

## THERMOSONIMETRY OF THE NBS—ICTA TEMPERATURE STANDARDS

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### ABSTRACT

Thermosonimetry (TS) curves for the NBS—ICTA recommended DTA temperature standards (NBS standard references materials 759 and 760) are reported. These materials generally show two regions of TS activity. The first (lower temperature) region is associated with a variety of processes such as fluid inclusion release, grain boundary motions and microcrack propagation, whereas the second (higher temperature) region is associated with the polymorphic transformations. Incorporation of a DTA specimen holder assembly into the TS equipment has provided evidence that the temperatures of the peak TS activity in the transformation regions correspond to the extrapolated onset temperatures of the DTA peaks, suggesting that the polymorphic transformations provide these crystals with mechanisms for relief of mechanical strain.

### 1 INTRODUCTION

In a previous article [1], instrumentation for obtaining thermosonimetry (TS) curves was described. In this apparatus, the sample is contained in a cup or on a platform at the top of a silica waveguide which stands on a piezoelectric transducer crystal detector. Noise emitted during heating of the sample is transmitted via the waveguide to the transducer crystal whose output is amplified, processed and recorded as a function of temperature. In effect, the sample is part of a self-exciting tuned resonator whose natural resonance frequencies are excited by noise from the sample and to which the transducer crystal is sensitive. A disadvantage of such a measuring system is that insertion of a temperature measuring device, such as a thermocouple, into the sample causes severe mechanical damping. In the absence of a direct measurement of sample temperature, the normal practice is to place a thermocouple as close to the sample as possible.

Using this method, TS curves of several substances have now been reported [2—7] and the temperatures of the TS peaks have been found approximately to correspond with the temperature of the DTA peaks. However, the precise relationship between the TS peak and the DTA peak for a given thermal event has not been established. A number of possibilities exist. For example, if the noise emitted during a polymorphic transformation is one component of the total free energy change at the transformation temperature, the TS peak should closely correspond with the DTA peak. On the

other hand, if TS activity is a measure of strain release prior to a thermal event, the temperature at which TS activity ceases should correspond with the onset temperature of the DTA peak.

In order to test the various possibilities, we have performed parallel TS—DTA experiments with the NBS—ICTA recommended DTA temperature standards [8,9] and here report on the temperature relationships between the respective peaks. A number of observations regarding the influence of sample particle size and heating rate on the temperatures of TS peaks are also made.

## 2. EXPERIMENTAL

NBS—ICTA DTA temperature standards [8,9]  $\text{KClO}_4$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{SiO}_2$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{BaCO}_3$  and  $\text{SrCO}_3$  were used as supplied in NBS standard reference materials 759 and 760. For investigation of the influence of particle size, coarser grained samples of AR quality from BDH were ground by hand and sieve fractionated.  $\text{SiO}_2$  was a sample of pure white silica sand.

Transformation temperatures of all materials were checked using a Stanton-Redcroft DTA 673-4 apparatus. The reference material was precalcined  $\text{Al}_2\text{O}_3$  and the specimen holders were dimpled 8 mm  $\times$  6 mm diameter platinum crucibles fitting into a 12 mm  $\times$  20 mm diameter ceramic specimen-holder assembly and locating over the beads of Pt/Pt, 13% Rh thermocouples. The  $T$  thermocouple was that of the reference crucible and the  $\Delta T$  thermocouple that of the sample crucible. Specimen weights were 250 mg and all experiments were performed in static air at 10 K  $\text{min}^{-1}$ .

