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THE α-β INVERSION IN SUBMILLIGRAM PARTICLES OF NATURAL QUARTZ

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The bacground to the supposed development of the 'Beilby layer' on fine-grinding quartz is briefly reviewed. It is shown, using single crucible thermal analysis and sub-milligram DTA, that grinding quartz can cause a dispersion of the α-β inversion over a temperature range of several degrees; this is a crystallographic effect rather than an impurity effect. The sub-milligram DTA apparatus used is described and some thermal effects, such as impurity zoning, are illustrated.

Keywords: natural quartz

History

Several decades ago it was widely believed that when quartz is subjected to intensive grinding, the particles become coated with a 'Beilby layer' which may result in an increased initial solubility rate, a decrease in density, and a lower proportion of quartz detectable by DTA. This belief possibly arose from a misunder- standing of the term 'vitreous'. Sir George Beilby [1] believed that solids could exist in two conditions: the normal condition and a vitreous condition produced from the first by polishing, in which the solid was assumed to melt momentarily giving a vitreous surface with a liquid-like smoothness, or by work-hardening caused by metal grains sliding over each other, melting at the contact points, and cementing the grains into a rigid structure. Belief in Beilby's ideas lingered longest in relation to quartz. This can be partly attributed to the fact that whereas metals cannot exist in a vitreous or glassy condition formed by melting and cooling, in the case of silica such a substance does exist. It is formed by melting and cooling any phase of silica to form a glass, often referred to as 'quartz glass' or, very confusingly, simply as 'quartz' as exemplified by 'quartz tubes', 'quartz halogen lamps', etc. Following Sosman [2], the least confusing name for this substance is 'vitreous silica'. It has a lower density than quartz and, being

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amorphous, does not show up on DTA. This was the substance thought to be formed as a layer on quartz particles, but Sosman himself [2] expressed serious doubts about Beilby's researches.

The logic of Beilby's deductions finally fell to pieces in the 1970s when the reported reductions in density were attributed to water adsorption from the atmosphere [3, 4]. If, for example, powdered quartz is heated at 200°C it rapidly achieves a constant weight, as if all the water has been liberated. But if reheated to 300°C, more water is liberated and so on, an effect occurring all the way up to 1200°C. Thus the investigations of that time, involving 'drying' at 200°C or less, erroneously supported Beilby's ideas. With corrections, even with the severest grinding of quartz into the submicron region, the density of the silica component remained unchanged [3]; X-ray diffraction confirmed that it was α-quartz changing to β-quartz when heated through the inversion temperature, yet no thermal effect was detectable by DTA.

The question thus arose: how could quartz exhibit this behaviour?

Further investigation was made concerning impurities [5, 6] which might smear the α-β inversion over a range of temperature by solid solution. However, more complicated phenomena arise – the grinding process influences the α-β inversion morphologically, revealed by single crucible thermal analysis (SCTA) [7] and submilligram DTA [8]. With sub-milligram DTA the gradual change of thermal properties of α-quartz as a function of temperature can be eliminated from the ΔT trace at low heating rates whereupon dynamic thermal effects, highly sensitive to crystal damage, became apparent. Effects of impurity-zoning [9] were often encountered but these are useful in demonstrating the capabilities of the apparatus and are of geological interest.

Construction of a submilligram DTA apparatus

The apparatus (Fig. 1), similar to the design of Mazières [10], was constructed with assistance from the late Mr. Dennis Hopper. Thermocouple beads, formed by arcing from a vibrating electrode, were drilled to form 'crucibles' 0.7 mm in diameter. Thermal noise was eliminated by paying attention to two features:

(i) The thermocouple wire became noise-sensitive when threaded through the ceramic tube, so an excess of wire was stretched and work-hardened to facilitate threading, and then cut off.

(ii) Convection currents occurred around the sample, so the silver block and base were remelted and the chamber made as small as practicable.

Temperature calibration (to 1°C) was by means of K_2SO_4 but temperature differences down to 0.02°C were resolvable at heating rates <0.1 deg/min when the drift of ΔT was negligible even with the reference crucible empty.

