

SOME THERMOPHYSICAL PROPERTIES OF THE CHALCOGENIC GLASS $Te_{70}Ge_{10}As_{20}$

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The present paper describes the temperature dependence of the thermal diffusivity k , the thermal conductivity λ and the effective specific heat gc of the chalcogenic glass $Te_{70}Ge_{10}As_{20}$ in the temperature range including the transformation region, crystallization and melting. The nonstationary pulse method with a planar heat source was used in the arrangement for the measurement under dynamic conditions. The thermophysical characteristics were continuous and their changes in the transformation region were accounted for by the excitation of the thermal polymer $Te_{70}Ge_{10}As_{20}$ to rotating oscillations and by the partial destruction of its structure. The thermal diffusivity reflected very sensitively the changes of the microstructure of this chalcogenic glass.

1. INTRODUCTION

The investigation of the physical properties of the semiconducting chalcogenic glasses is very interesting from the theoretical and practical point of view. There has been no general theory of the amorphous solids so far. The existing Zachariassen hypothesis of the random network, the crystalline hypothesis, the aggregate one, the hypothesis of undercooled liquids and the polymer hypothesis do not describe all the varieties of the real existing glasses.

The diffraction analysis, the optical spectroscopy and the resonance methods inform only about the nearest neighbourhood of the investigated atom. It is just the thermophysical parameters that characterize the transport phenomena (the scattering, the generation, the diffusion and the recombination of photons). Therefore they can give information on the intermolecular bonds, on the structure of the substance and on the processes causing their changes.

The glass temperature T_g is related to the cooling rate $q = -dT/dt$, the mean relaxation time $\tau(T)$ and to the activation energy $V_g(T)$ of the system [1] if

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$$T = T_g \rightarrow q\tau = \frac{kT_g^2}{V_g} = const., \quad (1)$$

where k is the Boltzmann constant.

The glass process is the consequence of the interrelaxation relation between the cooling process (determined by q) and the retarded equilibrating (determined by τ). The glass temperature $T_g(q)$ is proportional to the cooling rate q .

In the real substances the glass transformation and softening do not occur at the limited temperatures T_g and T_w . The transformation is a progressive process in the anomalous so-called transformation region.

The glass form and other properties depend on the cooling rate q as well as on any heat treatment — the thermal history of a sample. At any moment and at the given temperature $T < T_g$ the investigated glass is found at a certain point of equilibrating. The final process of equilibrating is the crystallization of a undercooled highly viscous liquid.

The frequency of homogenous nucleation I (Fig. 1) may be expressed by [2]:

$$I = \exp \left[A - \frac{\Delta G_{visk}}{RT} - \frac{\Delta G^*}{RT} \right], \quad (2)$$

where A — the collision factor, ΔG_{visk} — the free activation energy for the viscous flow, ΔG^* — the free energy of the formation of the critical nucleus, R — the gas constant. The growth of crystals, determined by the velocity of crystallization $G(T)$ (the $G(T)$ formula is similar to the relation (2), Fig. 2) and by the existing nuclei, occurs theoretically at any temperature $T < T_g$

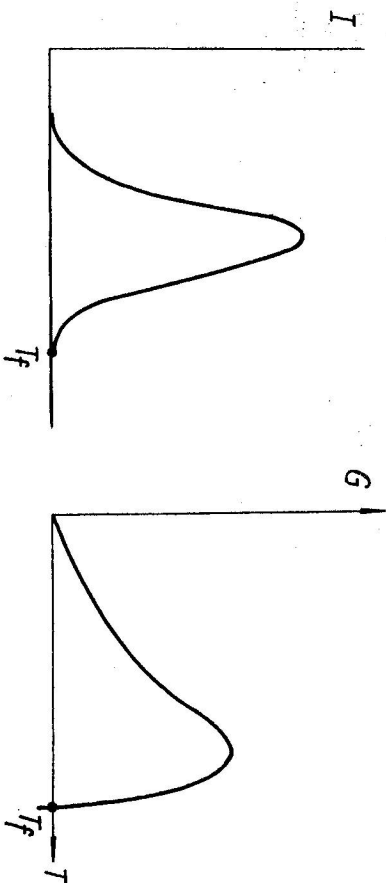


Fig. 1. The thermal dependence of the frequency of homogeneous nucleation in an undercooled liquid. Fig. 2. The thermal dependence of the velocity of crystallization.

and becomes negative at the melting temperature T_f . The superposition of the functions $I(T)$ and $G(T)$ determines the dependence of crystallization of a glass on the undercooling ΔT . In the many-component glasses the situation is often complicated [3]. Every component or crystalline modification has its own frequency I_i and velocity G_i .

