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THERMOSONIMETRY

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ABSTRACT

A status report on thermosonimetry, presented during the 8th ICTA Workshop on less common methods of thermal analysis, is given. The definition, means of detecting sonic effects and some applications of thermosonimetry are described. Prospects for these methods are outlined.

DEFINITION AND PRINCIPLES OF THE METHOD

Thermosonimetry (TS) is by definition a technique based on the measurement of the sound emitted from a substance during cooling or heating [1].

The fact that noise or sonic effects are created in heated or cooled material has been known for a long time and the recording of these signals was a question of the availability of appropriate technical apparatus. In the pure sense, sonic impression is a means of energy transport by mechanical waves. Practically available vibrations cover a broad range of frequencies, from audible (of a few hertz) up to very high inaudible ultrasonics (of several megahertz).

Sonic signals can be described by several parameters, e.g., the intensity, amplitude and frequency distribution. These signals represent continuous oscillations and separate bursts of noise. Analysis of the signal makes it possible to gain information about solid-state processes. For example, mechanical disturbances taking place in a sample are caused by a series of microscopic processes, such as motion of dislocations, propagation of cracks, chemical reactions, nucleation of the new phase, relaxation processes and discontinuous alterations of physical parameters (thermal expansion, compressibility, elastic modulus, electrical conductivity, etc.) In spite of the fact that the relationship between the elastic waves measured as the sonic signals and the corresponding processes have not been fully established so far, some useful information can be drawn from the results of thermosonimetry. The repeated occurrence of sonic bursts indicates the rate of solid reactions and of the energy transport.

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Detection of acoustic signals and apparatus for thermosonimetry

The experimental system for thermosonic detection is illustrated in Fig. 1. The sample to be measured is placed on the head of the seismically mounted fused-quartz glass stethoscope. The acoustic emission that takes place in the sample during the thermally stimulated processes causes mechanical vibrations in the stethoscope, which are converted into electrical information by the piezoelectric cell at the bottom. The temperature is monitored by a thermocouple situated close to the sample.

Figure 2 is a block diagram of the signal flow and the experimental data processing.

Examples of application

Study of phase changes. The high sensitivity of TS measurements permitted the study of phase changes that are not detectable by DTA. Figure 3 shows the TS curve of CaI_2. The acoustic effect around 300°C is connected with the phase transition and the effect in the temperature range 310–450°C has been ascribed to the annealing of the defects in the newly formed phase. Melting starts at 760°C, which is indicated by acoustic bursts.

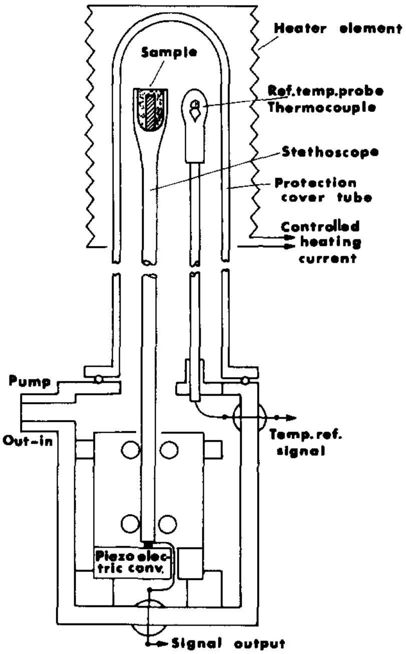

Fig. 1. Scheme of the system for thermosonic detection.