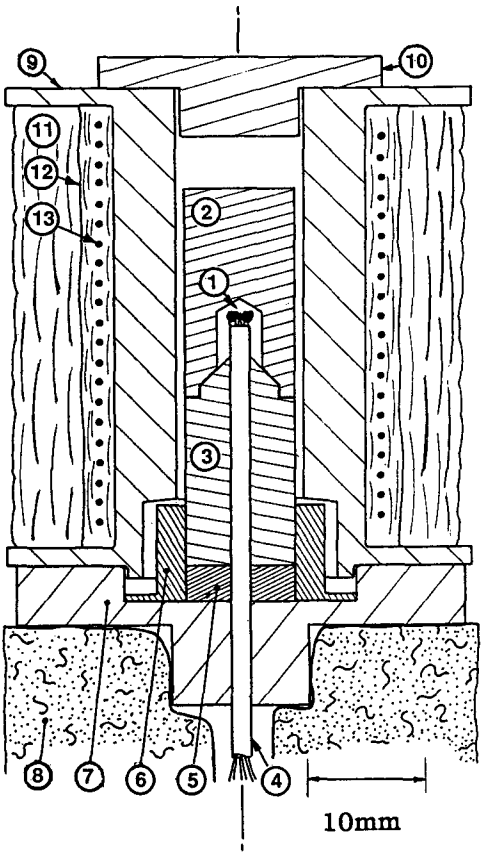

Fig. 1 Sub-milligram DTA apparatus. 1. Chromel-alumel thermocouple junctions formed into crucibles. 2. Silver block. 3. Silver base. 4. Ceramic tube – Dégussa Aérosil Standard TK800. 5. Agaline washer. 6. Brass cuff. 7. Brass furnace locator. 8. Magnesium oxide brick. 9. Brass furnace former. 10. Agaline cap. 11. Ceramic filler. 12. Glass fibre tape. 13. Kanthal heating wire. Ceramic wool encased the apparatus to obtain low heating rates

Results and discussion

A 50 g crystal of Brazilian quartz was crushed in a fly-press and two particles each of 420 μg selected. Results with one particle (Fig. 2) gave spikes, reproducible at any given heating rate, and at high heating rates they combined into one peak. The gradual change of properties of α-quartz gave an exponential-type leading edge to the peak at high heating rates and a similar trailing edge on rapid cooling. At high heating rates the β-quartz side of the peak was very steep irrespective of cooling or heating. As the heating rate was reduced, with purer

samples, $d(\Delta T)/dt$ exceeded the heating rate, leading to the conclusion that the inversion is neither a first-order nor a second-order phase change [8].

