Thermochimica Acta, 126 (1988) 365–374
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

POWDERED QUARTZ TESTED BY SINGLE CRUCIBLE THERMAL ANALYSIS (SCTA)

GUY S.M. MOORE

Physics Group, School of Natural Sciences, Hatfield Polytechnic, College Lane, P.O. Box 109, Hatfield, Herts AL10 9AB (Gt. Britain)

(Received 13 July 1987)

ABSTRACT

Single crucibles of different radii were constructed in which the temperature difference between the wall and the core of the sample was measured. This is called the "temperature lag" and is a useful parameter with respect to powdered quartz in which the $\alpha-\beta$ inversion is smeared over a temperature range. The temperature lag can be increased by increasing the rate of heating or cooling or by increasing the radius of the crucible. If the temperature lag becomes greater than the temperature smearing of the $\alpha-\beta$ inversion, then the inversion peak has a large amplitude regardless of the severity of grinding. Conversely this explains why micro-DTA is very sensitive to structural damage of the quartz, requiring only a few hours grinding for the inversion peak to disappear altogether.

SYMBOLS

γ	heating rate (negative for cooling) ($^\circ$C min^{-1})
ΔT	differential temperature ($^\circ$C)
θ_A	sample temperature measured close to the crucible wall ($^\circ$C)
θ_B	sample core temperature ($^\circ$C)
$(\theta_A - \theta_B)$	temperature lag ($^\circ$C)
S	temperature range over which the inversion becomes spread following powdering ($^\circ$C)
τ_{min}	time which elapses between a particle at the centre of a sample reaching a specified temperature and a particle near the outside of the sample reaching the same temperature (s)

INTRODUCTION

The powdering of quartz results in the attenuation of the $\alpha-\beta$ inversion peak seen on DTA, and it has been established [1] that this is due to the smearing of the inversion over a temperature range. A few hours grinding in an agate mill smears the inversion over at least 0.7 $^\circ$C, which is detectable by micro-DTA but not by normal DTA. In this paper evidence will be pre-

0040-6031/88/$03.50

sented that powdering quartz into the micron range smears the inversion still further over several degrees.

This subject has been adequately reviewed and discussed [1], and as pointed out, it is not easy to determine the "width" of an inversion peak by conventional DTA, which is why micro-DTA with so many advantages was developed and used to study this problem. It has been demonstrated that the inversion in quartz involves two distinct thermal effects: (1) A gradual change of properties of α-quartz several hundred degrees prior to the normally accepted inversion temperature in the vicinity of 573°C. This causes severe difficulties with respect to baseline construction and renders the concept of the "width" of an inversion peak unscientific. (2) A dynamic if nearly adiabatic or impulsive thermal effect within each particle, which cannot be readily appreciated during the more orthodox DTA of an aggregation of particles.

In contrast to normal DTA, micro-DTA at low $|\gamma|$ is insensitive to the first effect but readily responds to the impulsive thermal effects. The latter are so sensitive to structural damage of the quartz that only a few hours grinding in an agate mill is enough to cause the inversion peak to disappear altogether, whereas this duration of grinding has hardly any noticeable effect upon normal DTA. Micro-DTA is thus unsuitable for studying severely damaged quartz because the inversion is totally obliterated when studied by this method.

This paper concerns a different thermal technique employing perhaps a novel breed of crucible referred to by the author as single crucible thermal analysis (SCTA).

It is not suggested that SCTA has commercial potential. Difficulties of loading, unloading, cleaning and mass determination make it awkward to use, but as a research method it provides valuable data additional to those provided by DTA. With respect to quartz, the data revealed by DTA can be highly misleading: it is definitely the case that the assumption of a direct proportionality relationship between the peak area and a heat of inversion does not apply and can also be dangerous: finely divided quartz, in an energetically modified condition and possibly highly pathogenic, evades detection by DTA so *on no account should DTA ever be used to assess whether quartz is present in a dust.* SCTA has few advantages in this respect, but provides valuable data on the properties of powdered quartz. To understand the method it is essential to have a good qualitative picture of what happens during the heating of an aggregation of particles.