In crystals in which the thermal current is carried by phonons, the thermal diffusivity k is given by the formula [4]:

$$k = \sum_j \int d\omega C_j(\omega) v_j l_j(\omega), \quad (3)$$

where $C_j(\omega) d\omega$ is the distribution of phonons of the polarization j and the frequency ω , $l_j(\omega)$ is their mean free path and v_j is the magnitude of the group velocity.

The phonon scattering is directly proportional to the defect contents in the crystal, the thermal diffusivity is in an inverse ratio to them. In [5] it is supposed that in the non-crystalline solids at low temperatures the relation (3) is valid too. Glasses might be similar to crystalline solids with very low values of l_j . Therefore it can be expected that in the transformation region the thermal diffusivity decreases because of the decomposition of the fixed structure of glass.

II. THE PREPARATION OF SAMPLES AND THE METHOD OF MEASURING

The chalcogenide system $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ (20g) was prepared from 99.999% pure elements with a 0.1 mg accuracy of weighing. Tellurium was distilled in hydrogen atmosphere and the arsenic annealed in air. The homogeneous mixture was prepared after an evacuation for 4 hours to 4×10^{-4} mm Hg and by fusion in a sealed quartz ampoule of the diameter of 10 mm for one hour at the temperature of about 900°C and for five hours at 1000°C. The tube was shaken several times during heating because of the homogenization of the sample. The melt was gradually cooled for 2 hours to 900°C and then rapidly by submerging ring the ampoule into water.

The glass made by the technology of fast cooling was very brittle and porous (air bubbles formed caused by the radial gradient of temperature, by the dilatation, by the presence of the gas phase and so on). The compact sample was prepared by pressing the glass powder of the mean particle size 100 μ into the rings of the quartz ampoule of the dimensions $\varnothing = 10$ mm; $x_1 = 3$ mm; $x'_1 = 1.83$; 1.85; 1.70 mm (see Fig. 3).

X-ray diffraction patterns were obtained in a Debye-Scherrer camera using $\text{CuK}\alpha$ radiation. The glass structure was confirmed at room temperature and the crystalline one after heating to 250°C. Temperatures T_w , T_x , T_f were

estimated by the differential thermal analysis DTA at the heating rates $W = 10^\circ\text{C}/\text{min}$ and $W = 4^\circ\text{C}/\text{min}$, using the DUPONT 900 Thermal Analyzer.

For the determination of thermophysical quantities of the $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ system the dynamic pulse method with planar heat source was used [6-9]; the arrangement is shown in Fig. 3.

The infinite isotropic and homogeneous system was simulated by the cylindrical sample (1) surrounded by two environments (2) of sufficient dimensions from the same material as the sample. The whole system was surrounded by corundum powder. The planar heat source (3) giving a one-directional heat flow [8] was on one side of the sample and the thermocouple Te_2 (4) was on the opposite side at a precisely defined distance x . The other weld of the thermocouple was in the differential sample (5) made from the same material under thermal conditions equivalent to those of the measured sample but without the active heat source (eventually with the same heat source off).

From the analysis of the distribution temperature function in our samples the relations for the thermal conductivity λ , the thermal diffusivity k and the effective thermal capacity ρc were obtained [6].

The real process in the sample is a superposition of the linear increase of the temperature T_0 in the furnace at the rate W and of the pulses generated from the heat source and described by the temperature function [6].

