The concept of polymer nano-heteromorphic structure and relaxation of the glass-forming substance by chalcogenides, oxides and halides example. Some results and perspective

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The concept of polymer nano-heteromorphic structure and relaxation of the glass-forming substance considers the glassforming systems comprised of one or more components. The concept of polymer-polymorphoid structure and relaxation of one-component glass-forming substances (or an individual chemical substance (ICS), element or chemical compound) is the unique focus of this concept. One-component glass and glassforming liquid was constructed from co-polymers in varying degrees polymorphoids or crystal structure nano-fragments of different polymorphic modifications (PMs), which do not have translational symmetry (long-range order), but having short and intermediate-range (medium-range) orders. Polymorphoids may be missing (non-polymorphoids glass) in the glass containing more than one component. There is a genetic relationship between the glass and its crystal and liquid analogues, which has been manifested in the response to the external influences. The main feature of such glass reaction containing various PM polymorphoids was their inter-conversion, which is analogous to the inter-conversion of polymorphic modifications in the crystalline substance. This feature makes it possible to quantify the structure nano-diagnostics in glasses containing PM polymorphoids and determine their concentration ratio (CRP) for example for such compounds as S, Se, GeS_2, $GeSe_2$, As_2Se_3, B_2O_3, SiO_2, GeO_2, H_2O, $BeCl_2$ etc.

1. Introduction

In our opinion, the key to the most objective solution to the glass-forming substance structure and relaxation problem is the main rule of physico-chemical analysis. The Kurnakov-Tananaev's rule reads as follows: the properties of substance are a function of their most fundamental physical and chemical properties such as chemical composition, structure, dispersion [1, 2]. In turn, the structure of substance is a function of their chemical composition and dispersion.

The goal of this work is to analyze the structure of the glass-forming substance in a liquid, viscous and solid, as well as the structural changes in the process of relaxation of the substance. Relaxation of substance is a transition from one equilibrium state at ambient conditions (temperature, pressure, exposure to light, and others.) to an equilibrium state at the other conditions. Relaxation occurs under both the decrease of the intensity of external effects (temperature, pressure, etc.) and the increase of intencity. During the transformation of the external conditions, the substance tends to reach equilibrium, which characterizes the external exposure at any specific time. The main attention in this work is paid to two types of glass-forming substance relaxation and the corresponding changes in its structure. The first type is the relaxation of the cooling glass-forming melt until its solidification with the subsequent aging of the formed glass and then possible crystallization. The second type is the relaxation under the heating of a solid glass-forming substance that accompanies devitrification, the formation of a viscous-flow of liquid, possible crystallization, and the subsequent transition into a liquid state. Examples of the glass-forming substance relaxation under the effect of the photo irradiation have been presented. All kinds of glass-forming substance relaxation were associated with parallel changes in its structure, with reversible transitions such as equilibrium liquid - viscous liquid, viscous liquid - solid glass, liquid - crystal. The notions, as a relaxation and a structure in a glass-forming substance, are inseparable. Therefore, these notions are close in the concept title and they reflect equally the essence of the phenomenon, which is the glass-forming substance.

2. The existing concepts of glass-forming substance structure

Critical analysis of numerous works, most of which reflect the following models and concepts of glass structure, which preceded the concept of heteromorphic polymer nano-glass structure creation:

- crystallite hypothesis - Frankenheym (1835) [3], Lebedev (1921) [4],

- polymeric concept - Mendeleev (1864) [5], Sosman (1927) [6], Tarasov (1959) [7],

continuous disordered network concept - Zachariasen (1932) [8],

- polymer-crystallite concept - Poray-Koshits (1959) [9],

- concept of complexes - Krogh-Moe (1965) [10],

clusters of structurally independent polyforms concept - Goodman (1975) [11],

- chemically ordered continuous random network concept - Lukovsky and Hayes (1979) [12].

The analysis of these concepts has been given in [13-15]. The provisions presented in these concepts have revealed a number of objective aspects of the glass structure and at the same time, many do not agree with the experimental data nor explain some of the phenomena observed during relaxation of the glass-forming substance.

One of these provisions contained in the Frankenheym, Lebedev, Poray-Koshits, Goodman concepts, as well as other researchers, in particular, Randall et al. [16] is the following. The glass is composed of randomly arranged, extremely small crystals (crystallites), as evidenced by the broad diffuse rings in their X-ray diffraction patterns, while crystallite material is characterized by clear rings. This point of view was refuted by Warren [17]. He has showned that the observed broadening lines in the diffraction patterns is possible only when assuming the crystalline size is slightly greater than the size of the unit cell, i.e., "crystallite," which in glass has no translational symmetry, and does not have a crystal. The enumerated above concepts have been devoted mainly to the single-component glass- forming individual chemicals.