MODEL OF THE HEATING OF AN AGGREGATION OF PARTICLES

Mathematical descriptions of DTA, taking into account the varying specific heat of quartz and various phenomena occurring at the inversion

together with the important role of temperature gradients, are absent from the literature. With respect to quartz, however, a good qualitative model of the processes within a system of particles undergoing a phase change is still possible.

Imagine a quantity of solid of constant specific heat and thermal conductivity heated at a uniform rate, as in Fig. 1. After an initial transient response, all points within the sample will rise in temperature at an equal rate. The case of radial heat flow is illustrated. At the instant t_1 a typical temperature profile is illustrated, having a temperature lag of $\theta_A - \theta_B$; θ_A and θ_B are the temperatures at the outside and centre of the sample respectively. At the next instant t_2 all points in the sample have risen in temperature by equal amounts to give a new profile higher up the diagram

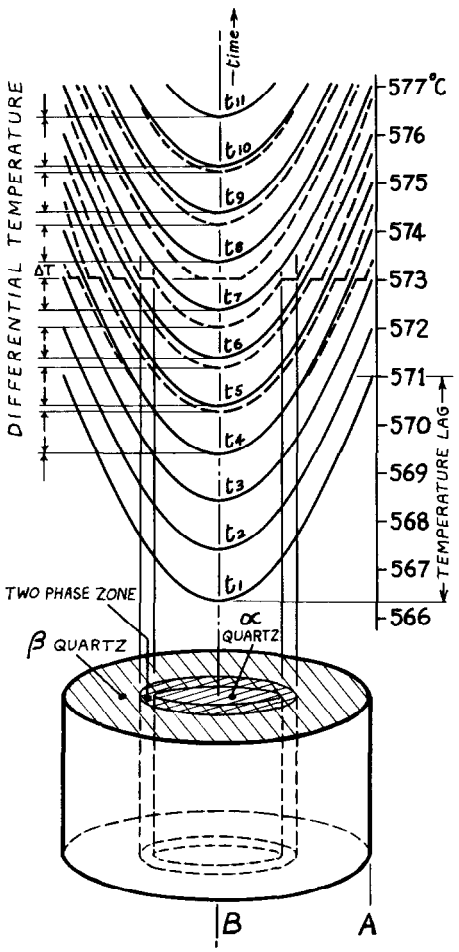

Fig. 1. Hypothetical temperature distributions in an inert reference sample (full curves) at different times, for radial heat flow and a uniform rate of heating. The broken curves relate to a sample exhibiting a latent heat type of phase change.

and so on; ideally the full curves would represent the behaviour of the inert reference sample of DTA.

On the same diagram the broken curves indicate the behaviour of a test substance, such as quartz, in which some thermal event occurs. If the reference matches the properties of the test sample, then ideally no temperature difference is detectable until the event begins to occur. The temperature difference ΔT could be the difference in temperature measured between the two sample cores. (The common case where the temperatures monitored are the temperatures of the crucibles, the latter of small enough thermal capacity to give a variation from linearity when a thermal event occurs, is not pursued in developing this model.)

A latent heat phase change is illustrated for the sake of simplicity in Fig. 1 (broken curves), and in the case of quartz this assumption will be corrected later. When the phase change resulting in additional heat absorption begins to occur in the outer regions of the sample, between t_3 and t_4, the difference between the curves, ΔT, at the centres of the samples is still close to zero. The transmission of heat to the core decreases as the phase change proceeds causing it to lag behind the reference and gives rise to an increasing ΔT deflection. Briefly a two-phase zone exists in the form of a tube, but the particles at the centre soon change phase and subsequently the test and reference samples reach the same temperatures and ΔT falls to zero, near instant t_{11}.

The direct proportionality between the temperature lag $(\theta_A - \theta_B)$ and γ is an essential feature of this kind of heating. Thus if a small thermal event occurs at a fixed temperature, the time τ_{min} which elapses between the event occurring in the outermost and innermost particles is $(\theta_A - \theta_B)/\gamma$. Since $\theta_A - \theta_B$ is directly proportional to γ, the elapsed time τ_{min} is independent of γ, and the reaction cannot be made to proceed any quicker, however fast the sample be heated. A "small thermal event" is equivalent to one requiring a large amplification to reveal it, which applies in the case of quartz. If the thermal event be large, then τ_{min} represents a lower limit for the event to occur in all the particles in the crucible.