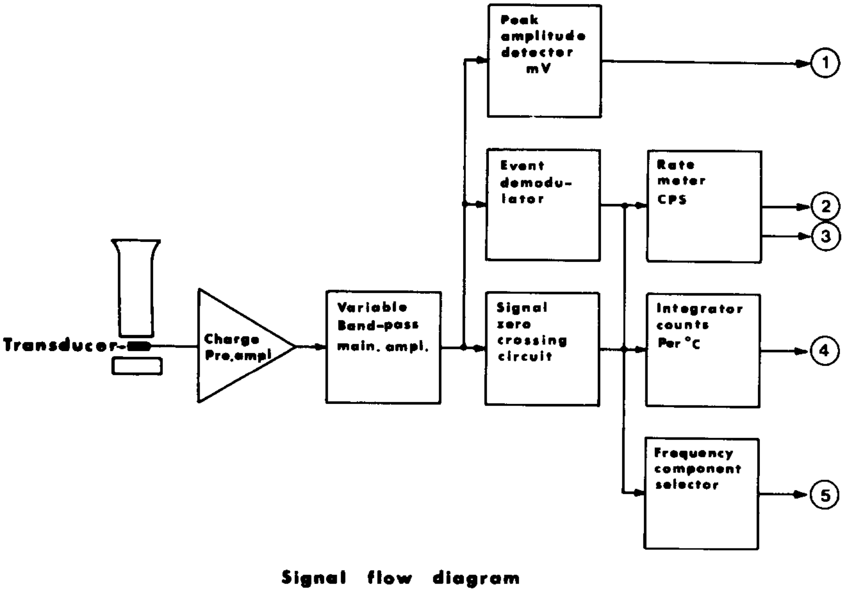

Fig. 2. Scheme of the signal flow and experimental data processing system.

Thermosonimetry has also been applied in phase diagram studies of salt systems. Figure 4 shows the TS curve of the system 15 mol-% NaCl–85 mol-% CsCl [2] and the phase diagram constructed. The $\beta \rightarrow \alpha$ transition in

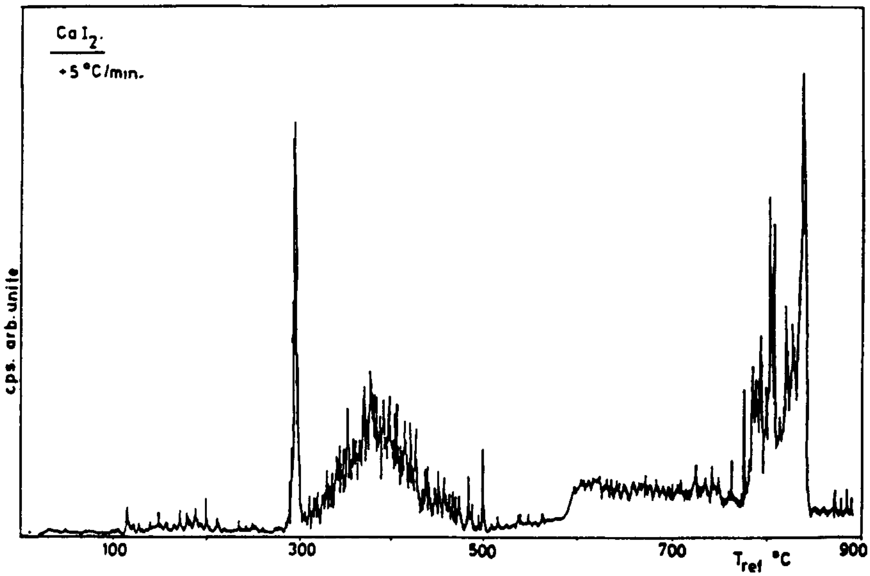

Fig. 3. Thermosonic curve of CaI_2. Heating rate, 5°C min^{-1}.

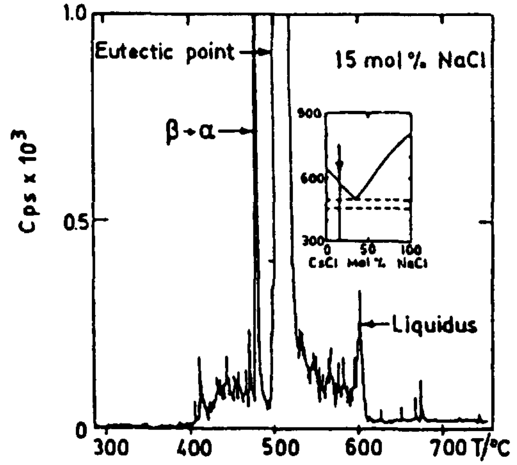

Fig. 4. Thermosonic curve of the mixture 15 mol-% NaCl–85 mol-% CsCl. Heating rate, 10°C min^{-1}.