In the late twentieth century, there are three new structure concepts (models) relating mainly to a multicomponent oxide glass, which continue to develop at the present time.

1. The concept of the chemical structure of glasses has been developed by Shahmatkin, Vedishcheva and Wright. It emphasizes the important role of structural and super-structural units and allows the setting of the quantitative relationships between structure and properties of multi-component oxide glasses [18]. The concept is based on the thermodynamic approach, using experimental data and X-ray scattering, NMR, EPR, IR and Raman spectroscopy in the glasses and crystals study.

2. The constant stoichiometry groupings (CSG) concept of oxide glasses has been developed by O. Yanush et al. It allows the predicting of the existence of new crystalline compounds with a corresponding symmetry of these groupings, to determine the partial properties of CSG, and calculate the dependence of the refractive index, density and linear expansion coefficient of the composition [19]. The concept is based on the analysis of the glass forming substance Raman spectra.

3. The analysis of the atomic structure of glass with the use of a fragmentary model developed by Aleinicova et. al. [20] shows by comparison of the experimental and model functions of atom radial distriction (RDF), that the glass contains groups similar to those in the crystalline phase. The model considers not only the multi-component, but also one-component glass compositions (SiO_2, As_2S_3).

These concepts are consistent with a number of the available experimental data, but they do not take into account the effect of the polymorphism on the glass-forming substance formation and properties.

3. The concept of polymer nano-heteromorphous structure and relaxation of the glass-forming substance

The appearance of the concept relates to the 1980 - 1990 decade of the last century [13, 21-23]. The original concept was known as the concept of "polymer polymorphous-crystalloid glass structure" [23].

Nano- heteromorphism is the concurrent existence of different structural fragments of the nanometric scale without translation symmetry (long-range order) in glass [24]. The concept of polymer nano-heteromorphous structure and relaxation of the glass-forming substance considers two types of structural fragments: (1) fragments, which are characterized only by a certain chemical composition, and (2) fragments characterized by the chemical composition and membership of the various polymorphous modifications of the substance.

The one-component glass (individual chemical compound or chemical element) always contains nano-fragments (polymorphoids) of different polymorphous modifications (PM) [25]. The multi-component glass contains both types of structural fragments - glass components in the various PM and components which have only one PM. Thus, the structure of the one-component glass is a special case of a glass-forming substance with nano-heteromorphic structure. That is, the concept of polymer nano-heteromorphous structure and relaxation of glass contains a special case: the concept of polymer-polymorphoid structure and relaxation of a one-component glass-forming substance consisting of nano-fragments (polymorphoids) belonging to different polymorphs modifications.

4. The main theses of the concept of polymer-polymorphoid structure and relaxation of one-component glass-forming substances [13-15, 26-28]

1. The glass-forming substance is the copolymer of nanofragments (polymorphoids) of a different polymorphic modification without translation symmetry (long-range order)

Glass-forming liquid is the glass analogue in a depolymerized state, which is characterized by fluid viscosity, increasing with polymerization.

2. A polymorphoid is a crystal structure nanofragment, consisting of an group atoms bonded together by chemical bonds using the rules of stereometric ordering, which are inherent in a crystalline material of one from PMs, and does not possess the translational symmetry of the crystal. In a polymorphoid, there is no long-range order (LRO), even in a minimal extent of two neighboring unit cells of the matter structure capable of an interacting broadcast.

3. The notion of "polymorphoid" was directly related to the notions of short- and intermediate-range order. Short-range order (SRO) is the stereometrically particular combination of atoms, including the atom taken as the reference point (the central atom) and the surrounding atoms within the first coordination sphere. Short-range order is characterized by the coordination number, species (varieties) of its constituent atoms, the distance between the atoms, and angles between bonds. The intermediate (medium) range order (IRO) is the stereometrically particular combination (topology) of the short-range orders within the polymorphoid characterized by the parameters of all SRO (coordination numbers, distances between atoms, and angles between bonds) and the dihedral angles. The intermediate range order has dimensions less than two periods of the crystallographic lattice, on at least one of the crystallographic axes. Otherwise, the polymorphoid becomes a crystallite – a minimum fragment of a crystalline substance.

4. Each glassy material has two or more SRO, two or more IRO (multiplicity SRO and IRO) and no long-range order (LRO). The number of IRO types equals the number of polymorphs participating in the formation of a glassy substance. In one-component non-crystalline material, there may be one, two or more SROs, but only one type of IRO and LRO.