A variation of thermal properties of the test sample from the reference prior to a phase transformation gives rise to differing temperature lags and a finite ΔT is then recorded. It follows that since the temperature lag is increased the larger the sample or the greater $|\gamma|$, DTA is more sensitive to the slowly changing thermal properties of quartz which herald the $\alpha \rightarrow \beta$ inversion under conditions of large temperature lag, i.e. in large samples or with large $|\gamma|$ or both. The converse argument, viz. that with small crucibles and at low $|\gamma|$ it may be possible to eliminate these slowly changing thermal effects from the ΔT trace, which proves possible, steered the research into the area of micro-DTA [1] as discussed above.

The effect of any smearing of a phase transition over a range of temperature upon the appearance of a DTA peak may be deduced using the above

model. If a latent heat remained of the same quantity but became smeared over a temperature range of S degrees, then provided S was several times less than $(\theta_A - \theta_B)$ little change in the peak appearance would be expected. If S were to become greater than $(\theta_A - \theta_B)$ then the peak appearance would be seriously affected. This is because at any instant when the thermal event has begun to occur in particles at the core of the sample, others near to the walls have not yet started; thus the rate of heat absorption at any instant is less even if the total heat absorbed remains the same, so the peak is of diminished amplitude. In this case reducing $|\gamma|$ does cause the phase change to proceed more slowly, and if $S \gg (\theta_A - \theta_B)$ the time for the phase change to occur is given approximately by S/γ.

Studying the relative behaviours of quartzes under various conditions of temperature lag can form the basis of an experimental method. The temperature lag may be varied in two basic ways: (a) by varying $|\gamma|$. Thus when the inversion has become attenuated following grinding, it becomes more apparent at greater $|\gamma|$ (see Fig. 2); (b) by varying the size of the sample and keeping γ constant.

A coarse and a fine sample of quartz tested in a large crucible may show inversion peaks of comparable magnitude, whereas in small crucibles the fine quartz sample may show a more diffuse peak if $\theta_A - \theta_B$ has become less than S (Fig. 2).

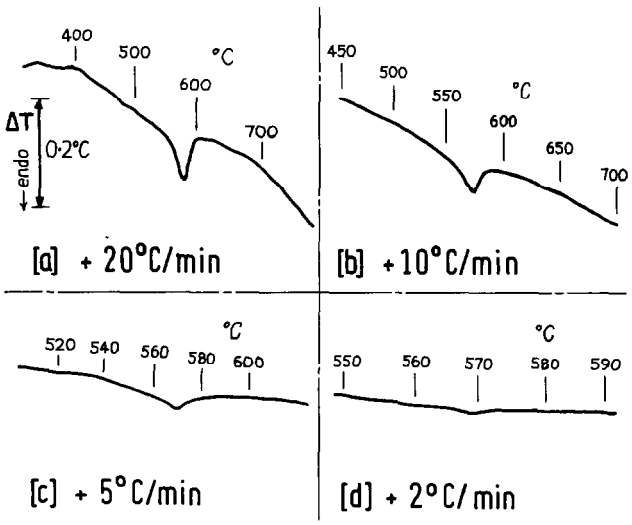

Fig. 2. DTA of "fine quartz", vibration milled to 1 μm mean size, at different rates of heating. Samples, 0.285 g.

VARYING THE TEMPERATURE LAG USING SCTA

The blocks of Fig. 3, which fitted on to existing DTA equipment, enabled the greatest range of size of test sample and dispensed with the reference sample. Under ideal conditions the temperature of the metal walls of the crucible is uniform and rising at a constant rate γ, and any temperature gradient within the block would be considerably less than within the sample. The ΔT monitored between the walls and sample centre is the temperature lag. Although the crucibles here were made of brass, at $\gamma = +5\,^{\circ}\mathrm{C\ min}^{-1}$ the several brass transitions were well away from the quartz inversion (nickel would be more suitable for the crucibles, but this research was done on a shoe-string!). In Fig. 4 the full curves correspond to the "coarse quartz", (a quartz sand from Chatteris, Cambridgeshire, U.K. of 72/120 Endecott mesh size). The broken curves correspond to the "fine quartz", which was the same substance after vibration milling for 100 h (mean size 1 μm).