CsCl was described at 470°C, the temperature of the eutectic point being 500°C.

Another salt system, $CsCl-BaCl_2$, was also studied by thermosonimetry and the TS curves were used for the construction of the phase diagram [2].

Frequency distribution of acoustic waves

Various processes that give rise to acoustic emission can be characterized by the distribution of the frequency of the acoustic waves. It should be taken into account that the recorded frequency spectra are slightly modified owing to the transfer of the acoustic waves in the stethoscope. Moreover, the recorded frequency distribution spectrum represents a combination of the natural resonances of the detection system and the proper acoustic waves of the sample. The former should be eliminated before the evaluation of the results of thermosonimetry. Figure 5 shows two examples of the frequency distribution corresponding to (a) $K_2Cr_2O_7$ and (b) K_2SO_4 [3].

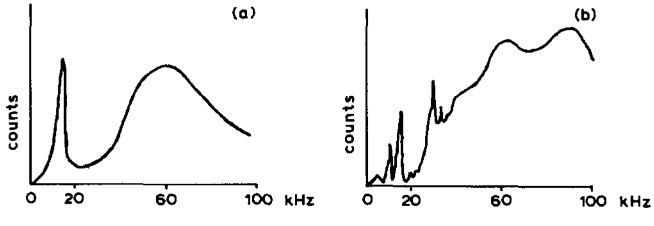

Fig. 5. Frequency distribution of the TS signal for (a) $K_2Cr_2O_7$ and (b) K_2SO_4 samples.

