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THERMOSONIMETRY (TS) OF TRANSITIONS IN INORGANIC GLASS MATERIALS

K. Lønvik
Div. of Physics, Univ. of Trondheim, N-7034 NTH Trondheim (Norway)

SUMMARY

This preliminary investigation proves that the softening process of common glasses are detectable by use of the method of thermosonimetry (TS). The experiments have been worked out with graded samples of crushed glass material. Besides a clear indication of the structural glass transition temperature, some of the recordings also turn up with a double peaking. This stepwise performance is believed to depend on the thermal pre-history of the glass, mainly the rate of cooling. Observations experienced by TS technic might probably also serve as a basis of evaluating thermal properties of the sample.

EXPERIMENTAL PROCEDURE

The experimental set-up is given elsewhere, ref. [1]. The sample material is in the form of pre-crushed inorganic glass, and the experiment itself is run in open air atmosphere. The TS-recordings are displayed as counted number of TS-signals pr °C (bit units called the rate R of the TS-activity), and the cumulative curve of these numbers (noted as the integration value I), both presented as a function of the reference temperature.

EXPERIMENTAL RESULTS

A typical result obtained is best illustrated by figure 1. The TS-information and the reference temperature are here simultaneously recorded as a time function. The curves show that the TS-signal bursts [cps] are broad banded, as seen in this case from separated registration within two frequency split areas ([LF] for lower and [HF] for higher frequencies). The distinct multistep characteristics are observed with different intensity and time resolution depending on the frequency band used.

In figure 2 is the cumulative curve I of the TS-activity response R compared with a dilation measurement of a solid piece of the sample material. Both the curves are corresponding very well to each other up to the point where the softening of the material start (the dilatometer sensor is prestressing the

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sample). The stepped performance of the I-curve indicates then that this might be a volume activated process (detectable by TS). There is a good agreement to the softening temperature and the peaking in this TS-activity.

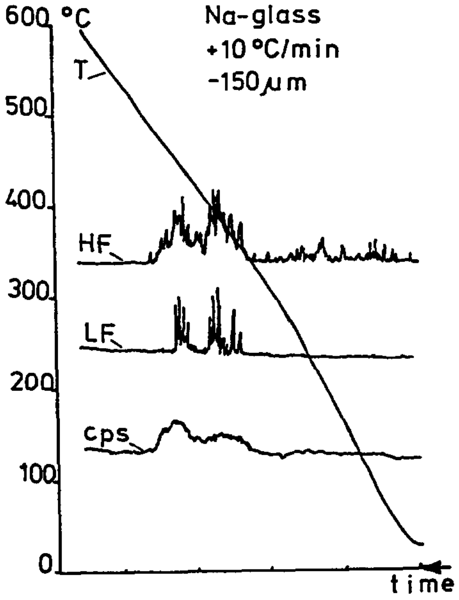
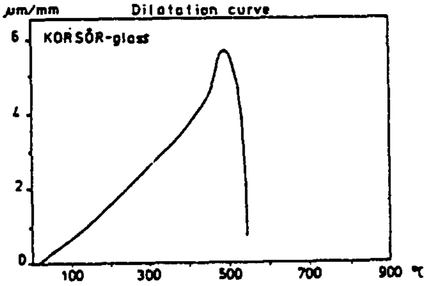
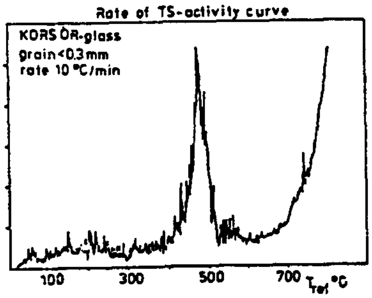


Figure 1. TS-information simultaneously recorded as function of time, with a rising temperature of 10 °C/min in open air atmosphere.
a) [cps] is the rate meter reading of TS-signal burst with a relatively big time constant for the purpose of smoothing.
b) [LF] is the amplitude outswing for signals in the frequency range 4-9 kHz with a rather small time constant.
c) [HF] is high frequency, 18-120 kHz range, signal amplitudes with a relatively big time constant.





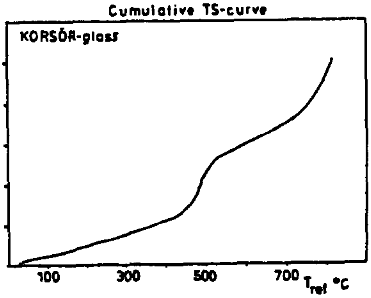


Figure 2. Detected TS-activity from grained Danish soft-glass (Korsør) compared to a dilation measurement. Both the glass-transition T_g and softening temperature T_s can easily be determined from the graphs.