The TS apparatus was essentially as described previously [1] but with some additional data processing units, see Fig. 1, and a demountable ceramic DTA specimen-holder assembly of dimensions 20 mm  $\times$  13 mm  $\times$  11 mm located alongside the TS sample holder. The three specimens (DTA sample,

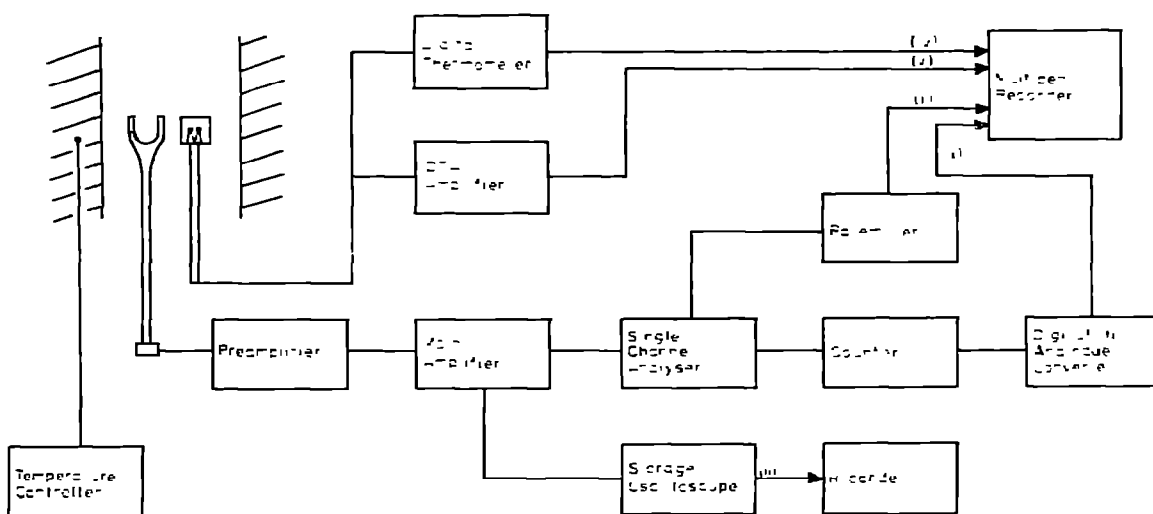


Fig. 1. Schematic of TS—DTA apparatus.

DTA reference and TS sample) were positioned equidistant from the protective sheath and the furnace wall. The use of a wide-bore furnace (5.0 cm) ensured that, although the DTA specimen-holder assembly was not in the geometrical centre of the furnace, the  $\Delta T$  baseline was essentially flat up to 1000°C. The specimen holders and the  $T$  and  $\Delta T$  thermocouples were exactly as specified above for the DTA 673-4.

A schematic of the TS signal processing equipment is given in Fig. 1. TS-(rate) curves were obtained by route (i), the total accumulated "ring-down" count was obtained by route (ii) and preliminary frequency and signal shape data by route (iii). For all experiments, the sample weight was 0.40 g, the main amplifier gain was 640, the single channel analyser window was set between 0.5 and 10.0 V, the rate meter was operated in the log mode, the time constant being 0.3 s and identical to that set on the digital to analogue converter. Rate (cps), total counts,  $T$  (route iv) and  $\Delta T$  (route v) were recorded simultaneously with a multi-pen recorder.

Hot stage microscopy was carried out using a Stanton-Redcroft HSM-5 unit.

### 3. RESULTS AND DISCUSSION

#### 3.1. Temperature calibration of the TS-DTA apparatus

Observed extrapolated onset temperatures for the NBS-ICTA standard materials using the DTA 673-4 apparatus and the TS-DTA apparatus, both at 10 K min<sup>-1</sup>, are given in Table 1. Standard deviations between these onset temperatures and the ICTA mean extrapolated onset values ( $T_{\text{ICTA}}$ ) are -1.5 K and -6.5 K, respectively. The deviation of the DTA 673-4 is negligible and, although that of the TS-DTA may indicate a  $T$  thermocouple calibration error, it is within the  $\pm 5$ -8 K standard deviation of the  $T_{\text{ICTA}}$  values [9]. The  $T$  thermocouple of the TS-DTA apparatus was therefore considered