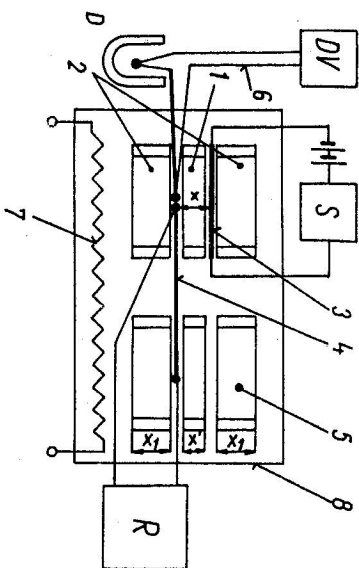


Fig. 3. The arrangement of the dynamic pulse method: 1 — The particular sample in the ring of a quartz ampoule of the thickness x ; 2 — the environment from the measured material in the ring of the quartz ampoule of the thickness x_1 ; 3 — the planar heat source (0.1059 cal/cm²) [10]; 4 — the thermocouple Te_2 ; 5 — the differential sample; 6 — the thermocouple Te_1 for the measurement of the temperature T_0 ; 7 — the furnace for the linear increase of the temperature T_0 [10]; 8 — the ceramic tube filled with corundum powder; 9 — the could junction of the thermocouple Te_1 in the Dewar; DV — the digital millivoltmeter; S — the switch for the rectangular pulse [10]; R — the recorder.

The derivation of these pulses supposed the temperature T_0 to be constant during the time t_m of the transport of the thermal pulse from the source to the indicator. Therefore the rate W must be negligible compared with the velocity of the propagation of the pulse. Eventually the values of quantities k, λ, gc characterize the interval $\langle T_0; T_0 + Wt_m \rangle$.

The temperature of the furnace T_0 was recorded by the thermocouple T_{e1} (Fig. 3, 6). The other weld of T_{e1} was in a Dewar flask (D) filled with water of a known temperature. The time of the maximum temperature response t_m at the pulse measuring did not exceed 30 seconds for all measurements. The values of the thermophysical quantities were determined in the interval $\langle T_0; T_0 + 0.38^\circ\text{C} \rangle$ maximally ($W_{max} = 0.75^\circ\text{C}/\text{min}$).

The thermocouples were made from 0.1 mm Cu and 0.075 mm constantan wires. Their calibration curve [10] was obtained by measuring the melting endotherms of 99.999% pure second class normals — In, Sn, Pb, Cd — in the simple DTA apparatus.

To obtain the temperature dependences of the thermophysical quantities from the investigated temperature range between room temperatures and the melting ones of the sample (367°C), was relatively time-consuming (15–30 hours). On the other hand this time is much shorter than that of the stationary, eventually the quasi-stationary method.

The applied methods allow to determine the three thermophysical quantities k, λ, gc at a given temperature with the help of one measurement and allow to measure the temperature dependence in sufficiently fine steps of ΔT , which is necessary for a detailed study of the transformation, crystallization and melting ranges of materials.

One of the advantages of the planar heat source is the following: The heat of the source does not cause a local heating but a homogeneous linear thermal flow.

The theory of the pulse method with a planar heat source supposes an infinite sample, an infinitesimally thin heat source, an ideal thermal contact and an infinitely short heat pulse. The correction necessary because of all the disturbing factors of the measurement was made in accordance with [6]. With respect to the analysis of accuracy of this type of measurements [9], our measurement involved an error of 5%.

III. THE MEASURED RESULTS AND THEIR INTERPRETATION

In the present paper there were investigated the temperature dependences of the thermal conductivity λ , the thermal diffusivity k and of the effective specific heat gc in the temperature region $\langle 20; 367 \rangle^\circ\text{C}$. The dynamic pulse method with a planar heat source was used. The three measurements with different heating rates are illustrated by graphs: $W_1 = 0.75^\circ\text{deg}/\text{min}$, $W_2 =$

$= 0.40^\circ\text{deg}/\text{min}$, $W_3 = 0.21^\circ\text{deg}/\text{min}$. The fourth measurement with the rate of $W_4 = 0.75^\circ\text{deg}/\text{min}$ was carried out on the third sample, which had crystallized during a previous experiment. From the obtained characteristics we can deduce the following:

The thermal dependences of the parameters k (Fig. 4), gc (Fig. 5), λ (Fig. 6) of the glassy and the crystalline $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ differ greatly but both types of curves are typical.

All three quantities k, λ, gc indicate one softening region (e.g. Fig. 7) $T_w \in \langle 125; 150 \rangle^\circ\text{C}$, one region of pronounced crystallization $T_x \in \langle 170; 230 \rangle^\circ\text{C}$ and the melting temperature $T_f = 367^\circ\text{C}$ in the investigated temperature range.