5. Significant changes in the structure and properties depending on the particular realization of an equilibrium process and inter-conversion of polymorphoids of different PMs take place in the glass-forming melt and glass:

$$A_k+B_l+C_m+...+Z_x \xleftrightarrow{\textit{T, P, Ph, H, t}} A_p+B_q+C_r+...+Z_y,$$
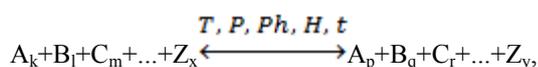
wherein A, B, C – polymorphoid of different PMs of substance with concentrations k, l, m, ..., p, q, r, ..., x, y, which are changed depending on the conditions (temperature T, pressure P, irradiation Ph , electric field E and magnetic field H, time t, and others.) from 0 to 100% and remaining in the amount equal to 100%.

6. Stereometrically ordered polymorphoids of various PMs unite (copolymerize) with each other, leaving some broken chemical bonds due to differences in the short- and medium-range orders, statistically alternating of different PMs. The result is a disorganized polymer polymorphoid glassy structure of matter in which order (nano-level) and disorder (micro- and macro-level) organically coexist.

7. Glass structure and properties are determined by the concentration ratio of polymorphoids (CRP) of the various PMs inherent to the glass and dependent on the state of the starting material, as well as the conditions for obtaining and subsequent treatment.

8. The process of a glassy substance forming is the process of emergence, inter-conversion and copolymerization of polymorphoids of different polymorph modifications of crystalline substances in a disordered (at the level of long-range order) polymer-polymorphoid glass structure (network, tangle of chains, tapes).

9. The relaxation processes in glass and glass-forming liquids (glass transition, devitrification, change in viscosity, glass softening, latent effects of pre-crystallization, photo (thermo) enlightenment and photo (thermo) darkening, invariant and dual thermal and photo crystallization, glass aging, etc.) basically have uniform physical and chemical natures. This means the inter-conversion (changing) of the concentration ratio of different polymorphoids' polymorph modifications and the accompanied polymerization-depolymerization processes in varying degrees.

10. The basic physico-chemical cause of the gradual viscosity increases in the melt and the formation of the glass is the presence of the polymorphoids with different polymorph modifications, which are able to reach copolymerization with the decreasing temperature in the melt. Melt cooling containing polymorphoids only one PM (non-glassforming melt) leads at the melting temperature, T_m, to the sharp viscosity increase and crystalline material formation.

The cooling of the glassforming melt in the temperature range of stable existence of the high temperature polymorph modification (HTPM) (in the range from the melting point T_m to the temperature polymorph transformation T_{tr} of crystalline substance) with a speed lower than the critical value leads to the conversion of the polymorphoid of different PMs (especially the most unstable in this range of low temperature polymorphs modification (LTPM)) into high temperature PM polymorphoids, and the crystallization of the melt in the form of an HTPM. Glass-forming material, cooling at a rate less critical in the area of LTPM stability, leads to the polymorphoid transformation HTPM → LTPM and crystallization in the form of an LTPM.

11. The reversible inter-conversion of polymorphoids of high and low temperature polymorphs modifications (HTPM↔LTPM), characterized by a reversal temperature $T_{w\text{-rev}}$ in the glass-forming substance, is the analog of the polymorphic transformation in the crystalline substance that is characterized by the transformation temperature T_{tr}. The temperature $T_{w\text{-rev}}$ is an analogue of the currently used glass transition temperature T_g, which reasonably replaced the Tamman temperature T_w (from German *"windung"* - inflection) - temperature of inflection point of the curve "property-temperature" [29]. True glass transition temperature (softening) – Tamman's T_g (Tg (T)) today is identified as the pre-endo effect temperature (sub-T_g

endoterm), which is located at 10-70 ° C lower than the conventional T_g [30], i.e. T_{w-rev}.

12. The general scheme of the structural relaxation processes in the condensed glass-forming substance (Fig. 1) reflects the essence of the processes occurring within it when the temperature changes.
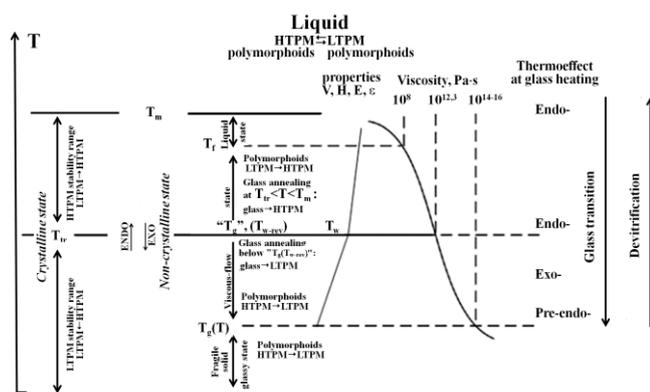