TABLE 1

Extrapolated onset temperatures of NBS-ICTA standard reference materials 759 and 760

| Material                        | ICTA mean extrapolated onset temperature [9], $T_{\text{ICTA}}$ (°C) | Observed mean extrapolated onset temperature, DTA 673-4 (°C) | Observed mean extrapolated onset temperature, TS-DTA (°C) |
|---------------------------------|--|--|---|
| KClO <sub>4</sub>               | 299  | 300  | 294   |
| Ag <sub>2</sub> SO <sub>4</sub> | 424  | 427  | 416   |
| SiO <sub>2</sub>                | 571  | 570  | 563   |
| K <sub>2</sub> SO <sub>4</sub>  | 582  | 579  | 576   |
| K <sub>2</sub> CrO <sub>4</sub> | 665  | 663  | 661   |
| BaCO <sub>3</sub>               | 808  | 806  | 800   |
| SrCO <sub>3</sub>               | 928  | 923  | 921   |

TABLE 2

Temperature differences between the TS and DTA holders in the TS-DTA apparatus

| Heating rate<br>(K min <sup>-1</sup> ) | Temperature at DTA reference<br>(°C) | Temperature at TS sample<br>(°C) |
|--|--------------------------------------|----------------------------------|
| 10                                     | 200                                  | 230                              |
|  | 600                                  | 620                              |
|  | 1000                                 | 1005                             |
| 25                                     | 200                                  | 260                              |
|  | 600                                  | 635                              |
|  | 1000                                 | 1015                             |
| 40                                     | 200                                  | 290                              |
|  | 600                                  | 655                              |
|  | 1000                                 | 1025                             |

capable of giving an acceptably accurate measurement of the temperature of a thermal event.

Except for small variations in peak area arising from the different particle sizes, the DTA peaks of the BDH materials were indistinguishable from those of the NBS-ICTA standard materials.

In the TS-DTA apparatus, the TS sample is contained in a 10 mm diameter fused silica glass holder and the DTA sample and reference materials are contained in 6 mm diameter platinum crucibles within a ceramic specimen-holder assembly. In a rising temperature experiment, the different thermal properties of the holders will create a temperature difference between the centre of the DTA reference crucible (from where the temperature of the DTA event is monitored) and the centre of the TS sample. To estimate this difference, a Pt/Pt, 13% Rh thermocouple, identical with that of the DTA reference, was placed in the TS sample and the output of this thermocouple and also that of the DTA reference were passed to the multi-channel digital thermometer and to two channels of the multi-pen recorder. Typical values for various heating rates and temperatures are given in Table 2 and show that the centre of the TS sample was always hotter than the DTA reference, presumably because the total heat capacity of the TS sample holder is less than that of the DTA specimen-holder assembly. Temperatures quoted for TS events have been corrected accordingly and are considered to be accurate to  $\pm 5$  K. The values in Table 2 refer to the centre of the TS sample and were found to be independent (within  $\pm 5$  K) of the nature of the sample in the TS holder. At the edge of the TS holder nearest the furnace wall, the difference was approximately twice as large, in accordance with previous estimates of the temperature gradients existing in samples undergoing thermal analysis [10-13].

### *3.2 General features of the TS curves and the influence of operational variables on the total emission count*

Although there were individual variations, in general the NBS-ICTA standard reference materials each emitted detectable TS (rate) signals in two

