SOFTENING AND CRYSTALLIZATION KINETICS OF Ge-S SYSTEM GLASSES

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The dynamical method with a planar pulse heat source was applied to the investigation of the temperature dependences of the heat capacity ratio $\varrho C(T)/\varrho C(T_0)$ and the thermal diffusivity ratio $k(T)/k(T_0)$ of powdered glassy and crystalline samples of $GeS_{1.25}$, $GeS_{1.3125}$, $GeS_{1.375}$, $GeS_{1.4375}$, and $GeS_{1.5}$, at temperatures ranging from room temperature up to the melting points. The thermal behaviour of Ge-S glasses was also studied by DTA. The evolution kinetics of an undercooled liquid formed during softening in a temperature range above 325 °C and crystallizing in two stages at temperatures above 380 °C and 450 °C, respectively, has been recorded in detail by $k(T)/k(T_0)$ and $\varrho C(T)/\varrho C(T_0)$ dependences as well as by DTA. With an increasing sulphur content in the glass the softening and mainly the low temperature crystallization temperature have increased.

КИНЕТИКА РАЗМЯГЧЕНИЯ И КРИСТАЛЛИЗАЦИИ СТЁКОЛ СИСТЕМЫ Ge-S

В работе исследована температурная зависимость относительной теплоёмкости $\varrho C(T)/\varrho C(T_0)$ и относительной температуропроводности $k(T)/k(T_0)$ порошкообразных стекловидных и кристаллических образцов $GeS_{1.25}$, $GeS_{1.3125}$, $GeS_{1.375}$, $GeS_{1.4375}$ и $GeS_{1.5}$, в интервале температур от комнатной температуры до температуры плавления. Исследование проводилось с помощью динамического метода с плоским пульсирующим источником тепла. Термические свойства стёкол Ge-S изучались также с помощью метода дифференциального термического анализа. Зависимости $k(T)/k(T_0)$, $\varrho C(T)/\varrho C(T_0)$ и метод дифференциального термического анализа детально воспроизводят кинетику переохлаждённой жидкости, которая возникает при размягчении в области температур свыше 325 °C и двухстадийного перехода в кристаллическое состояние при температурах свыше 380 °C и свыше 450 °C соответственно. Температуры размягчения и в первую очередь температуры низкотемпературной кристаллизации с возрастающим содержанием серы в стёклах повышаются.

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I. INTRODUCTION

It has been shown lately that chalcogenide glasses form a separate subgroup among all glassy materials. The glassy state of these systems is due to chains of non-chalcogenide elements (Ge, Si, C, As, P, B, etc.) which can form, when combining with chalcogenides, several characteristic structural figures only [1]. The practically used ternary and multicompound chalcogenide systems are formed by adding specific elements or by combining these basic units. Therefore, the study of any binary chalcogenide system (e.g. Ge-S) yields valuable informations about the properties of the basic structural units of more complex systems[1] and, simultaneously, it enables to investigate properties common to all binary chalcogenide glasses.

Among the chalcogenide binary glasses much attention is paid especially to the Ge-S system. Here occur — similarly as in the Ge-Se system [3] — two glass-forming regions [4, 5, 6]. The published references dealing with the determination of the size of these regions exhibit great differences caused by differing conditions during the glass preparation, by a different purity of the raw material, the choice of the identification method, etc. DTA measurements [6, 7], thermal expansion, extraction of S_8 molecules in CS_2, Vickers hardness, density, IR, optical and photoelectrical properties measurements [8, 9], electrical properties [10] and the study of the radial distribution function [5, 11] show that there are relatively simple covalent bounds in the whole system, however, the glasses in these two regions do not have the same structure.