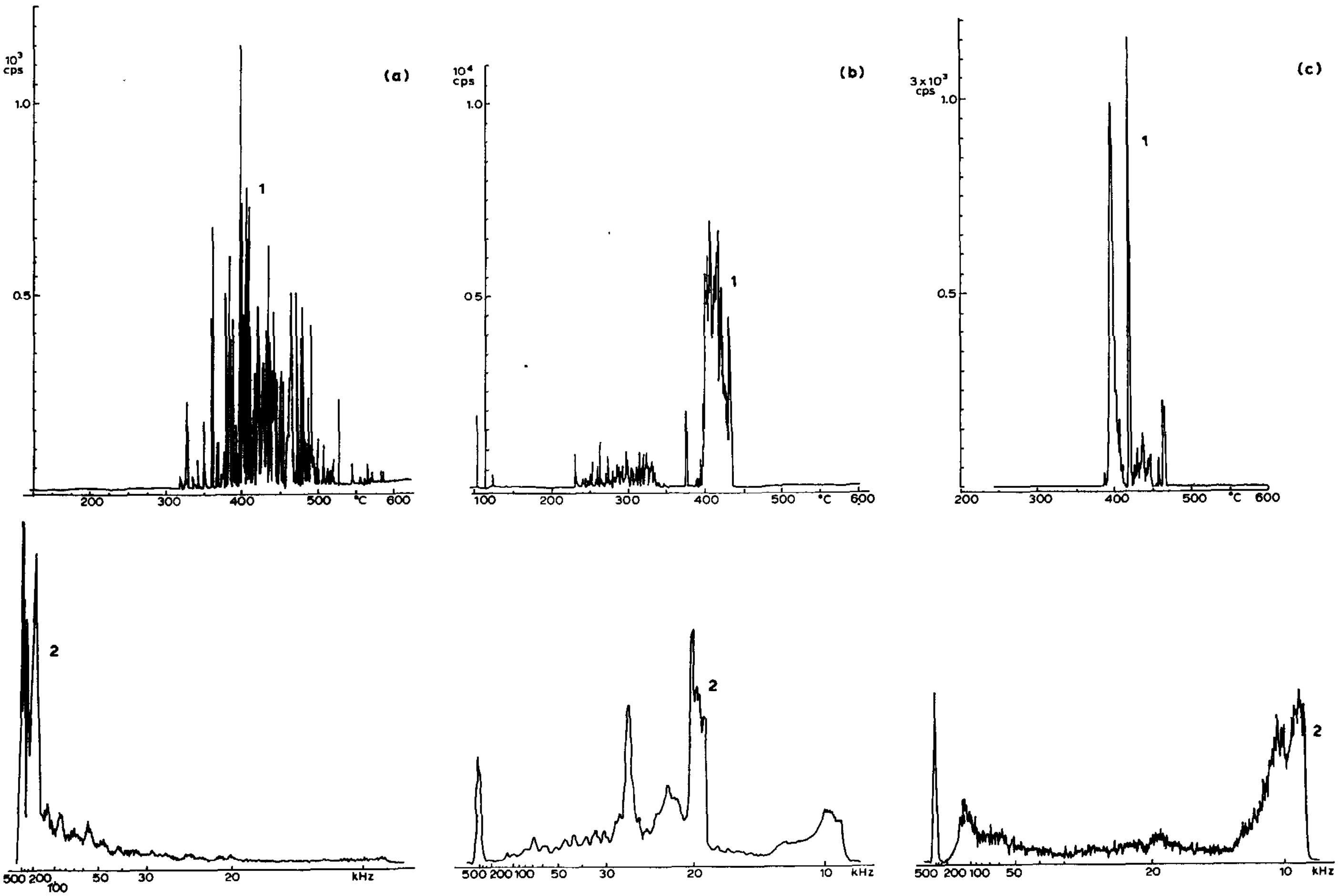

Fig. 6. Thermosonic curves of brucite samples originating in (a) Tyrol, (b) Pennsylvania, U.S.A. and (c) Løngbon, Sweden. The brucite samples from Tyrol were crushed and those from Pennsylvania and Løngbon were in the form of pieces of minerals. Heating rate, 2°C min^{-1}. 1, Differential FS curves; 2, frequency distribution curves.

Figure 6 shows that the frequency distributions of acoustic emission of brucite samples differ, depending on the origin of the mineral [4]. It should be taken into account that the frequency distribution of the TS spectrum can differ for powder and compact samples.

Time of conversion of quartz to cristobalite

The transformation of the high-temperature modification of quartz to cristobalite is a slow, solid-state process taking place above 1470°C. The grain size of the sample and the presence of impurities influence the grow rate of cristobalite. It was shown that quartz samples of different origins require different times for conversion to cristobalite at 1470°C. When a constant firing time (1 h) is used, different degrees of conversion were obtained for quartz samples of different origins (the TS spectra are illustrated in Fig. 7). The analysis of the conversion of quartz to cristobalite is of practical importance when determining the heating rate during the melting of quartz.

Characterization of minerals

Two types of vein quartz, dull and white, have been investigated by thermosonimetry [5] (see Fig. 8). The curves in Fig. 8 show differences in intensity and temperature of thermosonic activity. The low temperature rate

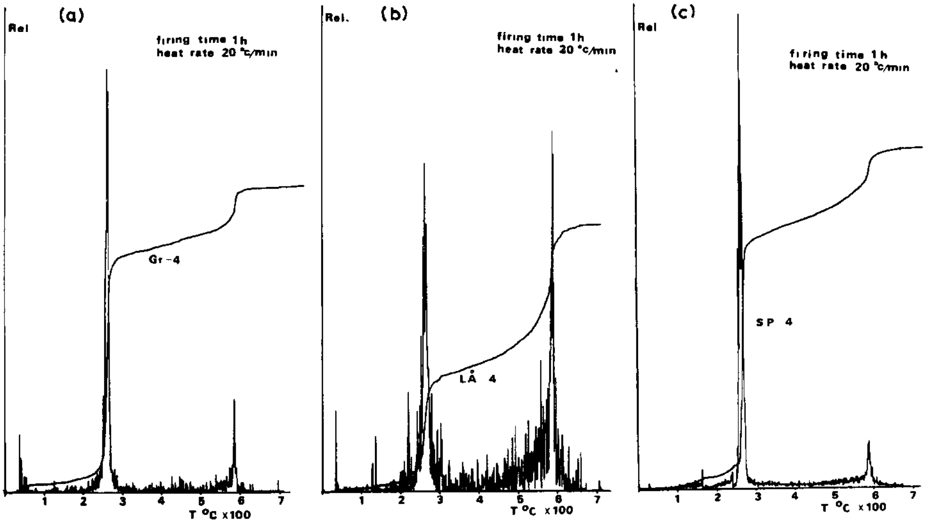

Fig. 7. Thermosonic curves (in differential and integral form) of three quartz samples originating in (a) Greece (Gr-4), (b) Sweden (La-4) and (c) Spain (Sp-4). Heating rate, 20°C min^{-1}. The samples were heated for 1 h at 1470°C prior to the measurements.