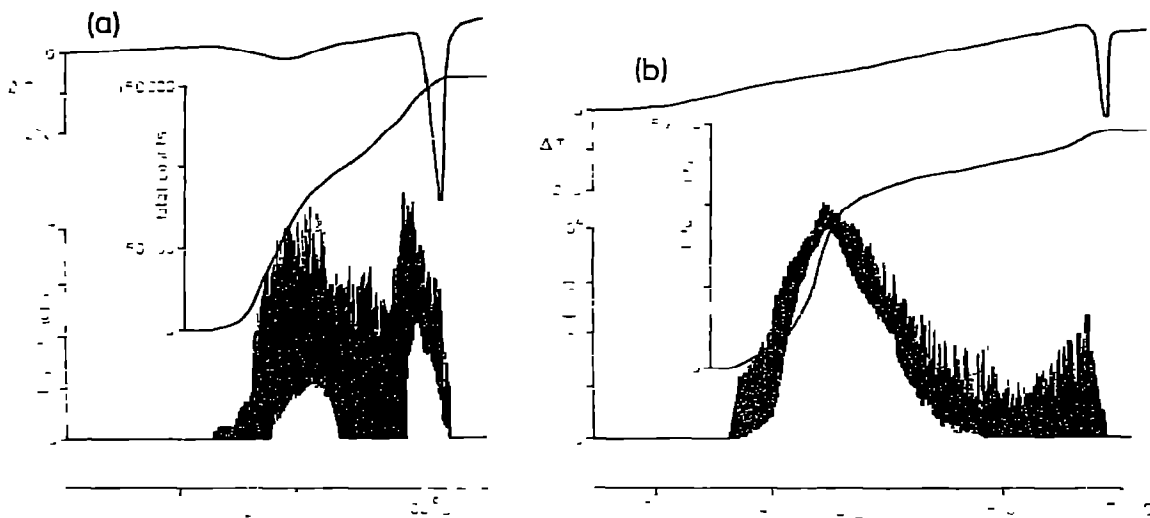


Fig. 2. TS rate, TS total count and DTA curves for (a) NBS-ICTA  $\text{KClO}_4$  and (b) NBS-ICTA  $\text{K}_2\text{CrO}_4$ . Heating rate  $10 \text{ K min}^{-1}$ .

more or less distinct temperature regions, see, for example, Fig. 2(a). Signals emitted in the lower temperature regions arise from microcracking and release of fluid inclusions etc. (see Sect. 3.4), whereas those emitted in the higher temperature regions are associated with the polymorphic phase transformations (see Sects. 3.3. and 3.5). In this section, some observations regarding total accumulated activity levels and their variations are discussed.

The total number of counts emitted during heating was dependent on factors such as the nature of the material itself, the particle size and the heating rate. For example at  $10 \text{ K min}^{-1}$  NBS-ICTA  $\text{KClO}_4$  ( $T_{\text{ICTA}} = 299^\circ\text{C}$ ) typically emitted  $1.5 \times 10^5$  counts over the temperature range ambient to  $325^\circ\text{C}$ . Approximately  $1.0 \times 10^5$  of this total appeared in the lower temperature region and the remainder in the transformation temperature region  $250\text{--}325^\circ\text{C}$  [Fig. 2(a)]. On the other hand, NBS-ICTA  $\text{K}_2\text{CrO}_4$  ( $T_{\text{ICTA}} = 665^\circ\text{C}$ ) also typically emitted  $1.5 \times 10^5$  counts but of these only approximately  $5 \times 10^3$  counts appeared in the transformation temperature region  $625\text{--}700^\circ\text{C}$  [Fig. 2(b)]. Thus it seems that some transformations are inherently acoustically active whereas others are acoustically less active, however, it is not yet possible to relate the level of acoustic activity to any structural, kinetic or mechanistic features of the transformations.

It has been shown previously [5] that a factor which influences the count rate is the sample particle size, samples consisting of larger particle sizes emitting at higher rates. This relationship is also shown by the total count. For example, samples of BDH  $\text{KClO}_4$  sieved to 20–60 mesh and 60–120 mesh emitted  $7.6 \times 10^5$  and  $6.3 \times 10^5$  counts, respectively, at  $10 \text{ K min}^{-1}$  up to  $325^\circ\text{C}$ . These values can be compared with the  $1.5 \times 10^5$  counts emitted by the NBS-ICTA materials in which the predominant particle size range is 200–240 mesh. For NBS-ICTA  $\text{BaCO}_3$  and  $\text{SrCO}_3$ , the particulate range is 240–300 mesh and these materials did not emit in their transformation

temperature regions. However, 200–240 mesh fractions of BDH  $\text{BaCO}_3$  and  $\text{SrCO}_3$  did emit weakly [Fig. 3(f) and (g)]; thus small particle sizes in addition to transformations of low acoustic activity are probably responsible for the lack of activity of the NBS–ICTA materials. It is worthy of note that the higher temperature ( $982^\circ\text{C}$ ) transformation of  $\text{BaCO}_3$  appears to be acoustically more active than the lower temperature ( $808^\circ\text{C}$ ) transformation [Fig. 3(f)].