The thermal diffusivity k (Fig. 4) of the glassy sample practically does not depend on temperature. In the softening region it decreases by 34% and in this way it forms a typical "S"-type transition. In the undercooled liquid in the low value of the thermal diffusivity at the beginning does not depend on temperature, then — during the crystallization — it increases more than twice. When the crystallization ends, the quantity k again does not depend on temperature, only in the melting range k suddenly drops.

The effective thermal capacity gc (Fig. 5) shows a very pronounced anomaly in the interval $\Delta T = 30^\circ\text{C}$ of the softening region and it increases continuously by as much as 40%. This increase is partially caused by the "false maximum" depending on the dynamic cycle of the measurement, i.e. by the difference between the actual and the fictitious temperature in the sample. The false maximum is not observed if either the measurement is performed in the cooling cycle, or the quasi-stationary method is used [11].

It is shown in [3] that values T_w and T_x are dependent on the composition of the Te-Ge system. The width of the range of the linear temperature dependence of the specific heat — the so-called plateau — is determined by T_w and T_x . From our experimental results $gc(T)$ and from [12] it follows that the chalcogenite glass $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ has one crystallization region so close to the transformation region that we have not been able to measure any plateau with the help of the applied method.

With regard to the relation $\lambda = kgc$ the thermal conductivity λ (Fig. 6) is calculated from the experimentally obtained functions k, gc .

Fig. 7 illustrates the reciprocal relations among the relative values of the thermal quantities. The heating rate W_2 is used. The transformation and crystallization regions of the functions f_1, f_2, f_3 are approximately identical.

In our pulse measurements no influence of the heating rate W on the temperature T_w — according to [1] has been observed, because of the interval $W_1 - W_2$ and the used evaluating methods. That temperature of the crystallization increases remarkably with the heating rate W (see Fig. 5), the

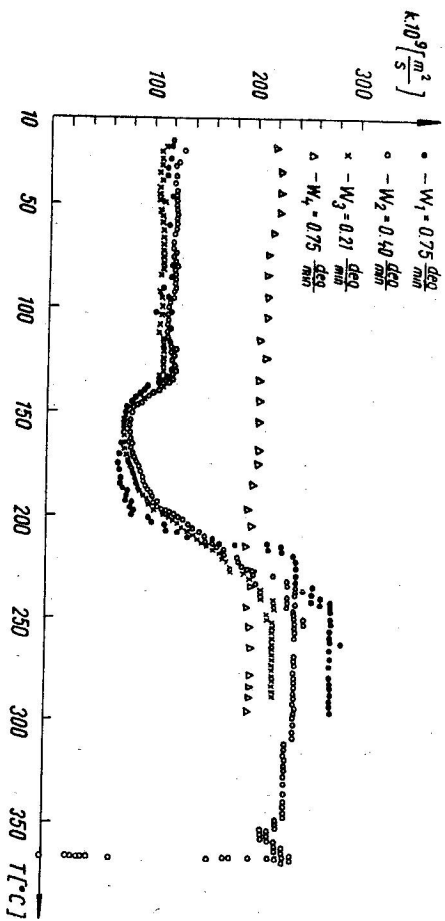


Fig. 4. The temperature dependence of the thermal diffusivity of the glassy and the crystalline $\text{Te}_{0.6}\text{Ge}_{0.4}\text{As}_{80}$ (● — $W_1 = 0.75$ deg/min, ○ — $W_2 = 0.40$ deg/min, x — $W_3 = 0.21$ deg/min, Δ — $W_4 = 0.75$ deg/min).

