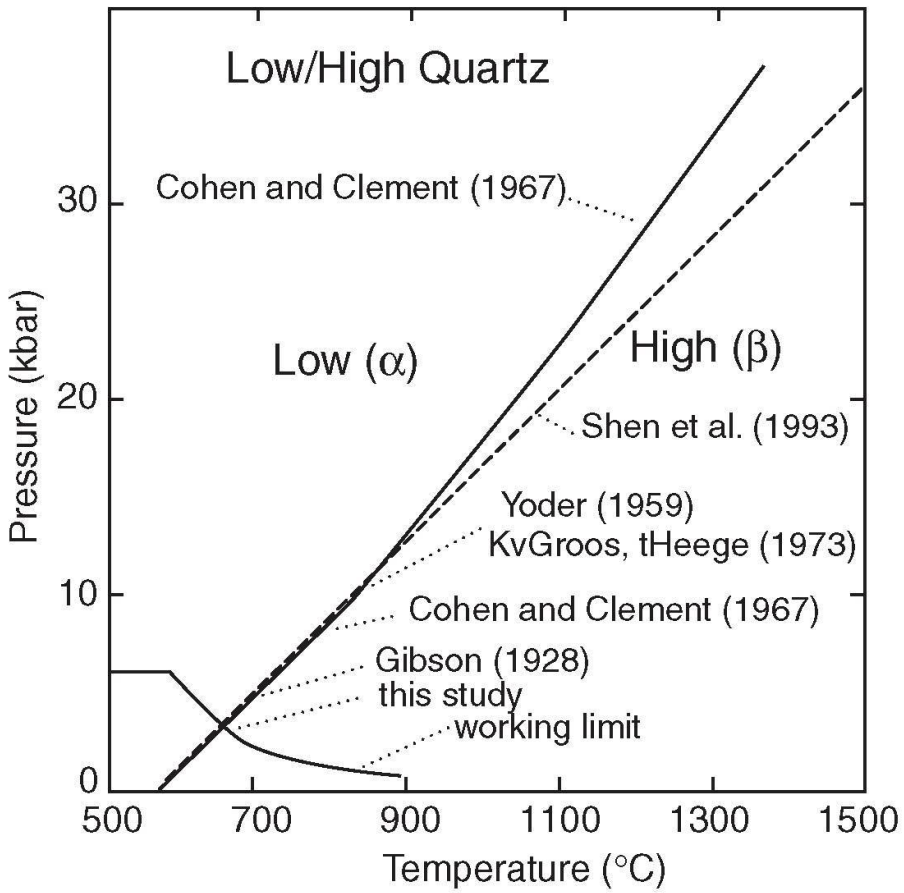

Fig. 1 Some experimentally determined phase boundaries of low- and high-quartz (Gibson, 1928; Yoder, 1950; Cohen and Klement, 1967; Van Groos and Ter Heege, 1973; see recent summary by Hemley et al., 1994). The working limit of our apparatus (Raz, 1983) is shown up to 0.6 GPa at 500 °C and 0.05 GPa at 900 °C. Shen et al. (1993) obtained the relationship $Tc = 574.3 + 25.9P - 6.406 \times 10^{-5} P^2$ (with dT/dP = approx. 25.6 °C/kbar) for the α–β quartz transition.

and the sample. TA offers a simplified experimental set-up; however it requires high speed and high resolution measurement of low EMF voltages (20 readings/sec, 0.1 μV, 40 mV full scale, resulting in roughly 20 bit resolution). Baselines were determined by numerical fitting.

Control of the experiments (temperature ramps and cycles, stepwise pressure bleed off) and