The influence of heating rate was less predictable than that of particle size. In general, there was an increase in total counts with increase in heating rate but wide variation of behaviour was noted. For example, NBS–ICTA  $\text{KClO}_4$  showed no statistically meaningful variation in the total counts emitted between 3 and  $40\text{ K min}^{-1}$ . However, over the range  $10\text{--}40\text{ K min}^{-1}$ , the mean total count emission from NBS–ICTA  $\text{K}_2\text{CrO}_4$  increased from  $1.5 \times 10^5$  counts to  $1.9 \times 10^5$  counts and over the same heating rate range, the mean emission from NBS–ICTA  $\text{K}_2\text{SO}_4$  increased from  $5.5 \times 10^5$  counts to  $9.0 \times 10^5$  counts. This variable behaviour suggests that for different materials there may be different mechanisms of emission or there may be threshold heating rates whose magnitudes may be related to the elastic properties of the materials and the thermal gradients necessary for catastrophic crack propagation.

The total number of counts emitted during cooling was always very much greater than that during heating. For example, on cooling NBS–ICTA  $\text{KClO}_4$  at  $10\text{ K min}^{-1}$  from  $325^\circ\text{C}$ , a mean  $2.0 \times 10^6$  counts were emitted. Slower cooling produced fewer signals, for example at  $3\text{ K min}^{-1}$ , a mean  $2.9 \times 10^5$  counts were obtained, but the total count on subsequent reheating was not influenced by the cooling rate. Since bulk moduli of solids are normally considerably larger than Young's moduli, this behaviour is in accord with the ability of most solids to withstand the surface compressive forces experienced during heating better than the surface tensile forces experienced during cooling [14].

### *3.3 Temperature correlations between DTA peaks and TS rate peaks for the transformations*

The DTA and TS (rate) curves for NBS–ICTA  $\text{KClO}_4$  illustrated in Fig. 2(a) show that the DTA event approximately corresponds to the clearly resolved second region of activity in the TS (rate) curve. At the higher heating rate, Fig. 3(a), the second TS event is less resolved and shows only as a distinct second component or shoulder, but the correspondence with the DTA event remains evident. TS (rate) curves for the remainder of the NBS–ICTA materials and the BDH  $\text{BaCO}_3$  and  $\text{SrCO}_3$  are also illustrated in Fig. 3. Although the corresponding DTA curves are not shown in this figure, temperature similarity between the DTA event and the second region of TS (rate) activity was noted for all these materials.

As a consequence of the disparity in temperature between the DTA reference and the TS sample during the heating regime and the resultant need to correct the temperatures of TS events according to Table 2, the true temperature relationships between the DTA peaks and the TS (rate) peaks could not