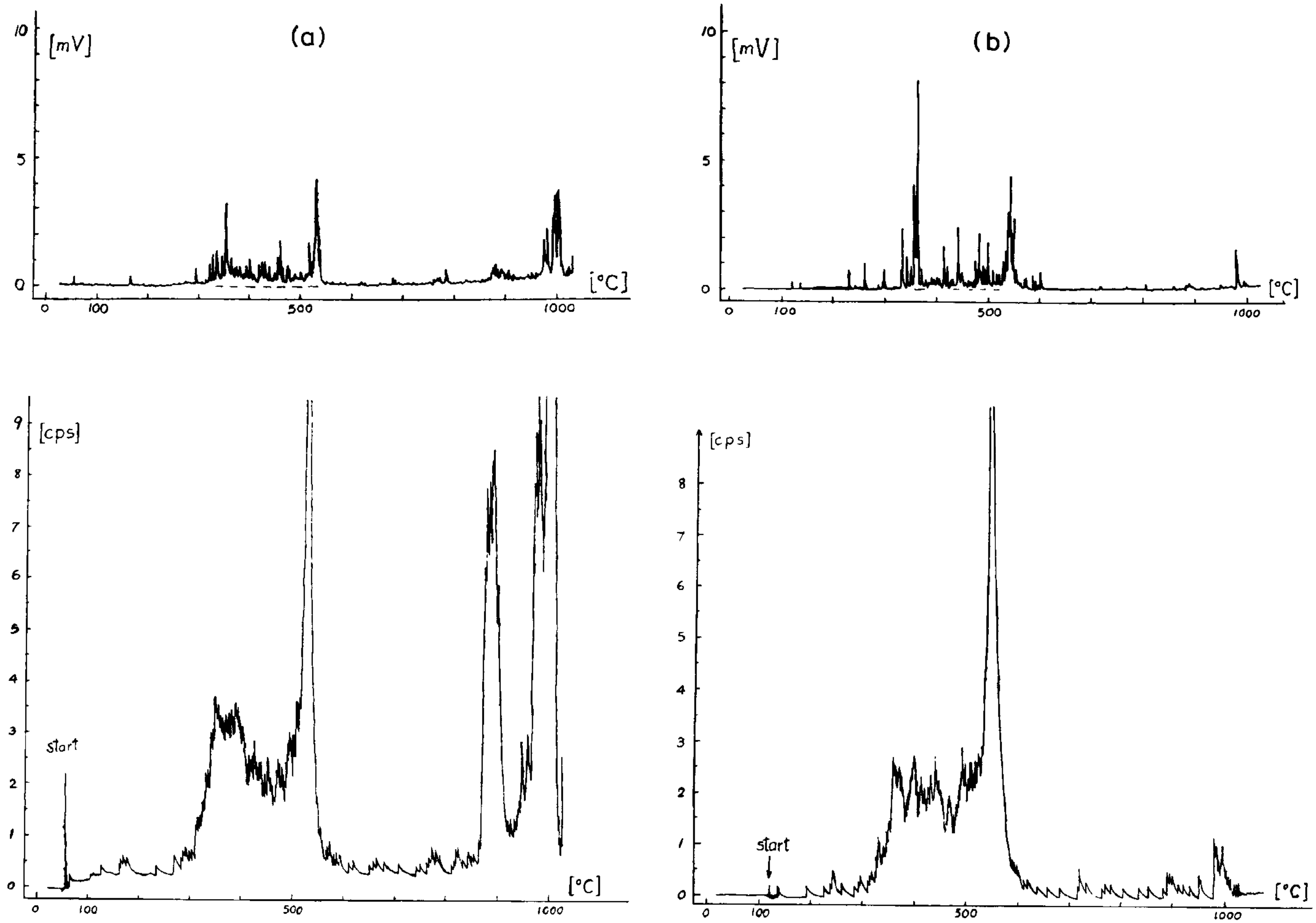

Fig. 8. Thermosonic curves of (a) dull vein quartz and (b) white vein quartz.