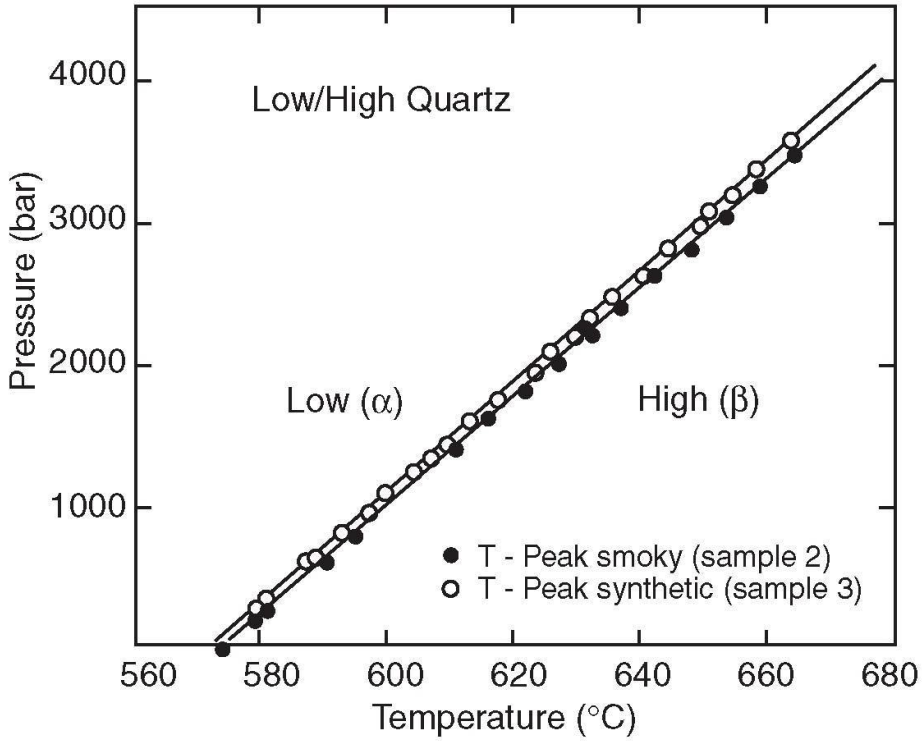

Fig. 2 The location of the peak temperatures for the synthetic and smoky quartz single crystal samples (3 and 2) determined in cooling runs with the TA apparatus to 3.5 GPa and 660 °C.

all data acquisition was accomplished with a DEC PDP-11 computer running the RT-11 operating system (Foreground-Background monitor). Voltages from thermocouples, LVDT amplifiers and pressure transducers were scanned with a low thermal-offset reed-relay scanner (HP 3495A) and routed to a digital voltmeter (HP 3456A). For instrument control, the HP-IB/IEEE-488 bus was used. Bias voltages driving temperature ramps were generated by a programmable digital to analog power supply (HP 59501A) and suitably arranged voltage-dividing resistors. Additional details on the apparatus may be found at our website: www.hydrothermal.ethz.ch.

3. Results of TA, PA and PVT measurements on quartz single crystals

Detailed PVT data obtained by high pressure dilatometry with this apparatus for quartz single crystals are reported by Raz et al. (2002). Three samples of quartz were used for the investigation of the thermal and volumetric properties and the low–high transition at pressures up to 0.35 GPa:

- sample (1) clear, colorless vein quartz (used for the development of the method)
- sample (2) smoky vein quartz cut parallel to the a-axis
- sample (3) synthetic quartz cut parallel to the c-axis

3.1. Observations during TA scans across the α–β quartz transition

At ambient pressure (Fig. 2) the transition temperature for the synthetic sample (3) was measured at 845 K, 2° lower than for the smoky sample (2). This difference increased consistently by approximately 1° up to 3500 bar (Fig. 2). In Thermal Analysis scans the peak height and area increased with the number of cycles over the transition. Peak width, however, appears to be insensitive to the sample's history. Thermal Analysis peaks for synthetic quartz (3) are symmetric whereas the natural vein-quartz sample (1) displays a split peak, i.e. latent heat is released in two distinct pulses (Fig. 3) – an effect observed already by Cohen and Klement (1974) and Keith and Tuttle (1952). This effect was confirmed by strain analysis in the high pressure dilatometer only for the high to low quartz reaction whereas the low to high reaction was always continuous in a very narrow temperature and pressure interval. Thermal-Analysis-Peak splitting is attributed to a short lived stable intermediate phase as determined by neutron scattering by Bachheimer (1980) and Dolino et al. (1984a,b).

3.2. Observations during isothermal PA

The low–high quartz transition was also investigated with a further set-up of the dilatometer allowing isothermal pressure scans. An empty

bomb was connected to the dilatometer's pressure vessel, pressurized and then cooled or heated independently. This arrangement allowed very slow pressure scans of approx. 1 bar/min. These experiments revealed an onset-of-reaction reaction hysteresis of approximately 50 bar for single crystals of vein quartz/sample 1 (Fig. 4). The reaction from low to high quartz commenced always at a well defined pressure and temperature and could never be stopped at an intermediate stage by reversing the scanning direction. However, the reverse reaction, going from high to low quartz, was slow. It had no well defined onset and was spread out over an interval of 10 to 20 bar. It could be stopped at any point of this interval and held in a stationary state (the stability field of the incommensurate phase?) for more than 15 minutes. All described phenomena could be observed equally at different scanning rates. This coexistence of low and high quartz has been observed by several other authors, for example, Arnold (1976), van Tendeloo et al. (1976), Shapiro and Cummins (1968).