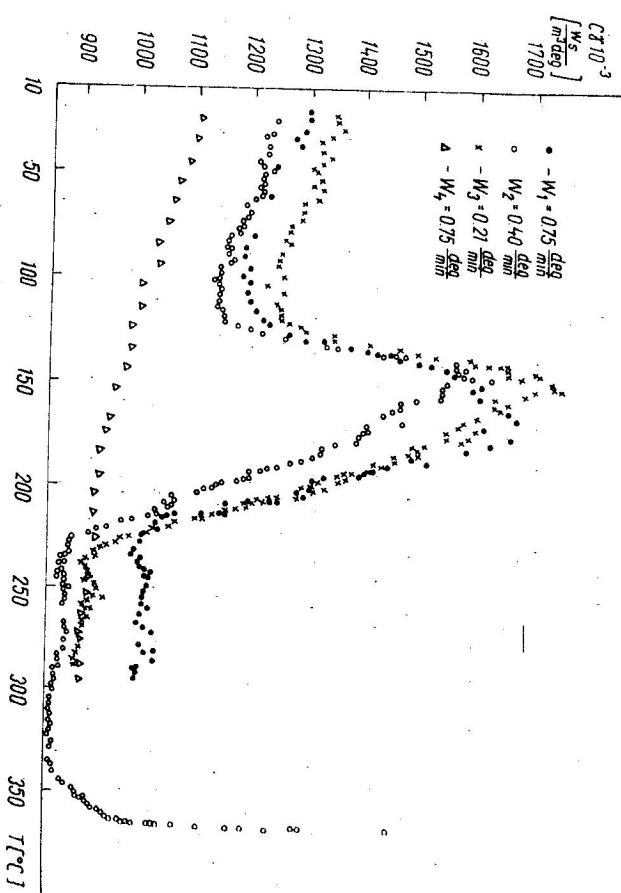


Fig. 5. The temperature dependence of the effective thermal capacity of the glassy and the crystalline $\text{Te}_{0.6}\text{Ge}_{0.4}\text{As}_{80}$ (● — $W_1 = 0.75$ deg/min, ○ — $W_2 = 0.40$ deg/min, x — $W_3 = 0.21$ deg/min, Δ — $W_4 = 0.75$ deg/min).

shift of the inflex point in the obtained curves in the crystallization regions and the results in [12]).

The thermal dependences of the thermal quantities are in the interval between the room temperatures and the softening region linear and reproducible. A remarkable increase of the dispersion is probably caused by the deformation

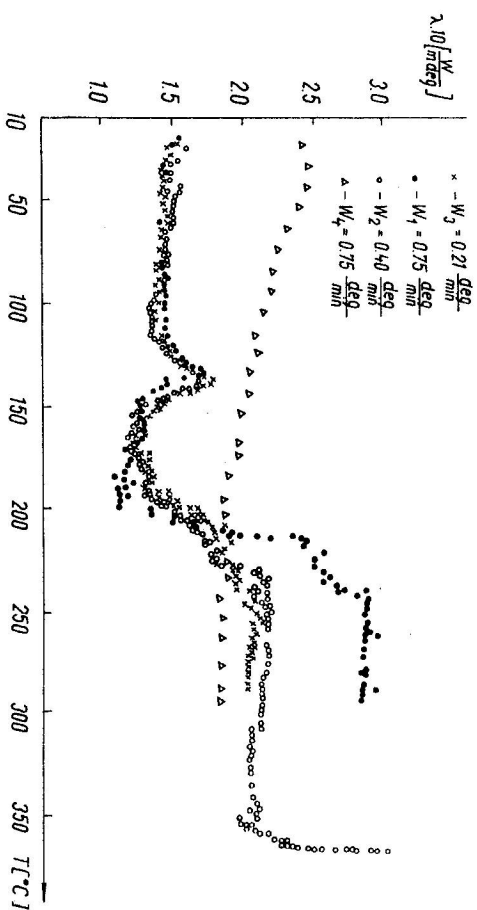


Fig. 6. The temperature dependence of the thermal conductivity of the glassy and the crystalline $\text{Te}_{0.6}\text{Ge}_{0.4}\text{As}_{80}$ (● — $W_1 = 0.75$ deg/min, ○ — $W_2 = 0.40$ deg/min, x — $W_3 = 0.21$ deg/min, Δ — $W_4 = 0.75$ deg/min).