Figure 3a) shows a typical recording of the TS-active R during the transition process of B_2O_3-glass former. The temperature at maximum rate is estimated to be 285 °C. The corresponding cumulative

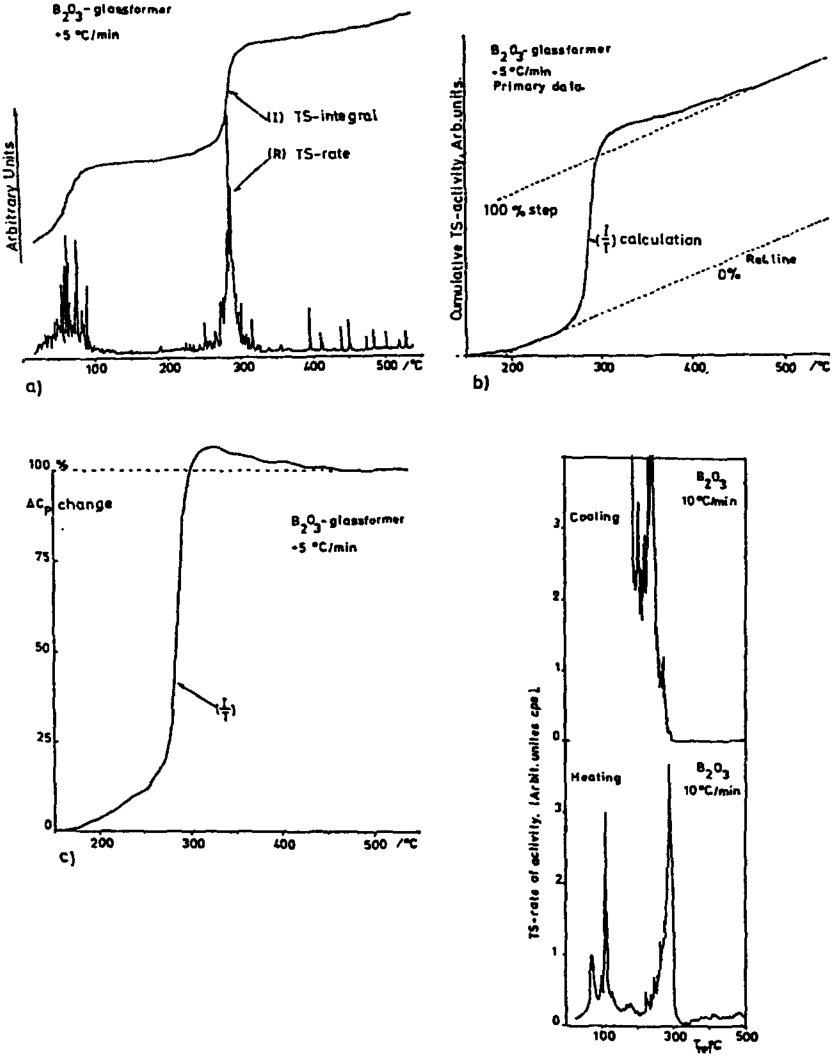


Figure 3. a) The primary TS-information in a rising temperature scan of B_2O_3-glass-former.
b) A worked-out cut for the observed phase change (250-350 °C).
c) The relative performance of the change in heat capacity during the phase transition as a function of the temperature level.
d) The heating and cooling cycle of the sample showing the temperature turning point of the phase transition.

curve I is drawn on the top of the graph. The integrated values I are now divided by the respective temperature level. This calculation is presented in figure 3b) for the limited region of the phase transition. From these data is the course of the step-change drawn, from the reference base-line 0% up to the line for 100 % of conversion. The normalized form of this curve is presented on figure 3c) as a function of the temperature level during the phase-change. The ordinate represents then the actual running value relatively to the total step change in the heat capacity.

APPENDIX

The formal correlation between step-changes of the temperature coefficients is expressed by Ehrenfest relations (relative atomic concentration constant);

$$1)\ T\cdot V\cdot(\Delta\alpha)^2 = \Delta\chi\cdot\Delta C_p \quad ; \quad 2)\ \frac{\partial P}{\partial T} = \frac{\Delta\alpha}{\Delta\chi} \quad ; \quad 3)\ \underline{\frac{\partial P}{\partial T} = \frac{1}{V\cdot T}\cdot\frac{\Delta C_p}{\Delta\alpha}} \qquad (1)$$

The TS-sensor actually detects pressure variations (waves). The actual change in the pressure parameter (~ I in text) is then supposed to be proportional to the third relation given.

The thermal expansion is approximated by the model equation

$$\alpha = a+b\cdot T+\underline{d\cdot\frac{E}{kT^2}\exp(-E/kT)} \qquad (2)$$

Since the additional contribution (third term) is proportional to $1/T^2$ the working relationship for describing the relative change in heat capacity will be:

$$\underline{\Delta C_p \sim (\text{instr.factor.})\cdot(I/T)} \qquad (3)$$

REMARKS

The different origins of thermosonic signals are very difficult to interpret. To specify the main source process of the most effective thermomechanical coupling will therefore be the important and demanding challenge for the use of the TS-technique in the future. This investigation is a first-step contribution to clear that problem. The potentiality in answering such questions might further be a kind of frequency analysis of the TS-information related to well known processes and theory.

REFERENCES

1 K. Lønvik, Thermosonimetry, Thermochimica Acta, 110(1987) 253-264.