In our experiments, hysteresis does not appear to be an artefact resulting from the specific design of our apparatus. Two types of hysteresis are discussed in the literature. The first "onset-of-reaction" or "sample" hysteresis is due to true kinetic reaction overstepping related to nucleation and growth of the new phase; the second type "device" or "container" hysteresis is related to the delay of attainment of P–T conditions in the "container" apparatus. We conclude from the observed rapid response times and very small gradients in temperature (1.5 °C/2.5 cm) within our apparatus (Fig. 4), that "container" hysteresis was minimal.

3.3. Observations during DTA scans across the α–β quartz transition

The differential thermal analysis (DTA) signals change their size with the number of cycles over the transition: Peak area and peak height increase whereas peak width remains unchanged.

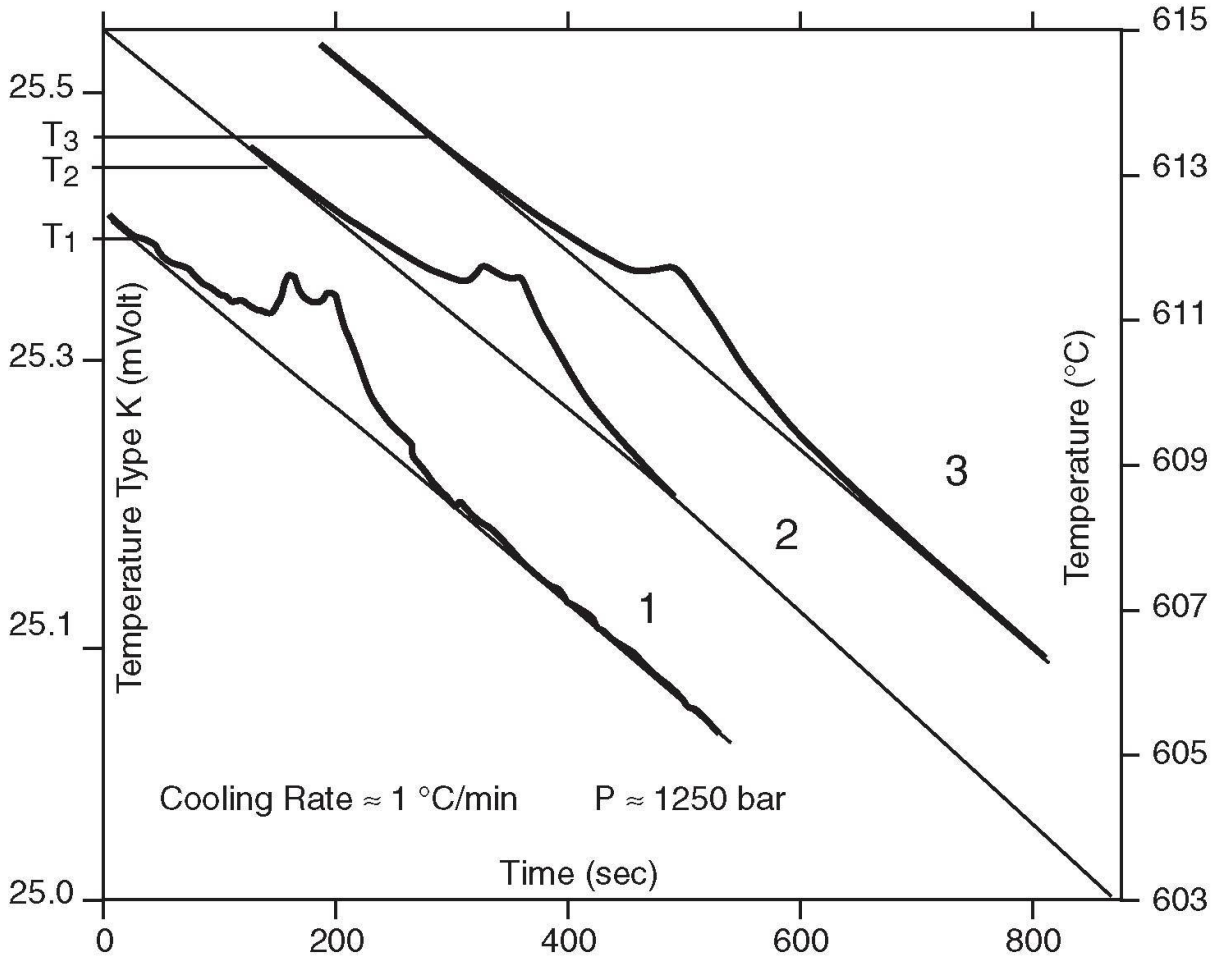

Fig. 3 Cooling TA curves at 1 °C/min at 0.125 GPa , for single crystals of (1) clear, colorless vein quartz, (2) clear, smoky quartz, (3) clear, synthetic quartz. T1, T2 and T3 mark transition onset temperatures.
Note the TA-peak splitting in the natural sample (as a possible consequence of impurities?).
The strikingly smooth curve (no double peak) for synthetic quartz is possibly a consequence of it's crystal water content. It remained unchanged even after more than ten transitions.