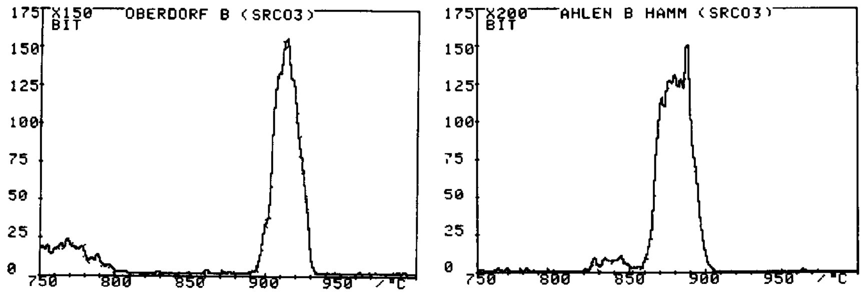

Fig. 9. Thermosonic curves of $SrCO_3$ of different origins.

is caused by the breakdown of pores filled by liquid. The conversion of quartz at 573°C described in the literature is indicated by the TS spectrum at 525–530°C (for white quartz) and at 540–545°C (for dull quartz). It is believed that the high thermosonic activity of white quartz in the high temperature region is caused by dehydration of the sample.

Thermosonimetry can serve as a useful method for studying the nature and mechanism of structural transformations between low- and high-temperature modifications of quartz and other minerals. In Fig. 9, the TS curves of $SrCO_3$ samples of various origins show the influence of physical defects, crystallinity and chemical impurities on the structural transformation of $SrCO_3$ [6].

KINETICS OF CRYSTALLIZATION OF GLASSES

Thermosonic spectroscopy represents a new method for the study of different mechanisms and kinetics of glass crystallization. Figure 10 shows

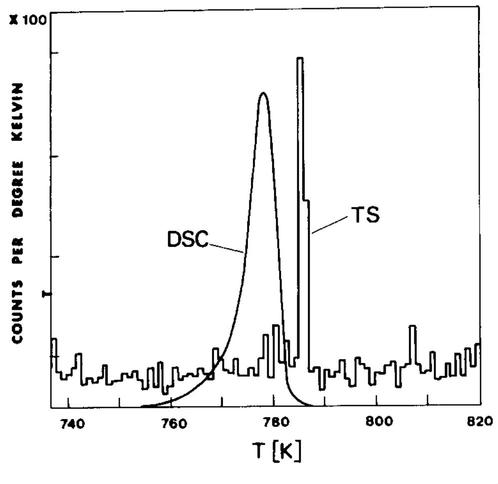

Fig. 10. Thermosonic and DSC curves of Metglass 2605 A. Heating rate, 10°C min^{-1}.

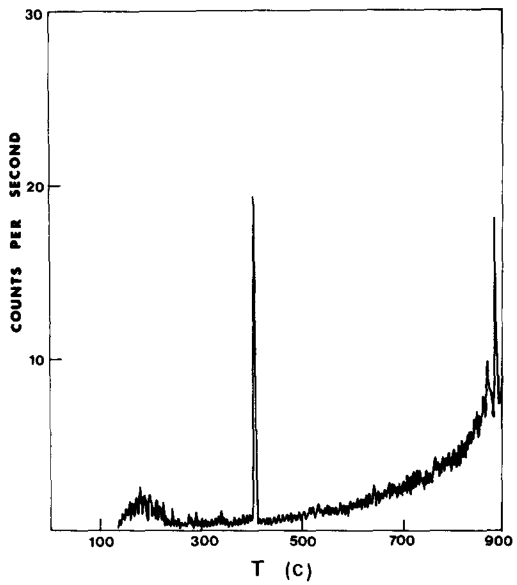

Fig. 11. Thermosonic curves of Metglass 2826. Heating rate, 10 °C min^{-1}.

the thermosonimetry results of the crystallization of the amorphous alloy Metglass 2605 A (nominal composition $Fe_{78}Mo_2B_{20}$), obtained during heating at a constant rate of 10 K min^{-1}. The DSC results are also presented for comparison. It was found that the structure of the TS signals depends on the signal frequency width. A good correlation between the TS and DSC maxima was found [7].