In GeS_x glasses with a sulphure content $1 < x < 2$ the occurence of two components, namely GeS_2 and GeS, is assumed, thus yielding two basic structural units: a GeS_2 tetrahedron and a GeS_8 octahedron. In this region the structural glass model is the network modifier model. Crystallographically GeS_2 is isostructural matter with an SiO_2-like 3-dimensional structure. It consists of GeS_2 tetrahedrons. The crystalline structure of GeS is of the type of a deformed NaCl lattice. It consists of GeS_6 octahedrons. It has been shown that in these glasses GeS is a covalent bond type with non-crystalline-like bonds. The RDF analyses of just this compound are ambiguous. Either the random covalent model or the threefold coordinate model is suggested for the structure of an amorphous GeS_x [5, 11]. Then a glassy material from the region of GeS_x (where $1 < x < 2$) could form a continuous structural pattern of the SiO_2-RO type (RO being e.g. MgO, CaO, etc.), where GeS_2 represents the basic glass structure modified by a glassy GeS, or the alloy could be phase separated to a glassy dichalcogenide with an SiO_2-like atomic arrangement

[1] For instance, in the Cu-Ge-S system — where a glass can be phase separated and the new low-temperature phase has a crystallization reaction below the matrix softening temperature, thus creating an advantageous memory effect [2].

and a threefold coordinated monochalcogenide. Because of the simultaneous occurrence of two different structural motives (GeS_2 and GeS) and the fact that in the region with a chemical composition between pure GeS_2 and GeS the glass-forming ability of the system is higher [6], one can expect the whole glass to be inhomogeneous. The probability of phase separation is also increased by the shape of the system phase diagram in this region [6] and the non-linear dependences of many physical parameters (e.g. softening temperature or density) on the composition.

The investigation of the temperature dependence of thermophysical properties of the above mentioned class of glasses (i.e. GeS_x systems with $1 < x < 2$) when we use the nonstationary pulse method and DTA enables to record in detail the evolution kinetics of the formed undercooled liquid thus extending the experimental knowledge about the binary Ge-S system.

II. METHODS AND EXPERIMENTAL RESULTS

II. 1. Preparation of the glasses

Chalcogenide glasses of nonstoichiometric composition, namely $GeS_{1.25}$, $GeS_{1.3125}$, $GeS_{1.35}$, $GeS_{1.375}$, $GeS_{1.42}$ and $GeS_{1.5}$ were prepared. Powdered germanium of $5N$ purity ($\varrho = 30\ \Omega$ cm, manufactured by VEB — DDR) and highly pure $6N$ sulphur (sublimated several times, made in Koch Light Lab. Ltd., London) were synthetized and homogenized in an evacuated quartz ampoule ($\varnothing = 9$ mm or $\varnothing = 4$mm for $GeS_{1.25}$) for 2.5 hours at a temperature of 950 °C.

The melt was mixed several times by shaking the ampoule. The system was always freely cooled in air, glasses of the $GeS_{1.25}$ composition were rapidly cooled by immersing the ampoule into water at room temperature. Especially the samples with the $GeS_{1.25}$ composition had often crystalline inclusions in the glassy matrix. They were excluded from our investigation. The glassy material prepared in this way was pulverized.

II. 2. Differential thermal analysis

The samples were tested by the DTA method the DSC cell of the DUPOND 900 Thermal Analyzer. Powdered ~20 mg samples were heated in aluminium pots at a rate of 10 °C/min in air. The empty aluminium pot was used as a reference sample.

Fig. 1 shows the DTA curves from room temperature up to 550 °C recorded in air of the following samples: B — $GeS_{1.5}$, C — $GeS_{1.42}$, D — $GeS_{1.375}$, E — $GeS_{1.35}$,

Fig. 1. DTA curves. A — crystalline $GeS_{1.375}$, B — glassy $GeS_{1.5}$, C — glassy $GeS_{1.42}$, D — glassy $GeS_{1.375}$, E — glassy $GeS_{1.35}$, F — glassy $GeS_{1.3125}$, G — glassy $GeS_{1.25}$ (heating rate ~10 °C/min, in air).
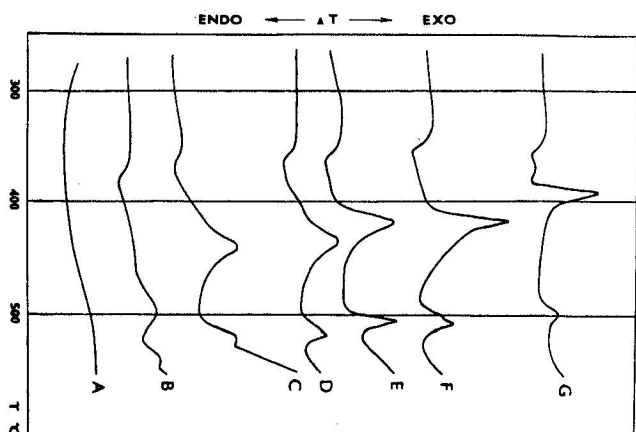
F — $GeS_{1.3125}$, G — $GeS_{1.25}$. The DTA B—G curves confirmed the glassy state of the samples. One softening region was recorded starting at the given heating regime at $T_g \sim 335$ °C (for $GeS_{1.25}$). With an increasing sulphur content the transformation region shifts up to $T_g \sim 350$ °C (for $GeS_{1.5}$). With further heating exotherms corresponding to two crystallization stages of the investigated material were observed. The increasing content of sulphur strongly shifts especially a low-temperature crystallization exotherm, which in some samples of $GeS_{1.5}$ — in contrary to the data published by Hruby [6] — merges in a high temperature crystallization.