The increasing peak size indicates that the transition progresses faster after a number of cycles. Annealing of structural defects, exsolution of water and other impurities, twinning of left and right handed crystals or the incorporation of the argon pressure medium into the structure may be possible causes.

4. Interpretations of observations

Among all phenomena observed during our measurements the hysteresis of the onset-of-reaction (observed in both, up and down P–T scans in Pressure Analysis and Thermal Analysis) remains most striking and is consistent with previous stud-

Table 2 Reported volume differences of the low–high quartz transition. The ΔH, obtained from calorimetric measurements or DSC (Differential Scanning Calorimetry), were converted to ΔV by the first order Clausius-Clapeyron equation dP/dT = ΔH/TΔV. These values are systematically higher than the measured ΔV obtained by dilatometry, PA or x-ray studies.

Author	ΔV [cm³/mol]	Method
Sosman (1927)	0.195	ΔH, calorimetry
Kelley (1960)	0.372	ΔH, calorimetry
Mayer (1960)	0.118	strain
Majumdar et al. (1964)	0.11	x-ray
Skinner (1966)	0.12	strain
Berger et al. (1966)	0.154	x-ray
Bystrikov (1966)	0.008	x-ray (?)
Stull and Prophet (1971)	0.223	ΔH, calorimetry
Ackermann and Sorrell (1974)	0.09	x-ray
Ghiorso et al. (1979)	0.205	ΔH, DSC
Mogéon (1988)	0.121	strain
This study	0.11 ± 0.01	dilatometry