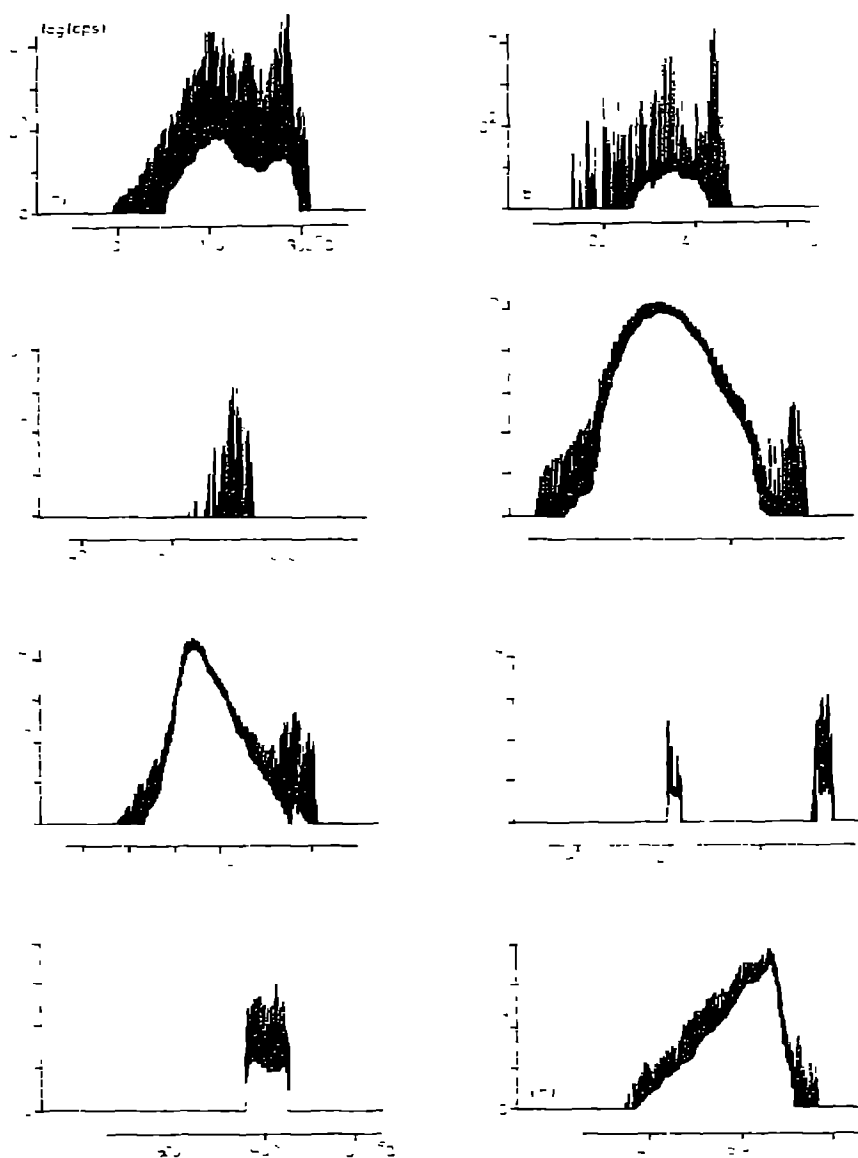


Fig. 3 TS rate curves for (a) NBS-ICTA  $\text{KClO}_4$ , (b) NBS-ICTA  $\text{Ag}_2\text{SO}_4$ , (c) NBS-ICTA  $\text{SiO}_2$ , (d) NBS-ICTA  $\text{K}_2\text{SO}_4$ , (e) NBS-ICTA  $\text{K}_2\text{CrO}_4$ , (f) BDH  $\text{BaCO}_3$ , (g) BDH  $\text{SrCO}_3$ , (h)  $\text{SiO}_2$  sand. Heating rate  $40 \text{ K min}^{-1}$ . Ordinate scales are  $\log(\text{cps})$ .

be established with accuracy. Nevertheless, the corrected data consistently indicated that the DTA peaks and the TS (rate) peaks were not coincident but, as shown for  $\text{KClO}_4$  in Fig. 2(a), the onsets of the DTA peaks coincided with the TS (rate) peaks. This correlation between the temperatures of DTA peaks and TS (rate) peaks is significant to the understanding of the origin and meaning of acoustic activity (see Sect. 3.5).

Heating rate and particle size had no measurably significant influence on this correlation except that increased heating rate and increased particle size decreased the resolution of the two components of the TS (rate) curve. For example, Fig. 3(h) shows the TS (rate) curve of the  $\text{SiO}_2$  sand sample

and is typical of the type of curve obtained from a sample of larger particulate size at fast heating rate in showing the polymorphic transformation only as a shoulder on the steeply sloping high temperature end of the principal peak.

### *3.4 TS activities at temperatures below the transformation temperatures*

The temperature at which TS (rate) activity commenced was also found to be dependent on the nature of the sample, its particle size and the heating rate. In general, increasing the heating rate and increasing the particle size, both of which increase the temperature gradient across the sample, caused a lowering of the temperature of initial activity.