In Fig. 1 curve A corresponds to a $GeS_{1.375}$ sample measured for the second time. We assume that the sample has crystallized in the whole volume during thermal treatment in the first measuring cycle — denoted as D — and the immediately following slow cooling. It does not involve any softening region nor crystallization regions of the undercooled liquid.

II. 3. Thermal diffusivity and heat capacity measurements by the pulse methode

The temperature dependence of the thermal diffusivity k and the bulk heat capacity ϱc of the glasses were measured by means of the non-stationary pulse

method described in [12, 13]. The method enables to determine both isothermally and nonisothermally the influence of temperature on the investigated structure. It allows a quasicontinous observation of softening, crystallization, melting and kinetics of glassy materials.

A planar pulse source was used. It consists of a net made of a Pt wire of the diameter $\Phi = 0.05$ mm. The temperature of the sample was recorded by a Pt-PtRh thermocouple with the diameter $\Phi = 0.1$ mm. The response of the thermal pulse was recorded by a differential thermocouple made of a Nickel-Nickelchrome wire with the diameter $\Phi = 0.1$ mm.

Powdered Ge-S system samples ($\Phi = 10$ mm, $x = 1.8$ mm, $x' = 3$ mm, [12]) put into corundum powder underwent a measuring cycle in an oven where the temperature increased quasi-linearly from 20 °C up to about 550 °C at the rate $W \sim 0.85$ °C/min. Samples with a holder in the same arrangement as in the oven
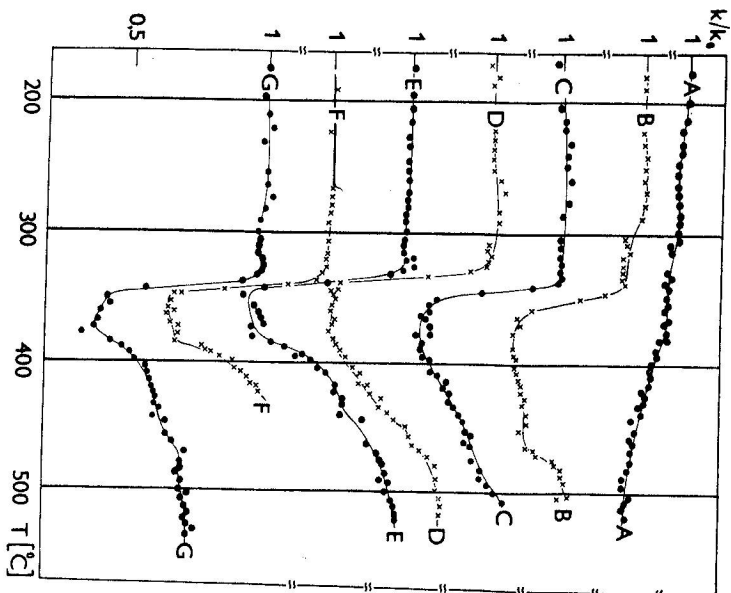
were freely cooled down to room temperature. Then, the measuring cycle was repeated with the obtained crystalline samples.

Our apparatus enables measuring within <1 % error [13]. The scatter of the measured data is due to the temperature instability at the measurement. With increasing temperature the scatter increases due to air flow. In the transformation region the scatter is caused by the pooring together of grains as well as by severe changes in the thermal parameters.