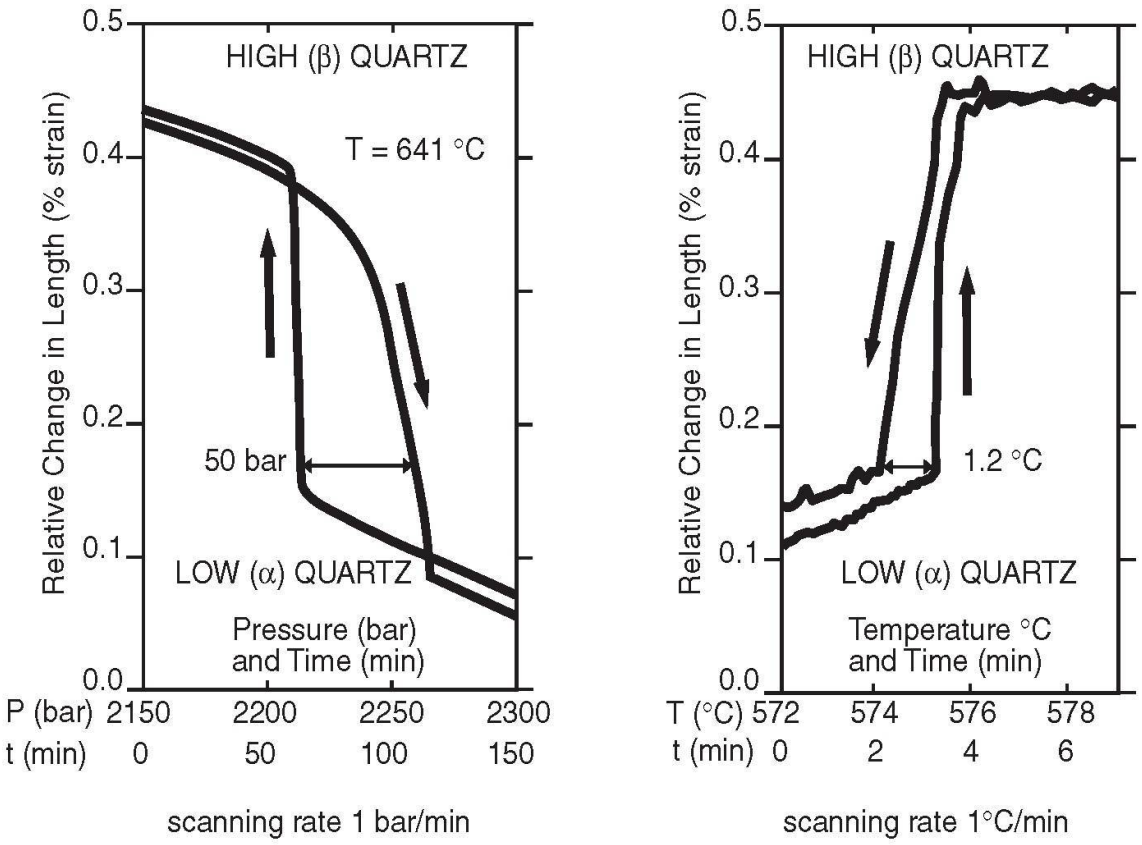

Fig. 4 Reaction hysteresis in terms of percentage strain of the low–high quartz transition in single crystals of vein quartz (sample 1).
Left graph showing a pressure scan (at one bar per minute) at constant temperature (641 °C).
Right graph showing a temperature scan (at 1 °C per minute) at constant pressure (1 bar).

ies. It is noteworthy that the onset-of-reaction hysteresis effect remained unchanged after cycling over dozens of times through the transition without any smoothing or merging for several different natural quartz samples. Further studies will have to investigate whether there are differences in the effect under isochoric, isothermal and isobaric conditions.

There are considerable differences in the volumetric properties reported by the various authors for the low (α) to high (β) transition in quartz (see Table 2).

Interestingly, ΔV values determined by direct measurement (x-ray, Pressure Analysis, dilatometry) are all systematically smaller than those derived from calorimetric ΔH values converted to ΔV by means of the Clausius-Clapeyron equation ($dP/dT = \Delta H/(T \cdot \Delta V)$). The differences range up to 100% and more. Resolving the equation for ΔV places ΔH in the denominator which in turn results in higher ΔV's for smaller ΔH's. This leads to the conclusion that the earlier calorimetric measurements of enthalpies systematically resulted in too small values for ΔH, partly due to poorly controlled radiation heat loss from the earlier calorimeters, and partly due to the difficulty of resolving the double phase transition. Dolino and Bachheimer (1984) using a Differential Scanning Calorimeter deduced a transition enthalpy of 4.2 J/g during cooling where the incommensurate