The points C and E in Fig. 4 indicate the range over which the slopes of the peaks approximately match the slopes of the "step responses". The "step response" of a crucible was determined by suddenly pouring in a sample of coarse quartz slightly warmer than the crucible (see Fig. 5); it then gave an exponential type of curve as it achieved equilibrium. One has to appreciate that the curvature of the peaks for the coarse quartz in Fig. 4 was influenced by the dynamic thermal behaviour of a sample. Step responses for the fine quartz were not determined because the fine powder could not be suddenly packed into the crucible at a different temperature. However, the thermal conductivity of the fine quartz was approximately halved compared to the

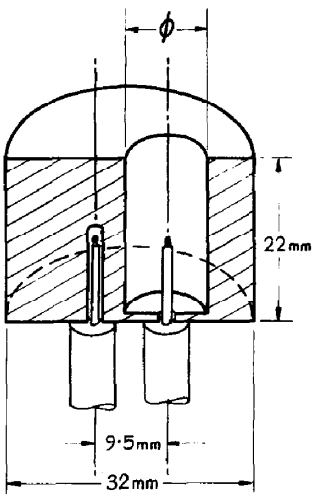

Fig. 3. SCTA crucible design in which the measured ΔT is the temperature lag. Crucible diameters were $\phi = 4$, 6, 8, 10, 12 and 14 mm.

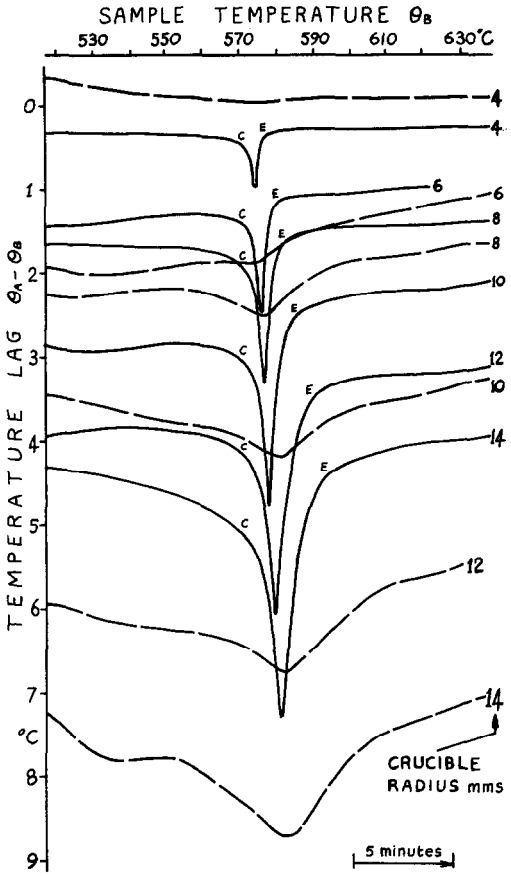

Fig. 4. SCTA results for "coarse quartz" (full curves) and "fine quartz" (broken curves).

coarse quartz, measured by Lee's disc for powder packed to the same degree; thus it may be assumed that the ranges C to E were approximately doubled for the fine quartz.

The decrease in thermal conductivity adequately accounts for the apparent increase in width of the peak for the fine quartz tested in the 14 mm crucible: the temperature lag for the fine quartz was approximately 8° C, some twice as large as for the coarse quartz, approximately 4° C, so it would take twice as long to sweep through the inversion. On the basis of this data alone there is no need to think in terms of temperature smearing of the inversion in the powdered quartz as an explanation. However the more diffuse peak for the fine quartz does disappear at a greater rate than the coarse quartz and is completely absent for the 4 mm crucible in accordance with the expectations of the effects of temperature smearing.