In order to establish whether any visible effects coincided with TS activity in the lower temperature regions, crystals of  $\text{KClO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{SiO}_2$  sand were visually examined during programmed heating using the hot-stage microscope. The greatest visual activity was displayed by  $\text{K}_2\text{SO}_4$  which at  $10 \text{ K min}^{-1}$  started to "bump" at  $350^\circ\text{C}$  and to fracture at  $420\text{--}450^\circ\text{C}$ . The temperature of maximum TS (rate) activity for  $\text{K}_2\text{SO}_4$ , Fig. 3(d), corresponds well with the temperature of fracture but the temperature of commencement of TS activity is considerably below that at which mechanical effects were visually detected. With  $\text{KClO}_4$ , the first visual effects were noted at  $225^\circ\text{C}$ . These took the form of small eruptions from the crystal faces, most of which occurred at  $270^\circ\text{C}$  but continued to  $300^\circ\text{C}$ . Again, these visual effects correspond with the maximum TS (rate) activity [Fig. 2(a) and 3(a)]. The silica sand sample showed no visual activity on heating at  $10 \text{ K min}^{-1}$  but at  $50 \text{ K min}^{-1}$  a small amount of "bumping" was observed between  $500^\circ\text{C}$  and  $575^\circ\text{C}$ , again corresponding with the maximum TS (rate) activity [Fig. 3(h)].

The coincidence of visual effects with maximum count rate in the lower temperature regions suggests that this TS activity is associated with mechanical parameters such as catastrophic crack propagation and fluid inclusion release. In the case of  $\text{KClO}_4$ , a very small and broad DTA endothermic event was often noted to coincide with this TS (rate) activity, see Fig. 2(a), and since the visual evidence suggests that gaseous inclusions erupt from the crystals at these temperatures, this seems to offer an explanation of both this DTA event and the TS (rate) activity. In the case of  $\text{K}_2\text{SO}_4$  (and to a smaller extent  $\text{SiO}_2$ ), catastrophic thermal shock fracture caused by microcrack propagation seems to offer an explanation of the TS (rate) activity in this temperature region.

Two further pieces of evidence support the view that  $\text{KClO}_4$  and  $\text{K}_2\text{SO}_4$  differ in the nature of their low temperature TS activities. Firstly, it was noted in Sect. 3.2 that the total counts emitted by  $\text{KClO}_4$  was independent of heating rate whereas the total counts emitted by  $\text{K}_2\text{SO}_4$  almost doubled on increasing the heating rate from  $10 \text{ K min}^{-1}$  to  $40 \text{ K min}^{-1}$ . The total counts associated with release of fluid inclusions would not be expected to vary with heating rate since increase in heating rate would not increase the number of inclusions released (although it would increase the rate of release). However, the total number of counts associated with microcrack



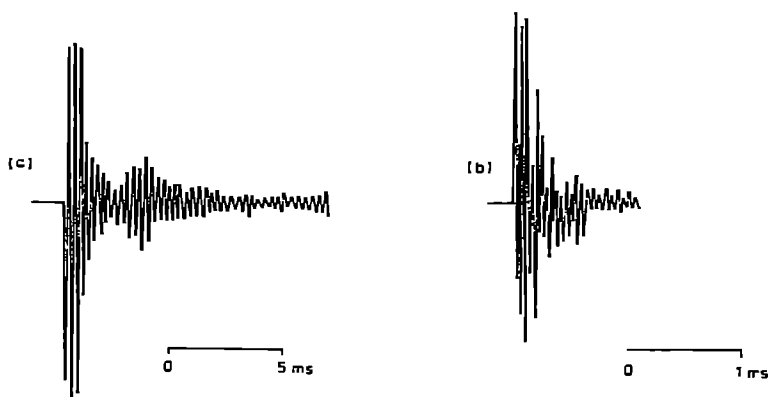


Fig. 4. Typical "ring-down" TS signals. (a) 4 kHz, (b) 20 kHz.

formation and propagation would be expected to vary with heating rate since an increase in heating rate would increase the thermal stress on the sample and hence the number of microcracks necessary to relieve the resultant strain within the sample.