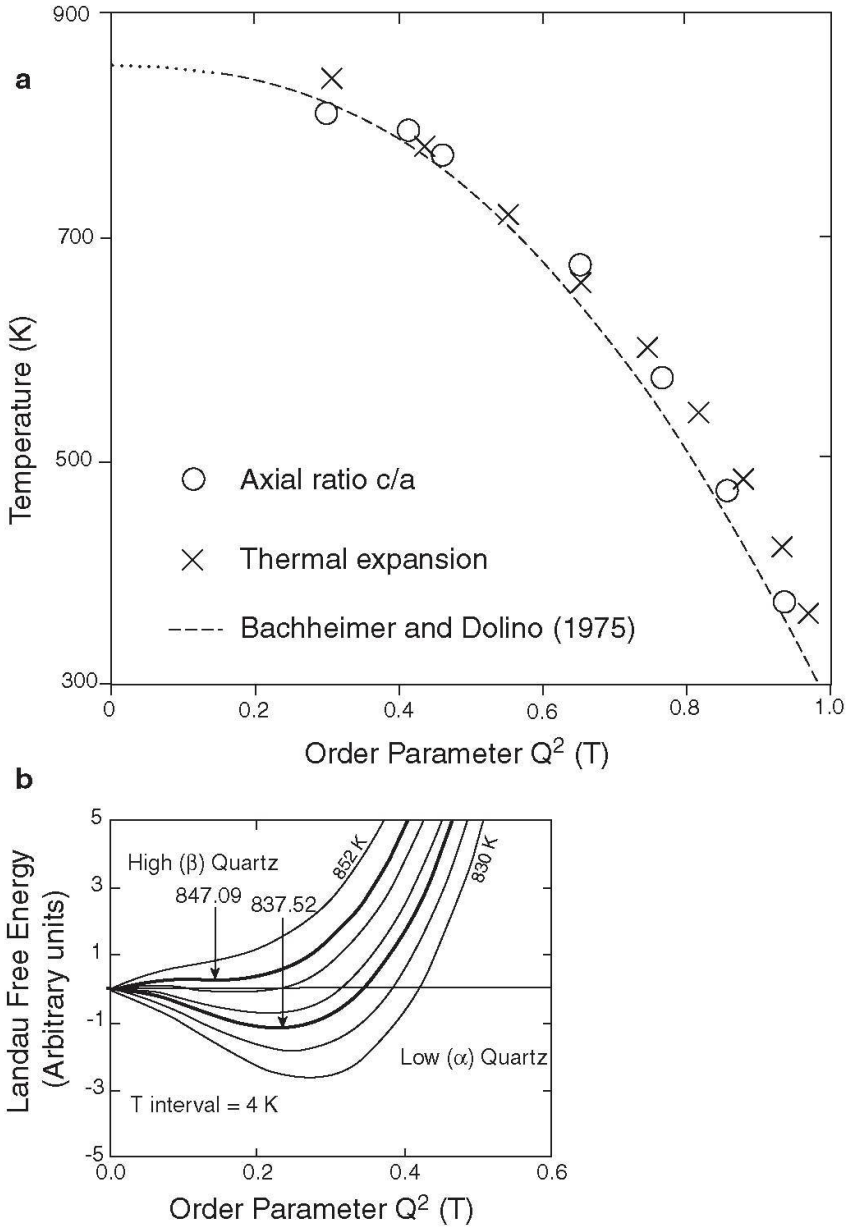

Fig. 5 The order parameter squared (Q^2) as a function of Kelvin temperature (a) and Landau Free Energy (b). Our results for thermal expansion and the axial ratio c/a (Raz et al., 2002) are compared with the optical measurements of Bachheimer and Dolino (1975). The parabola $e_1(T) = A' - A(1-T/To)^{1/2}$ with A = 0.01646 fits the data for thermal expansion and the square of the Landau order parameter (Dolino and Bachheimer, 1984, Fig. 4)

phase did not nucleate, and during heating an enthalpy of 5.5 J/g at Th = Tc + 1.4 K.

5. Distortions in the structure of quartz and their relation to phase transitions

The macroscopic behavior observed here in single quartz crystals (Figs. 3 and 4) has some explanations at the microscopic scale from various structural studies.

The low-quartz structure (with a space group of P3121 for left-handed and P3221 for right-handed twins) consists of two sets of chains of SiO_4 tetrahedra forming spirals parallel to the c-axis (see Liebau and Bohm, 1982; Heaney et al., 1994, p. 9; Hemley et al., 1994, p. 43; Ross, 2000, p. 259) and can be viewed as a distortion of the structure of high quartz. Three simultaneous mechanisms permit the quartz structure to decrease in volume with increasing pressure, (i) distortion of tetrahedra in response to changes in bond angle, (ii) decrease in bond length, but mainly (iii) rotation of linked tetrahedra (Jorgensen, 1978). Changes in the Si–O–Si angle and the tetrahedral tilt-angle control the thermal expansion, whereas smaller changes in the Si–O–Si angle and the tetrahedral distortion control isothermal compression (D'Amour et al., 1979; Levien et al., 1980). Sowa (1988) explains the high pressure behavior of quartz structures through the changes of anion-anion distances through packing of both the polyhedra and the anions. The transition from the α- to β-phase corresponds to the addition of a 2-fold symmetry axis parallel to c (from space group P3221 (α) to P6222 (β), and their enantiomorphs, Phillips, 2000, p. 219) that also relates the Dauphiné twin orientations of the α-phase.

5.1. Intermediate phases at the α–β quartz transition

Recent work on the α–β transition in quartz has detailed the stability of incommensurate phase(s) stable between 573 and 574.3 °C and encountered during the α–β quartz transition (summarized by Heaney, 1994, p. 2, 16; Heaney, 2000, p. 148). Anomalous behavior near the critical temperature had been detected in the 1930's by light scattering experiments (Steinwehr, 1932; Yakovlev et al., 1956) and later by Raman spectroscopy (Raman and Nedungadi, 1940; who observed the first "soft mode", and Shapiro and Cummins, 1968; see summary by Heaney, 1994, p. 16).