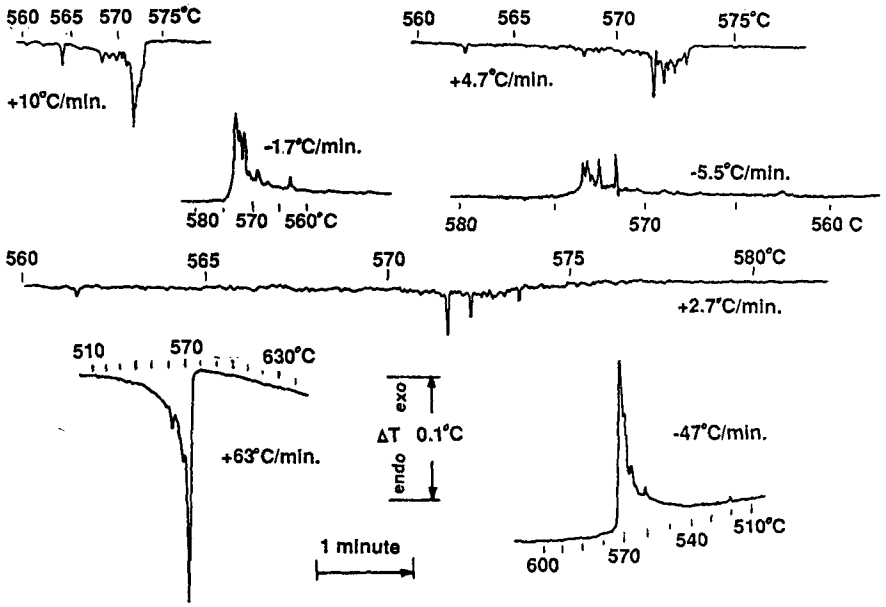

Fig. 2 Submilligram DTA of 420 μg particle of Brazilian quartz

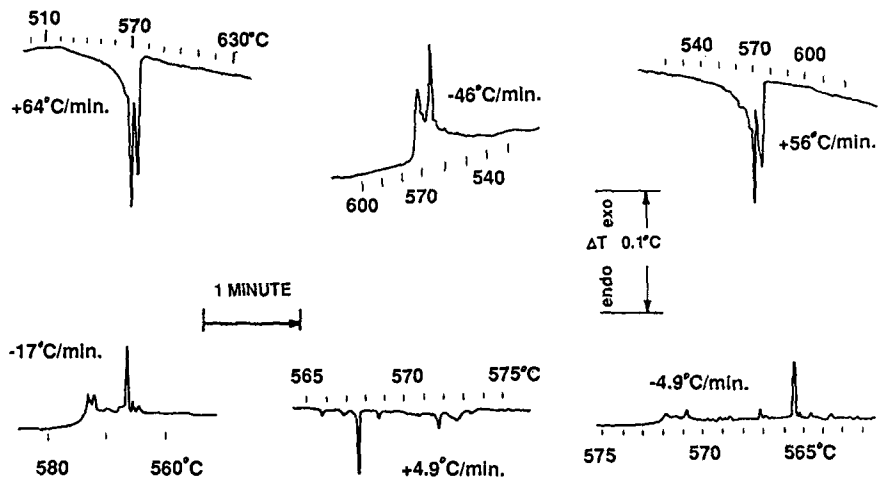

Fig. 3 Submilligram DTA of another 420 μg Brazilian quartz particle

At low heating rates 'heating spikes' occurred in reverse sequence compared to the 'cooling spikes', established either by the 'signature method' or the 'hysteresis method'. In the former the reversal of the characteristic spiky pattern was obvious; in the latter, the temperatures of the heating spikes were compared with the cooling spikes and any apparent negative hysteresis rejected. This established that the inversion peaks were not spread out on account of temperature gradients in the sample but were triggered and individually dependent on the temperature.

The other particle (Fig. 3) produced a doublet at high heating rate but as this decreased, one peak remained and the other fragmented and disappeared. This indicated different rate sensitivities of the inversion within a single particle and can be attributed to zones of lesser and greater structural damage, respectively [8].

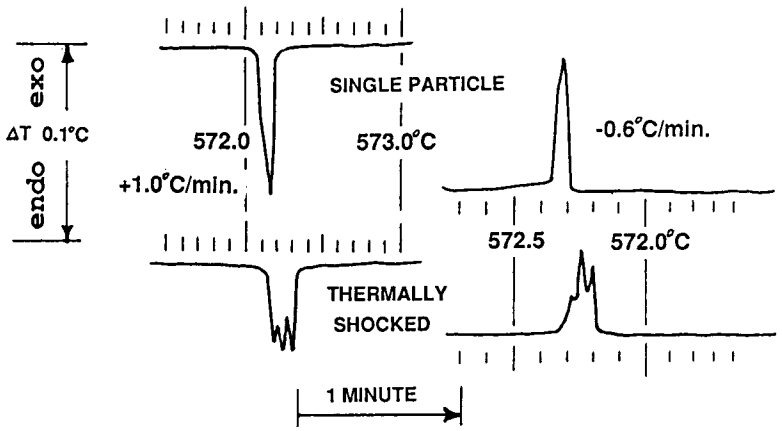

Fig. 4 DTA of 300 μg particle of FT243 oscillator Brazilian quartz, before and after thermal shock treatment

A 300 μg particle prepared from a wartime FT243 oscillator crystal, probably Brazilian [11], gave the curves of Fig. 4, before and after a thermal shock treatment, achieved by placing a particle into an indentation in a nichrome heating wire and plunging the yellow-hot particle into water.

In conclusion, submilligram DTA can reveal fundamental data on the quartz inversion, and is of interest to the electronic quartz industry in assessing quartz quality, and in geology for studying conditions of formation of quartz grains in rocks [12].

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Zusammenfassung — Es wird ein kurzer Überblick über die Hintergründe der angenommenen Bildung der "Beilby-Schicht" von feinmahlendem Quarz geschildert. Mittels Einzeltiegel-thermoanalyse und Sub-Milligramm DTA wurde gezeigt, daß das Mahlen von Quarz eine Ausweitung der $\alpha - \beta$-Umwandlung über einen Temperaturbereich von einigen Grad verursachen kann; dies ist eher ein kristallographischer als ein Unreinheitseffekt. Das eingesetzte Sub-Milligramm DTA Gerät wurde beschrieben und es werden einige thermische Erscheinungen, wie z.B. Zonieren von Verunreinigungen dargestellt.