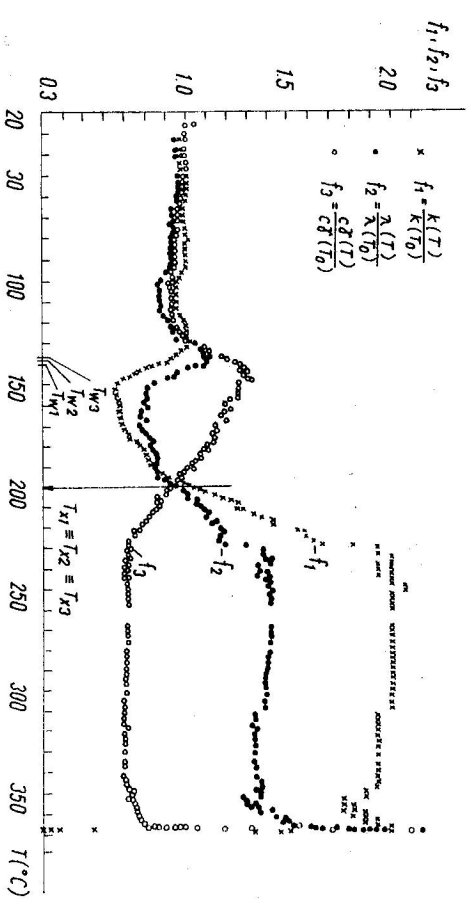


Fig. 7. The temperature dependence of the relative changes of the thermal diffusivity, the thermal conductivity and the effective thermal capacity.

of the sample above the temperature T_w in the highly viscous state and by the deformation during crystallization. The process of crystallization is greatly influenced by the thermal history of the sample, which is verified by the measurement with the heating rate W_1 : A small defect in the linear heating at 214°C causes changes in the development of all further crystallization.

All absolute values of the investigated thermophysical parameters are influenced by the change of magnitude of the contact resistance and so on.

With reference to [13] the chalcogenic glass $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ is a high polymer substance. It differs from the crystalline one in that its chains not parallel but they are disordered or form groups. The structure of such thermal polymer grows in a glass melt by the so-called undercooled polymerization in the temperature range between T_r and T_g .

By [14] below the temperature T_w the polymer molecules practically only oscillate in a linear polarised transversal way. The specific heats of the crystalline and glassy samples are nearly of the same magnitudes. Below the temperature T_w the amorphous polymer is in the state of an undercooled melt with a fixed structure. Near the temperature T_w the polymer units are excited to "rotating oscillations", which causes an increase of the interatomic distances. There is a difference between the polymers with chemical bonds and the thermal polymers. Among the chains of the thermal polymers there act secondary bonding forces. They are in the order of molecular interchain forces. Therefore the destruction of a thermal polymer occurs already closely above the temperature T_w . The destruction and rotating oscillations excite new "oscillators", therefore the specific heat of polymer glass increases intensively (Fig. 6).

In the softening region the fast decrease of the thermal diffusivity k (Fig. 4) is caused by a decrease of intermolecular bonds, by an increase of the scattering processes in consequence of the excitation of rotating oscillations and the thermal depolymerization.

The thermal conductivity λ of the chalcogenic glass $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$ (Fig. 5) has a different slope from that of the crystalline dependence $\lambda(T)$, but both conductivities coalesce near the melting temperature T_f . The existence of the characteristic maximum of thermal conductivity at the temperature T_w was confirmed. The maximum is determined from the relation $\lambda = kgc$, where c increases more sharply than k decreases [14].

IV. CONCLUSION

Finally it is necessary to say that the existing data concerning glasses are still not complete. Therefore the interpretation of the obtained quantities of such a thermal system is as yet very difficult.

Considering the required dimensions of samples it is comparatively difficult to produce the chalcogenic glass $\text{Te}_{70}\text{Ge}_{10}\text{As}_{20}$. In this work the variations of the thermophysical quantities as functions of temperature are investigated by the dynamic pulse method using a planar heat source. Our experimental results are in quantitative agreement with measurements obtained on other glasses. It has been shown that:

1. Softening and crystallization are not point phenomena but in the investigated chalcogenic glass they are realized in the temperature ranges of $T_w \in \langle 125; 150 \rangle^\circ\text{C}$, $T_x \in \langle 170; 230 \rangle^\circ\text{C}$.
2. The functions $k(T)$, $\lambda(T)$, $gc(T)$ are continuous in these ranges.
3. The thermophysical parameters — especially the thermal diffusivity k — detect sensitively the changes of the microstructure of glasses.
4. The processes of softening and crystallization are influenced by the magnitude and linearity of the heating rate in the sample.

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