Figure 11 shows the TS spectrum of Metglass 2826 (nominal composition $Fe_{40}Ni_{40}P_{14}B_6$). The crystallization of the glass is indicated by a sharp peak at 395 °C (extrapolated to a zero heating rate). The thermosonic activity in the temperature range 247–350 °C is ascribed to a structural rearrangement. A kinetics dependence according to Kissinger shows excellent agreement between the thermosonimetric and DSC results and an activation energy of about 93 kcal mol^{-1} was evaluated for the crystallization process [8].

Glass transition

It is assumed [8] that at the glass transition temperature a discontinuous change in the free volume occurs, generating elastic waves that cause a thermosonic effect. Inorganic glasses in a powdered form have been investigated by thermosonimetry, and Fig. 12 shows the results of thermosonimetry of the soft glass, together with the dilatometric curve. There is a good correlation between the TS and dilatometric curves. Both the glass transition temperature (T_g) and the softening temperature (T_s) can be easily determined from the curves in Fig. 12.

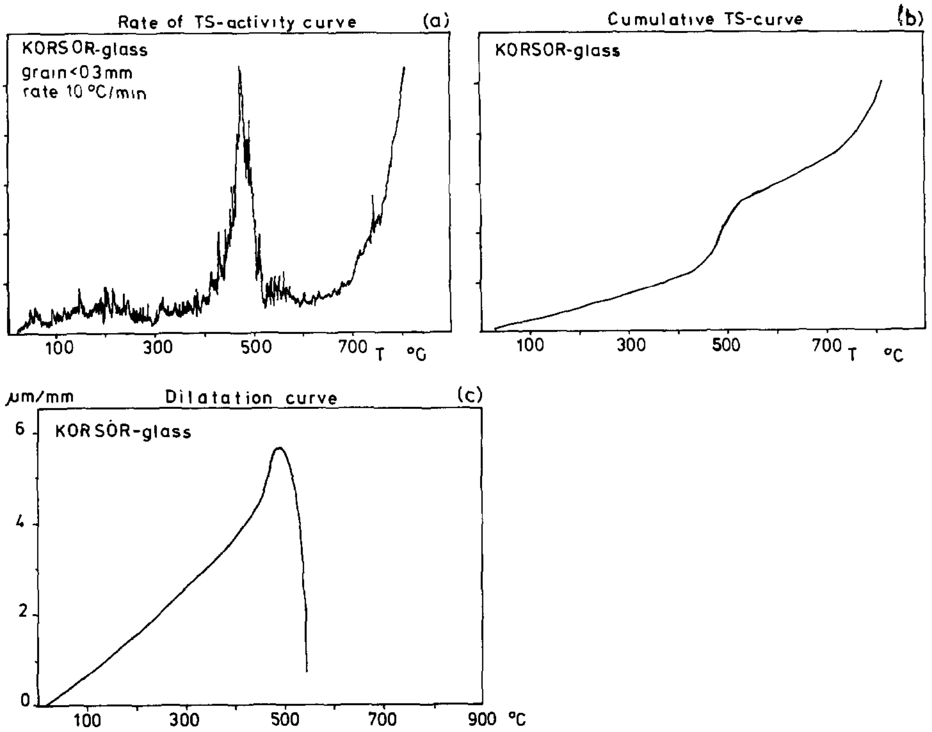

Fig. 12. Thermosonic differential (a) and integral (b) curves and dilatation curve (c) of Korsør glass sample. Heating rate, 10° C min^{-1}.