Fig. 1. The scheme of structural relaxation processes of the condensed glass-forming substances. Glossary to Fig.1.: T_m – melting temperature; T_f – boundary temperature of the liquid ("Flussigkeit" in German) and the viscous-flow states; T_{tr} – temperature of interconversion of high- and low- temperature polymorphic modifications in the crystalline state; T_w – Tammans winding temperature on a curve "property vs temperature" of glass-forming substance [29]; "T_g" glass transition temperature, accepted in literature [31], which unreasonably replaced T_w Tamman's one [26];

T_{w-rev} – reversing temperature of the direction of the polymorphoids interconversion of the high- and low-temperature polymorphous modifications in the glass-forming substance, identical to T_w temperature, proposed by Tamman [29]; $T_{g(T)}$ temperature transformation of a viscous-flow liquid into a solid brittle glass state, proposed by Tamman [29]; V – specific volume [29, 32], H – enthalpy [32], E – modulus of elasticity [32], ε – dielectric constant [29].

5. The concept of polymer nanogeteromorfous structure of glass-forming substance and supramolecular chemistry

In our view, there is a direct link between the concept of the nanogeteromorfous structure and the relaxation of the glass-forming substance (as well as the non-crystalline non-glass-forming substance [14, 15]), and supramolecular chemistry - the rapidly developing field of experimental chemistry. [33]

One of its founders, Nobel Prize winner J.M. Len [34] gave her definition as "chemistry intermolecular ensembles and intermolecular bonds".

The work [33] offers the following definition of a supramolecular compound: a group of molecular components, the individual properties of which are integrated into the properties of the whole ensemble

(covalent or noncovalent). As an example, non-covalent interaction is a hydrogen bond.

An example of a covalent interaction between the molecular components with covalent bonds in a nanogeteromorfous concept is the polymorphoids of Se, GeS_2, As_2Se_3, SiO_2, $BeCl_2$, et al. [14]. An example of the interaction via hydrogen bonds is glass-forming H_2O in a solid or liquid state [35].

Polymorphism and polymerization within the concept of the polymer nanogeteromorfous structure of the glass-forming matter [26, 27] are also characteristics of supramolecular systems [36].

Thus, the concept of the structure of the polymer nanogeteromorfous glass-forming substances can be considered to be closely related to the concept of supramolecular chemistry.

6. Relaxation and change of the structure of the glass-forming material upon cooling from the liquid state. The aging of the glass

The most important factor influencing the vitrification process is the structure of the glass-forming substance and, primarily, the structure of glass-forming fluid [27].

In accordance with [37] selenium melts slightly above the melting temperature (217 ° C) contains 40% monomer Se_8 (monoclinic low-temperature polymorphic modification - LTPM) and at 427 ° C - 25%. The rest falls on the hexagonal high temperature PM (HTPM), which is formd at the melting. As a result of the melting HTPM of the glassforming substance, the polymorphoids of the HTPM and LTPM appear in the melt. This is evidenced by the data summarized in [27] for such glassforming substances as $GeSe_2$ [38], S [39], SiO_2 [40], H_2O [35, 25], $BeCl_2$ [41, 42].

The following mechanism for the formation of polymorphoids of low-temperature PM in liquid is presented in [28].

At the dispergating of substance (both solid and liquid) the sizes of the individual fragments are reduced. The associated fluid [39] (including glass-forming liquids such as H_2O, SiO_2, $GeSe_2$, $BeCl_2$, and others) contains associates, in part linked to each other which constantly are ruptured and reformed (already possible between other parts of the associates) chemical bonds. With the increasing temperature of the melted substance, associates reduce in size, and in the part which is not connected at any given time with other associates, there is a surface tension that tends to reduce the free surface of the associates to the lowest possible limit, causing a certain overpressure inside the associate. This pressure will be greater the greater the degree of dispergating of the associates. The increased internal pressure is the main reason for the conversion of associates that have no long-range order, i.e., polymorphoids of one polymorph in other polymorph modifications, forms at elevated pressures [43, 44, 45]. For silica, it is the transformation of cristobalite polymorphoids into polymorphoids of denser quartz (see

experiment of Gerber et al. [40]). For H_2O it is the transformation of ordinary ice I (d = 0.92 g.sm^{-3}) polymorphoids in ice II (d = 1.18 g.sm^{-3}) and ice III (d = 1,15 g.sm^{-3}) polymorphoids [35, 25]. With further heating, the temperature factor of the substance structuring begins to prevail over the structuring factor associated with an increase in pressure. The concentration in the liquid quartz polymorphoidov SiO2i polymorphoidov heavy ice II and III in H_2O begins to decrease, and the density of the liquid falls. At a pressure of 1 atm water after melting, the endothermic effect is at T^+_k = 2,6 ± 0,4 °C. Water heated below this temperature while cooling exhibits equilibrium crystallization without supercooling. Heating water higher than T^+_k leads, at the lower temperatures, to its hypothermia followed by uneven-explosive crystallization [46]. Thus, above 0 ° C, there are two types of water with the different properties.