The source of the unusual behavior was suggested by Young (1962), on the basis of high temperature X-ray diffraction experiments, as being due to the replacement of Dauphiné twin domains by fine-scale microtwins during the α to β transformation. Subsequent transmission electron microscope studies by Van Tendeloo et al. (1976) and Malov and Sonyushkin (1976) showed, that large Dauphiné twins dispersed into a mosaic of triangular microtwin prisms elongated parallel to the c-axis. The work by Bachheimer (1980), who monitored thermal expansion, elastic compliance and birefringence simultaneously through the α to β transition, suggested at least one intermediate structure, with a first-order transition from α-quartz at 573 °C (=Tc) and a second-order transition to β-quartz at 574.3 °C (=Ti or Th). Hysteresis effects of the onset-of-transition were reported from Raman experiments (Shapiro and Cummins, 1968) and also from γ-ray and neutron diffraction studies (Bastie and Dolino, 1985; Dolino et al., 1984a,b).

The first-order nature of the α to β transformation was explained by a Landau expansion with an order parameter corresponding to the tetrahedral tilt angle Θ (Hoechli and Scott, 1971; Grimm and Dorner, 1975; Banda et al., 1975; Bachheimer and Dolino, 1975, Heaney, 1994 p. 16). The Landau expansion can also be related to measureable macroscopic parameters from our study (such as axial ratio c/a and thermal expansion, Fig. 5a). Aslanian et al. (1979, 1983, 1984) coupled Landau free energy with a term that related the order parameter to spontaneous strain enabling them to explain the observed microtwins thermodynamically (see Carpenter, 2000, p. 42). These works predict the existence of two stable incommensurate phases between the stability fields of α- and β-quartz (called 3q- and 1q-phases for periodicity in three or one dimension, by Aslanian et al., 1979, 1983, 1984), and α_I by Dolino et al. (1983, 1984) who considered the transition from β to α_I to be second order, and the transition from α_I to α to be first order. This region can be viewed in Fig. 5b where the Landau free energy is shown as a function of the order parameter near to the α to β transition temperature. Incommensurate structures are modulated with a well defined periodicity but which is not a multiple of the translational periodicity of the underlying lattice (see Putnis, 1992, p. 412). The triangular microdomains (honeycomb structure of Van Tendeloo et al., 1976) have been identified with the 3q-phase (Zeyen et al., 1983; Dolino et al., 1984a,b).

Satellite reflections associated with the 3q incommensurate phase were imaged by X-ray transmission topographies (see Heaney and Veblen, 1991). Bastie et al. (1988) noted that although the transition from 3q to 1q may be induced by non-hydrostatic stress, it can also occur at zero

stress, where the 1q phase is only stable over a few hundredths of a degree (see summary by Cohen, 1994, p. 397; Dolino and Vallade, 1994, p. 406). Despite evidence for a 3q- to 1q-transition at zero stress from neutron diffraction experiments (Dolino et al., 1987), Bastie et al. (1988) found no evidence for macrodomains in the 1q-phase (which they concluded is only stable over a few hundredths of a degree). Cohen (1994, p. 397) notes that the molecular dynamic simulation results of Tsuneyuki et al. (1990) suggest that these structures are governed by fluctuations on a time scale of 4 to 12 picoseconds (Cohen, 1994, p. 398). The observed coexistence of the 3q- and 1q-phases supports the possibility that the α to β transition is entirely first order (Heaney, 1994, p. 18).

Our own studies, as well as the experiments summarized above, clearly demonstrate that any further investigation of the intermediate phases will require control of temperatures and gradients down to the sub-Kelvin range. For this, thermocouple sensors used so far would need to be replaced by Platinum resistance thermometers (resistance temperature detectors, RTD's). However, Pt-RTD's are limited to temperatures below 500 °C, because above 500 °C re-crystallization of Pt rapidly decreases RTD accuracy and thus makes Pt-sensors totally unsuitable for temperatures higher than 600 °C. In any case control of temperature to about 1 degree Kelvin is possible in the hydrothermal apparatus used by us, which is much higher than in current diamond-anvil cell devices (at best about 5 degrees Kelvin, see Raz et al., 2002, p. 571). The stability interval of the 3q incommensurate phase is not more than 1.5 Kelvin, and in the best case T gradients in our apparatus are about 1 Kelvin over the entire sample (2.5 cm). Further modifications of our apparatus could be made with great effort to reinforce the above observations for the transition to the 3q incommensurate phase, but not for the supposed 1q incommensurate phase.