Figs. 2 and 3 show the corresponding temperature dependences of the thermal diffusivity ratio $k(T)/k(T_0)$ and the heat capacity ratio $\varrho c(T)/\varrho c(T_0)$, respectively, ($\varrho$ being the density and c denoting the specific heat) for $GeS_{1.25}$ (curves G), $GeS_{1.3125}$ (curves F), $GeS_{1.35}$ (curves E), $GeS_{1.375}$ (curves D), $GeS_{1.42}$ (curves C), and $GeS_{1.5}$ (curves B) glasses. The A curves in both figures (similarly as the A curve in Fig. 1) present the thermal behaviour of a $GeS_{1.375}$ crystalline sample crystallized

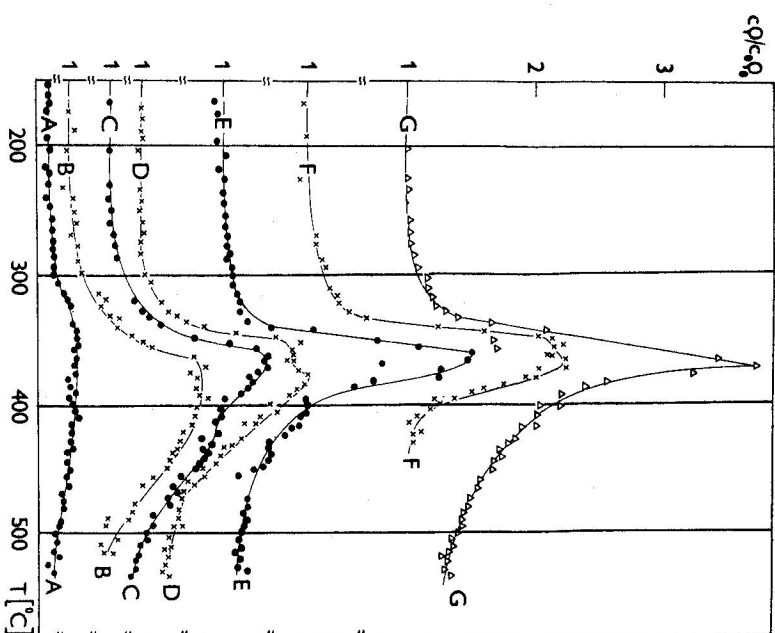Fig. 2. Temperature dependences of thermal diffusivity ratio. A — crystalline $GeS_{1.375}$, B — glassy $GeS_{1.5}$, C — glassy $GeS_{1.42}$, D — glassy $GeS_{1.375}$, E — glassy $GeS_{1.35}$, F — glassy $GeS_{1.3125}$, G — glassy $GeS_{1.25}$ (heating rate ~ 0.85 °C/min, in air).

Fig. 3. Temperature dependence of heat capacity ratio. A — crystalline $GeS_{1.375}$, B — glassy $GeS_{1.5}$, C — glassy $GeS_{1.42}$, D — glassy $GeS_{1.375}$, E — glassy $GeS_{1.35}$, F — glassy $GeS_{1.3125}$, G — glassy $GeS_{1.25}$ (heating rate ~ 0.85 °C/min, in air).

during the measuring cycle D. The symbols $k(T_0)$ and $\varrho c(T_0)$ denote the thermal diffusivity and the heat capacity of a sample at 200 °C in the given arrangement, respectively. All temperature dependences of one ratio are shown in one figure, with a y-shifted scale.

III. DISCUSSION

The quasicontinuous temperature dependences of the thermal diffusivity k and the heat capacity ϱc of glassy materials in transformation regions are at present not known. The analysis of such dependences is limited by the scatter of measurements which in the transformation regions — due to fluctuations — increases.

The thermal diffusivity k is a parameter that immediately reflects microprocesses in the structure of materials. For the thermal diffusivity k we can write

$$k = \frac{1}{3} v_c l,$$

where v_c denotes sound velocity in the studied medium and l is the phonon free path.

In the transformation region — where with increasing temperature a severe drop in the viscosity of glasses appears — the values of the easticity coefficient decrease [14]. This decrease causes a drop in the sound velocity in the glasses and, consequently, a drop in the phonon velocity v_c. The phonon free path in this tepmperature region is determined by the phonon-phonon interaction, and it is of the order of interatomic distance [15]. Thus, during softening a drop in thermal diffusivity appears due to a decreased phonon velocity.