Some questions concern the masses of the samples and data as given in Table 1. Admittedly the masses of the finely ground quartz were less than

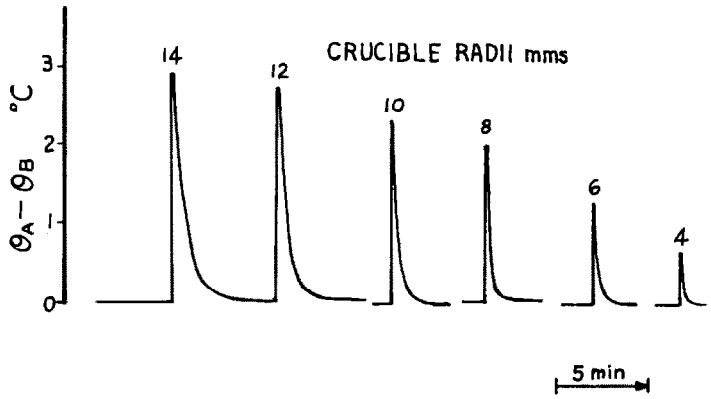

Fig. 5. "Step responses" of the SCTA crucibles.

TABLE 1

Masses of samples

Crucible diameter (mm)	Mass of 72/120 mesh quartz sand (g)	Mass of quartz milled 100 h (g)
4	0.414	0.216
6	0.844	0.501
8	1.503	0.953
10	2.437	1.548
12	3.466	2.239
14	4.789	3.206

the masses of the coarse quartz, but this does not fully explain the more rapid disappearance of the inversion peak for the fine quartz as the crucible radius was decreased.

DISCUSSION

These results could easily be explained if the inversion in the quartz became smeared over a temperature range of several degrees. Micro-DTA [1] indicates a temperature smearing of at least 0.7 °C for quartz milled just for a few hours whereas this has no noticeable effect upon the results of normal DTA. It seems logical that extended milling should increase the smearing until even with large samples, when S becomes greater than the temperature lag, the inversion peak begins to be affected and to appear of diminished

amplitude as in the case of the DTA of quartz milled for several hundred hours.

One notes that while micro-DTA demonstrates impulsive thermal effects in individually tested particles of quartz 0.5 mm diameter, when examined collectively by normal DTA [1] no such impulsive effects are detectable. In normal DTA the thermal inertia of the sample and crucible simply performs an integration of all the impulsive thermal effects of the individual particles within. Obviously the qualitative model developed above needs modification given that quartz exhibits impulsive thermal effects as opposed to a latent heat [1], but Fig. 1 then becomes impossible to illustrate. Nevertheless similar arguments apply with respect to the smearing of the impulsive thermal effects over a range of temperature, i.e. impulsive phenomena still occur but are scattered over a temperature range. When this range becomes larger than the temperature lag, the inversion peak has a reduced amplitude. The reason for impulsive thermal phenomena passing unnoticed in normal DTA is because the greatest rate of change of ΔT never exceeds $|\gamma|$ for powdered quartz under normal conditions.

The method of SCTA deserves some general comment. Like Darwin's theories of natural selection, normality often reinforces itself by trying out variations and then allowing them to die if they are unsuitable. SCTA probably comes into this category, but might survive as a rarely used research method. Whether or not the method of DTA will ever become extinct is another question— electronics has reached the stage where it is possible to examine very small changes of voltage without having to indulge in the artifice of getting rid of a large standing d.c. voltage by measuring temperatures with respect to a reference sample located in a similar thermal environment. This ingenious technique, contrived by our inventive forefathers to allow the amplification of small fluctuations in temperature from linearity, is little more than "an instrumental artifice" since the thermal properties of the reference sample are not explicitly involved in assessing the thermal properties of the sample under test. Perhaps the impetus of tradition, however, will preserve the method of DTA as the surviving species until long after one might have expected DTA to have fallen by the wayside.

SCTA has the advantage that at least the "reference" thermocouple junction is located in a useful position giving a measurement of the temperature lag, which DTA does not do. Apart from the difficulties of performing SCTA in terms of handling the samples, another difficulty concerns the basic thermal asymmetry of the system; if the furnace departs from a linear rate of temperature rise this will cause fluctuations in the measured ΔT, so it is essential to ensure good furnace control.

When one does research into the properties of quartz using a large range of sample size from fractions of a milligram [1] up to several grams as reported here, and at various heating rates, one often feels that some kind of "scale effect" operates. A small amount of grinding has the greatest in-

fluence on the thermal properties of the smallest samples. To bring about the same reduction in the inversion peak in a larger sample it is only necessary to increase the damage induced by grinding or reduce $|\gamma|$.

REFERENCE

1 G.S.M. Moore, Phase Transitions, 7 (1986) 25.