5.2. Possible mechanisms for the α–3q–β quartz transitions

Dolino and Vallade (1994, pp. 404–415) present evidence which shows that the α to β quartz transition is a displacive first-order transition (but very close to being tricritical, see Allen and Cahn, 1976; Carpenter et. al., 1998). But because of the large damping of the β-phase soft mode close to the transition it is difficult to distinguish the displacive from order-disorder behavior (Dolino and Vallade, 1994, p. 415, Dove et al., 2000, p. 22). Heaney (1994, p. 19, following Aslanian et al., 1983) notes that the α to β quartz transition is driven by a dynamical soft mode which couples briefly with a transverse acoustic mode to generate the incommensurate phase. Berge et al., (1985) and Vallade et al., (1992) identified a Rigid Unit Mode (RUM) in β-quartz at $k = 0$ which acts as the soft mode in the α to β transition in quartz. These workers also identified a branch of the RUM responsible for the incommensurate phase transition between α- and β-quartz.

The thermal behavior of both low pressure polymorphs of SiO_2, quartz and cristobalite, is similar. Each has two structural configurations, (α) observed at low temperatures, and (β) observed at higher temperatures (Parker et al., 2001). The first order displacive nature of the α to β transition in quartz and cristobalite, and the disorder of the β-phase at high temperature, has been deduced from the radial distribution function (RDF, Dove et al., 1997; Parker et al., 2001, p. 69). The RDF's for Si–O and O–O distances show that the α–β transition affects the arrangement of second order neighbors. The first peak observed in the α–β transition in cristobalite is associated with the rotation of rigid SiO_4 tetrahedra without any external distortion (Dove et al., 1997). At high temperature the decrease in the cell volume corresponds to the decrease in first Si–Si distance. The α–β transition in quartz and cristobalite is thus accompanied by the increase of disorder, which can be seen from the RDF's, particularly from the longer length scales (also for coesite, Parker et al., 2001, p. 70).

6. Summary

A double phase transition was observed for two of three single crystal quartz samples scanning through the classical low (α) to high (β) phase transitions using TA (Thermal Analysis), DTA and PA (Pressure Analysis). The transition peaks (at 573 °C and 574.5 °C at 1 atmosphere) maintained this 1.5 K separation at higher pressures, and after repeated cycling through the transitions. The displacements due to onset-of-reaction hysteresis in isothermal pressure scans, and in isobaric temperature scans, were consistent also after repeated cyclical scannings (as also noted by Dolino et al., 1983). This suggests that the causes for the double phase transitions are a long-term large-scale feature of the crystal structure. Liebau and Bohm (1982) considered that double phase transitions are characteristic when a high temperature phase transforms to twins of a low temperature phase during cooling. In the heating direction twin domains are produced in the low temperature structure (α-quartz) at temperatures just below the α to β transition.

It is noteworthy that our single crystal sample of clear synthetic quartz (sample 3, Fig. 3) showed only a single transition peak during scanning through the α to β transition. However, Dolino et. al. (1983, Fig. 3) found double transitions at the α to β transition in some synthetic single crystals from x-growth sectors but not from z-growth sectors. Fluid inclusions are expected to be present in our synthetic quartz sample, as it turned milky after some hundred transition cycles, whereas Thermal-Analysis-peaks remained smooth and never displayed any splitting (Fig. 3, curve 3, see also Bambauer et al., 1969). How charged defects relate to the stability of the 3q incommensurate phase remains to be shown.

Penetration of the pressure medium Argon into the quartz structure was proved qualitatively in a specimen of the colorless vein quartz of approximately 2 g weight that had been cycled through P (up to 2 kbar) and T (up to 650 °C) for several weeks. 100 mg of this sample were heated in an evacuated chamber up to 400 °C in order to remove subsurface absorbed argon. This specimen was subsequently heated to 500 °C in a high-precision gas mass-spectrometer. The amount of argon released thereby was too high to be quantitatively measured even after a five-fold split of the gas stream. Following this result the overall amount of Argon dissolved in the quartz lattice is estimated to be less than 0.5% by weight.

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