The second piece of evidence comes from the shapes of the signals that are emitted during the higher and lower temperature regions of activity in  $\text{KClO}_4$  and  $\text{K}_2\text{SO}_4$ . Figure 4 shows typical "ring-down" signal bursts, (a) and (b) corresponding to approximately 4 and 20 kHz, respectively. (N.B. These frequencies do not correspond to the frequencies emitted by the sample but to natural resonances of the measuring system induced by different emissions from the sample.) Although this aspect of TS is only in the earliest stages of development, we have noted that the majority of signals appear to be of type (b); however, lower frequency type (a) signals are more commonly observed during the low temperature activity of  $\text{KClO}_4$  than in any other material for which measurements of this type have been recorded. This suggests that the source of low temperature activity in the TS curve of  $\text{KClO}_4$  may differ from that in  $\text{K}_2\text{SO}_4$  and other materials.

The ability of the TS technique to monitor types of thermal activity not accessible to conventional thermoanalytical techniques has also been demonstrated recently for fluorite minerals [15]. These exist in a variety of colour variants, none of which show DTA events up to  $1000^\circ\text{C}$  but which do show characteristic TS (rate) activity in the  $300\text{--}800^\circ\text{C}$  region. Whether this activity originates from fluid inclusions, lattice defects or lattice strain is not known but it serves to illustrate the potential of the TS technique for investigations of structural integrity in mineral and other materials.

### *3.5. Meaning and origin of acoustic emissions during polymorphic transformations*

In a TS experiment, the detected signals are manifestations of the pressure waves (mechanical noise) arising from strain release in the thermally stressed sample. The individual effects that contribute to the total strain and its subsequent release are not yet fully established but major contributors will be

fluid inclusion release, dislocation and grain boundary motions, the generation and propagation of microcracks, etc. Whether atomic displacements occurring during solid I  $\leftrightarrow$  solid II phase transformations themselves cause acoustic emission is doubtful. For example, it has been stated [16] that only co-operative martensitic-type transformations are acoustically active and it has been estimated [17] that it requires  $10^5$ – $10^6$  dislocation breakaway events to produce one acoustic signal from an alkali halide crystal. However, irrespective of whether atomic displacements (albeit in large numbers) can produce detectable acoustic emission, there is no doubt that the existence of a phase transformation is sufficient for emission to occur. In Sect. 3.3, it was noted that for the solid I  $\leftrightarrow$  solid II transformations of the NBS–ICTA standard materials, the peaks of the TS (rate) curves correlated in temperature with the onsets of the DTA peaks. Since a peak in a TS (rate) curve represents a temperature of maximum rate of strain release and the onset of a DTA peak, although of no fundamental significance, provides a good estimate of the thermodynamic equilibrium temperature for a transformation [18], this correlation indicates that the commencement of a solid I  $\leftrightarrow$  solid II transformation provides a mechanism for strain relief. Thus a solid I may be considered to undergo a structural transformation when its rate of internal strain accumulation exceeds the rate at which its elastic properties permit release of that strain by dislocation motions, crack propagation etc. Complete reorganisation at the atomic level to a new structure of more favourable lattice energy (solid II) is then the only means of effecting the strain release. If no new stable structure is available, then complete fracture of the lattice occurs, i.e. melting. Relationships between elastic moduli and parameters such as lattice energy [14] and melting point [19] are well established. The TS (rate) peak corresponding to a phase transformation is therefore a measure of the strain build-up prior to the transformation and its subsequent decline when structural reorganisation at the transformation temperature occurs. This important role that stress factors play in transformations of materials has also been recognised in the dehydration of single crystals of potassium alum where crack propagation resulting from stress deformation has recently been microscopically observed to occur prior to nucleation of the product [20].

At high heating rates, the TS (rate) peaks corresponding to polymorphic transformations commonly exhibit enhanced activity just before or at the point at which the rate returns to baseline [see examples in Figs. 2(a) and 3]. On the temperature axis of the DTA curve, the corresponding point is approximately the peak temperature. In a rising temperature experiment, the increase in temperature at any point in the sample slows down and stops during a transformation and when the transformation is complete, the temperature increases very rapidly until it catches up with the furnace temperature [11]. This rapid increase is a brief but severe thermal stress on the sample and may be the cause of this enhanced activity.

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