Taking into account the following data Pauling [35], we can assume that the cause of supercooled water, which was cooled from a temperature greater than 2.6 ± 0.4 °C, is located in a complex mixture of associates consisting of ice I, II and III polymorphoids. The water heated to temperatures below 2.6 ± 0.4 °C, contains, evidently, much less (or no) concentration of ice II and III polymorphoids. This water immediately crystallizes in the form of ice I. Thus, the structure of glass-forming liquids is constructed from the polymorphoids of the different polymorphic modifications, the concentration ratio of which varies depending on the temperature of the liquid [27]. Melt cooling leads to the polymerization of different PM polymorphoids, with an increase in viscosity and the glass formation [14, 25].

This process is only provided if the cooling rate of the melt exceeds the critical cooling velocity V_{cr} [47]. At less than the critical cooling rate, and by exposing (annealing) the melt in the temperature range T_m – "T_g" (T_{w-rev}), it crystallizes into a high temperature PM. Annealing at a temperature below "T_g"(T_{w-rev}) leads to the crystallization of the low-temperature of the PM. Thus, according to [48] the glassy GeSe$_2$ has been crystallized into a HTPM at 425 ° C and into a LTPM at 325 °C. "T_g"(T_{w-rev}) of glassy GeSe$_2$, which is in the 335-392 °C range [38, 47, 49]. Vitreous selenium crystallizes at 28 °C into a monoclinic PM, and at 43 °C into a hexagonal PM [50]. Selenium "T_g"(T_{w-rev}) is 30,5 - 31,5°S [51].

These data once again confirm the position of the concept of the polymer - polymorphoid glass structure regarding the stability of HTPM polymorphoids and instability of LTPM polymorphoids at a higher reversing temperature (T_{w-rev}) HTPM↔LTPM conversion, and the stability of LTPM polymorphoids and instability of HTPM polymorphoids below (T_{w-rev}) [52, 14].

Thus, in glassy selenium occurs a process of HTPM → LTPM polymorphoids transformation, as well as the reverse process: LTPM → HTPM. That is, the property of enantiotropically substances [53] has been manifested, whereas crystalline selenium is characteristically the monotropic property, we mean only the monoclinic PM transformation into a hexagonal PM.

The equilibrium supercooled liquid region is below T_m. It borders the viscous-flow state area. Tamman marked this boundary as T_f [29]. The symbol «f» denotes «liquid, melted» («flussig» in German). Tamman denoted T_f as the temperature, at which the first signs of the liquid state can be seen in heated glass, i.e. when the first thread elongates from the glass. Tamman's softening interval lies between its $T_{g(T)}$ and T_f [29]. Currently, the term "glass transition interval" is often used [32, 47, 54], i.e. the same temperature range, but passed in the reverse direction. In accordance with the data [55], the viscosity in this range is within ≈10^8-10$^{14-16}$ Pa· s. The lowest temperature point of this range is characterized by the transformation temperature of the viscous-flow liquid into a solid brittle glassy state id est Tamman's $T_{g(T)}$ [29].

The glass transition process is a dual process of the copolymerization-depolymerization of a glass forming substance: (1) copolymerization of the HTPM and LTPM polymorphoids throughout the range of the glass transition and (2) depolymerization of the LTPM polymorphoids in the range from T_m (melting temperature) to «T_g» (T_{w-rev}) because of their instability in this range, and also the depolymerization of the HTPM polymorphoids below «T_g» (T_{w-rev}) according to their instability in the area. The viscosity of the glass-forming substance at «T_g» (T_{w-rev}) is ≈ 10^{12,3} Pa·s, i.e, «T_g» (T_{w-rev}), and is located approximately in the middle of the glass transition temperature range, which is characterized by a viscosity ≈10^8-10$^{14-16}$ Pa·s [55]. There is a process of transformation of the LTPM → HTPM polymorphoids above «T_g» (T_{w-rev}) and below «T_g» (T_{w-rev}), which is the transformation process of the HTPM → LTPM polymorphoids parallel with the depolymerization processes above and below «T_g» (T_{w-rev}). These processes are analogous to the polymorphic transformation processes in the crystal. The designation of «T_g»(T_{w-rev}) stresses a Tamman priority in finding and applying a given temperature, as well as its true physico-chemical nature - reverse the direction of the conversion of various PM polymorphoids. At the same time, the true temperature of the glass transition is the viscous-flow fluid transformation temperature into a solid brittle vitreous state – Tamman's $T_{g(T)}$. $T_{g(T)}$ is below its T_w [29], i.e. "modern" «T_g» (T_{w-rev}).