Thermal microcracking

The properties of heterogeneous materials such as ceramics are strongly influenced by thermal microcracking. During the cooling of ceramic samples from firing temperature, cracks are produced as a result of the stresses and strains in the material at the microscopic level. The creation of defects can be studied on the basis of thermosonimetry, as has been shown in a study of the CaF_2–NaCl system [9].

Quantitative measurements of the content of cristobalite in dust

The problem of determining small amounts of cristobalite in dust particles with a size of 0.15 µm and a surface area of 22 m^2 g^{-1} was solved by using the TS technique [10]. The area of the TS peak is suggested to be proportional to the amount of cristobalite present in the sample. X-ray analysis was not able to determine such a small amount of cristobalite.

Figure 13 shows the results of the thermosonimetry (in the form of

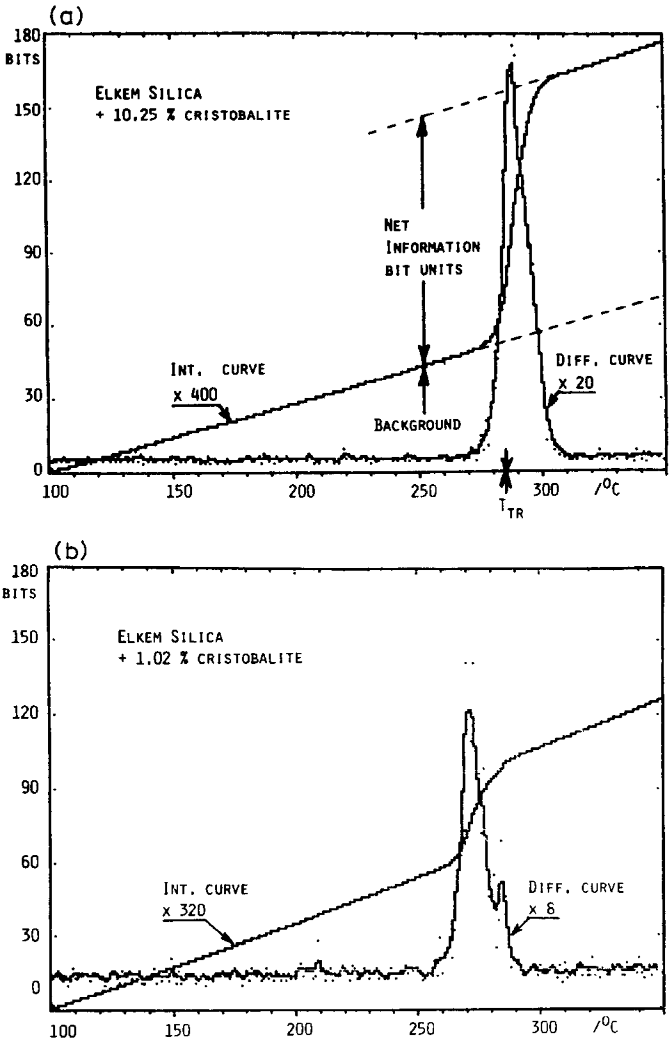

Fig. 13. Thermosonic differential and integral curves of the mixtures Elkem Micro silica with (a) 10.25% and (b) 1.02% of cristobalite.

differential and integral TS curves) of Elkem Micro silica in a mixture containing (a) 10.25% and (b) 1.02% of cristobalite.

Prospects for thermosonimetry

Thermosonimetry offers some advantages in the study of inorganic substances and minerals, for example in its high sensitivity and selectivity.

The future prospects of thermosonimetry depend on its further development, i.e., its quantification. The method has the potential to be useful for the characterization and quality control of different materials.

The modern instrumentation available for thermosonimetry permits measurements on the vibration state of materials and the diagnosis of materials and prefabricated materials. This is a type of fast Fourier analysis that could be used directly in comparative thermosonimetric studies of the quality, stability and technological control of materials.

The future development of thermosonimetry should not only concern the frequency content of the TS signal. It is also of interest to use the amplitude distribution of the TS spectrum as an indicator of the conversion of mechanical energy during thermally induced processes.

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