In the crystallization temperature region both the free path and the velocity of phonons increase due to an increasing order and a strengthening of bonds in the crystalline region. Therefore, there is a increase of thermal diffusivity in this temperature region.

The heat capacity ϱc measurements (ϱ being the density and c being the specific heat of glassy materials) exhibit during softening and /or glass formation non-equilibrium effects connected mainly with a time-dependent configuration displacement of molecules. At temperatures sufficiently lower than the transformation temperature T_g the configuration is frozen and the equilibrium is characterized by the glass heat capacity. This is, at very low temperatures, often similar to the heat capacity of crystals with a chemically identical composition. At temperatures higher than T_g the changes in configuration are so fast that their time dependence cannot be measured and the liquid possesses a certain equilibrium heat capacity. In the transformation region the heat capacity contribution corresponds to the changes in the motion modes (rotations or translations), and it is much smaller than the contribution due to configuration displacements (creation of holes and others).

In order to describe the time dependence of the heat capacity in the transformation region it is necessary to employ non-isothermal kinetics laws. So far no detailed theory has been developed. A very good description of these processes is provided by the kinetic hole theory of liquids and glasses [16]. The liquid (or glass) is considered as a quasicrystal with some molecules in the lattice sites and many unoccupied ones (i.e. holes). The equilibrium number of holes is given by temperature. The heat capacity increment $\Delta(\varrho c)$ caused by configurational displacement is equal to zero both above and below the transformation temperature, where it reaches a sharp maximum. During crystallization the value of the heat capacity is decreased by a configurational displacement contribution. In these crystalline regions the heat capacity is given by vibrational modes.

The analysis of the temperature dependences of thermophysical parameters measured by non-stationary pulse method with a planar source confirms in all glassy samples the above mentioned anomalous behaviour of the thermophysical properties (Figs. 2, 3). The softening and crystallization regions of a particular glass can be compared with the curves of DTA. The measured thermal diffusivity course in the GeS$_{2.5}$ sample (Fig. 2, curve B) confirms that in the course of the measuring cycle the sample softened near the temperature $T_g \sim 325 \div 350$ °C. With increasing temperature the undercooled liquid gradually became crystalline in two stages: at temperatures $T_{x,1} > 380$ °C and $T_{x,2} > 450$ °C, respectively. The absolute values of the heat capacity changes $\Delta(\varrho c) \sim 310$ % are also in the transformation region and at crystallization greater than the thermal conductivity changes ($\Delta k \sim 62$ %). The G—B curves in Figs. 2 and 3 (as well as in Fig. 1) show that with an increasing sulphur content in the samples the transformation temperature T_g and also the crystallization temperature region arise. In some samples the second crystallization is less pronounced because of an increasing scatter of measurement in the crystallization temperature region. In all the figures the A curves present the properties of crystallized powdered samples.

The analysis of DTA curves published for the same materials by various authors ([6, 7], Fig. 1) shows that the basic features characterizing the material are identical. The samples differ especially in the temperature region that characterizes the development of the undercooled liquid. We have found that these anomalies are influenced by the raw material purity, the size of the ampoule, homogenization and cooling methods, etc. Similar properties of glasses are mentioned in [6].

The relations between the temperature region of important structural changes (transformation region, crystallization region) in each investigated material as well as the course of these changes obtained by the DTA are in agreement with the measured courses of thermophysical quantities by the pulse method. The absolute values of softening and crystallization temperatures are functions of the glass heating rate during the experiment [17]. This explains the shift in these temperatures to lower values compared to the temperatures obtained from DTA.

The character of the observed structural changes in the Ge-S glasses yields the following conclusion. With increasing temperature the glasses pass through the softening point into the state of the undercooled liquid and then crystallize in two self-contained phases identified as GeS and GeS$_2$ [7]. In the transformation region the thermal diffusivity decreases due to the drop in phonon velocity. During crystalization the thermal diffusivity arises due to an increased velocity and the free path of phonons. In the range of the transformation temperature the heat capacity intensely increases due to configurational changes in the glass.

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