The process of the polymorphic transformation of the crystal high-temperature polymorph modification into the low temperature PM while cooling proceeds at a temperature T_{tr} (Fig. 1) with an exothermic effect [56, 57]. The same effect is observed in the transformation of HTPM polymorphoids into LTPM polymorphoids in a glass-forming material that reflects the relationship of the vitreous and crystalline states [58].

Fig. 2 [59] shows the thermogram of the differential thermal analysis (DTA) of glass forming selenium, illustrating the exothermic peak upon the melt cooling. This effect decreases in intensity when the temperature decrease is the cause of a glass enthalpy reduction below «T_g» (T_{w-rev}) and an increase of the content of the LTPM polymorphoids in glass.
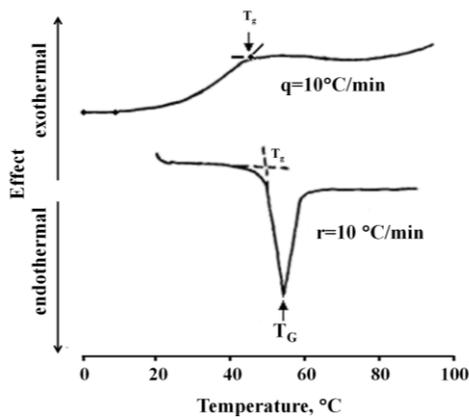
Fig. 2. Typical DSC heating and cooling scans on a-Se films: r=heating rate and q=cooling rate [59].

Fig. 3 shows the curves of differential scanning calorimetry (DSC) for the glass basaltic compositions 43.3 SiO_2 - 15.6 Al_2O_3 - 1.8 TiO_2 - 11.7 FeO - 10.4 CaO - 6.6 MgO - 3.9 Na_2O - 0.7 K_2O [60]. The pre-crystallization (induction) exothermic process of the concentration and copolymerization of the HTPM polymorphoids take place in the glass at cooling speeds slightly greater than the critical. In this process, the cooling curve is shown in the form of the first exothermic effect after melting at $\approx$980˚C. Another smooth exo peak has been observed below in the T_{w-rev} («T_g») region in the basaltic glass at the glass transition, testifying to the polymorphoid transformation: HTPM $\rightarrow$ LTPM. Apparently, polymorphoids were represented here by the compounds of SiO_2 with other oxides.
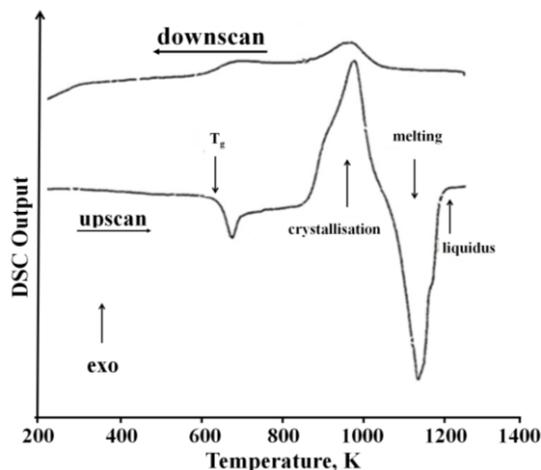

Fig. 3. Differential scanning calorimetric (DSC) measurements on a basaltic glass. "Exo" means exothermic response to the heating or cooling process. The measurements are performed in argon at the heating and cooling rate 20 °C/min [60].

The exothermic effect of the polymorphoid transformation HTPM $\rightarrow$ LTPM starts in the «T_g» (T_{w-rev}) region (viscosity $\approx 10^{12,3}$ Pa·s) and continues with the further cooling of the glass-forming substance. Upon reaching the level of viscosity $\approx 10^{14-16}$Pa·s [55] viscous-flow liquid turns into a solid brittle glassy state, with the fixed Tamman temperature $T_{g\ (T)}$ [29]. Below this temperature, the transformation process of HTPM polymorphoids into LTPM polymorphoids continues and the aging glass process begins. The theoretical approach to the aging process of glass was developed in the Nemilov papers [61, 62]. Much attention was paid to the glass aging process in the works of P. Bulchand and his colleagues [63-65]. The authors divide two- and three-component compositions in Ge-Se, As-Se, Ge-P-Se, etc. systems as "floppy" (under constrained with n_c <3, where n_c – the count of bonding constraints per atom), "stressed rigid" (over constrained (n_c> 3), and *"intermediate"* (n_c = 3) phases.

The non-reversing heat flow measured in glasses by modulated differential scanning calorimetry (MDSC) characterizes glass enthalpy. Non-reversing heat flow at T <T_g in "floppy" and "stressed rigid" glasses uniformly decrease and the glass gets old. For "intermediate" glass phase, this flow almost disappears. The glass transition in the "intermediate phases" is almost completely thermally reversibl, and aging is not observed [66].

In [65] the boundary compositions of system Ge_xS_{1-x}, the separation of the "intermediate phase" from the "floppy" and "stressed rigid" phases has been determined. "Intermediate" phase is in 20% <x<26 % range. These data are in good agreement with the data of R. Golovchak et al., whose papers also investigated glass aging problems [67-69]. The "Intermediate phase" in the system As_xSe_{100-x} [70] in the range 29% <x< 37% ($\triangle$x = 8%) for glass agin for three weeks. As a result of an eight-year aging, $\triangle$x was reduced to 7%.

In [68] the following conclusion has been drawn. The absence of physical aging is the most appropriate criterion for "self-organizing phase" identification (The terms "self-organizing phase," "intermediate phase" and a "window of reversibility" are equivalent.).

These facts and theoretical considerations, as well as the results of other studies, reveal certain physical and chemical properties of the glassy state and its relaxation, which are associated with aging glass, but they do not say anything about the structural changes occurring in the aging process.

This deficiency is filled in by other works, based on the polymer - polymorphoid structure of glass [14, 15, 26, 27]. They show that the transformation process of HTPM polymorphoids into LTPM polymorphoids is the physico-chemical basis for glass aging, which ends after a certain time (from several days to thousands of years for various compositions) [71, 72] with a crystallization of a low-temperature polymorph modification. It was also shown that in such binary systems like GeS_2 - S, $GeSe_2$-Se, As_2Se_3-Se etc., there are composition ranges (called by Bulchand [63] as "intermediate phases") that do not contain polymorphoids (non-polymorphoid compositions) of the first ($GeSe_2$, GeS_2 , As_2Se_3), or second (S, Se) component. In these compositions, the intermediate-range order characterizing polymorphs of these components is

divided into short-range orders ($GeSe_{4/2}$, $As_2Se_{3/2}$, $Se_{2/2}$) and mixed short-range orders ($Ge_{1/4}GeSe_{3/2}$, $As_{1/3}As_2Se_{2/2}$, $As_{1/3}SeSe_{1/2}$) by fragments of other components. The intermediate-range order is absent (the polymorphoids are absent) in these compositions, that is the reason for the lack of aging glass.

7. The relaxation and structure changes of the glass-forming substance in the solid state upon the application of heat (devitrification process)

The devitrification process of glass usually begins upon the application of heat below the Tamman's temperature $T_{g(T)}$. The glass turns into a viscous liquid state at $T_{g(T)}$ (with a viscosity $\eta = 10^{14-16}$ Pa · s [55]). Further heating at a rate greater than the critical heating rate [73] provides to a transformation of a viscous-flow liquid (with viscosity above ~10^8 Pa · s [55]) in an ordinary liquid. The devitrification is observed as a crystallization process of the glass-forming substance into the LTPM at $T<T_g$ (T_{w-rev}) or into the HTPM at $T_g<T<T_m$ (where the T_m is melting point and $T_g = T_{w-rev}$) at a heating rate lower than the critical rate and at constant temperature (annealed glass). During annealing at T_g (T_{w-rev}) the glass-forming substance is crystallized in the form of two polymorphic modifications: LTPM and HTPM.

The main condition of the devitrification process: the copolymerization rate of the HTPM and LTPM polymorphoids in the glass-forming substance is less than the depolymerization rate that results with a simultaneous polymorphoid conversion of one PM into another: LTPM → HTPM above T_{w-rev} and HTPM → LTPM below T_{w-rev} [26]. The greater percentage of the evidences of a polymer-polymorphoid glass structure, as well as the facts of the physico-chemical characteristics of the relaxation of the glass-forming substance were obtained in the process of devitrification.

We can see in Fig. 1, that the viscosity of the substance and other properties of a solid brittle glassy substance change slowly while heating the substance up to a temperature for transformation into a viscous-flow state (i.e. up to of devitrification), where the viscosity varies within 10^{14-16} Pa · s [26]. Here, there are the significant changes in the glass: an increase of the molecular motion, a loss of glass brittleness and an increase in the volume, heat supply and coefficient of expansion, so the glass begins to soften, which is fixed by the softening of Tammann's temperature $T_{g(T)}$ [29].

Nemilov's viewpoint [56] practically coincides with Tamman's one. The intensity of the vibrational motion and free volume, required to move the atoms, increases with an increase in temperature, whereas the free energy activation of viscous flow E_η, required of atoms moving, decreases. Conversely, the E_η value increases at the transition from viscous-flow to a solid glass state. The E_η value with viscosity 10^{15} Pa · s for the simple substances approaches to the breaking energy of the chemical bonds, which form a glassy frame (Table. 1). As a result, the heating process of the glass with a viscosity ~10^{15} Pa ·s leads to breaking down of a glass skeleton and the glass softens.

Thus, the data [29], [55] and [56] are consistent with each other and lead to the conclusion that the true softening temperature (glass transition) or, in other words, the transformation temperature of a brittle glassy state into a viscous-flow liquid (and vice versa), is Tamman's $T_{g(T)}$ softening temperature (or vitrifaction), when the viscosity was 10^{14-16} Pa · s. i.e., which lies well below the conventional T_g (T_{w-rev}), located at ~$10^{12.3}$ Pa · s [32, 47].

The undisputed evidence of this conclusion is a detection of the pre-endoeffect (pre-endoderm, or sub-T_g-endotherm) on the differential scanning calorimetry curves, discussed in [26] and which is usually up to 10-70°C below the T_g, that inexplicably changed Tammann's T_w temperature [27] i.e. the temperature of the bending on the curve "property-temperature".

Table 1. The free activation energy of the viscous flow E_η at the transition into the brittle state in comparison with the energy of chemical bonds E_d for simple glass in kcal · mol^{-1}[56].

Substance	SiO_2	GeO_2	B_2O_3	BeF_2	As_2S_3	As_2Se_3	$GeSe_2$ (extrapolation)	Se_6
E_η	114±10	73±4	38±3	55±3	47±1	45±2	52±1	31±1
E_d	110±5	82±3	124±5	89±1	61	43±3	52±3	41
Δ% E_d	2.5	11	70	38	23	4.5	0	24.5

The pre-T_g-endoeffect was analyzed in [74] for the B_2O_3 glass after the sub-sub-T_g relaxation (stabilization glass) in the process of annealing at T_{anneal} less than T_g under 100 K ($T_{anneal} <T_g - 100$ K). The authors do not explain the physical and chemical nature of the stabilization process during the glass annealing. According to the concept of polymer-polymorphoid glass structure [14, 26] the pre-T_g-endoeffect always presents in one-component glass, because it is a manifestation of the conversion process of solid glass into the viscous-flow liquid, which is accompanied by the rupture of a large part

of the chemical bonds forming the frame of the glass [29, 55, 56].

This effect is negated by its opposite exothermic effect under certain conditions of of glass synthesis, in particular, with the rapid cooling of the melt. Quickly tempered glass consists essentially of the HTPM polymorphoids since these polymorphoids during rapid quenching have no time to be transformed into the LTPM polymorphoids at the temperature lower then T_{w-rev} [14, 26]. When a solid glass is transformed into viscous-flow liquid at the temperature $T_{g\,(T)}$, the endothermic effect of the cleavage of chemical bond led to the formation of the HTPM polymorphoids. These polymorphoids are not stable at a temperature below the T_{w-rev}. As a result, the conversion reaction of the HTPM into the LTPM polymorphoids proceeds with exothermic effect. This exothermic effect neutralizes the endothermic effect of chemical bonds cleavage and at a sufficient number of the HTPM polymorphoids (at a sufficient fast rate of cooling of the melt) reduces the endothermic effect to zero.

As a result, the temperature of the endothermic effect of Tg (T) or Tamman's temperature for a rapidly quenched glass is not detected by differential scanning calorimetry.

Hence it becomes clear why the Tamman's term "softening temperature Tg (T)" has disappeared from scientific literature. This temperature was below the Tw temperature on the curve "property-temperature", which was assigned by the symbol «Tg» [32, 25]. It also appears, in the 70-80s of the last century, of the concept of "sub-sub-Tg-relaxation", "sub-T_g-endotherms", "sub-T_g endoeffect", "pre-endoeffect" and other definitions, related to glass [74, 30].

Let us consider the experimental results of the vitreous boron oxide B_2O_3 ($T_g = 583$ K), which was annealed at 460 K at different times annealing [74]. The Fig. 4 shows the growth of sub-Tg endoeffects with an increasing annealing time (1 hour, 3, 10, 30 hours) of the glass, i.e. when in the sample accumulation of the LTPM polymorphoids and a reducing of the HTPM polymorphoids happens. As a result, a compensation of endoeffect of the broken chemical bonds decreases in the exothermic conversion of the HTPM into LTPM polymorphoids [26]. At the end, there is a gradual merging of sub-T_g endoeffect with T_{w-rev} endoeffect (conversion of the LTPM in HTPM polymorphoids).

The annealing effect on the relaxation enthalpy for the rapidly quenched vitreous calcium metaphosphate (cooling rate up to 10^6K/s) (Fig. 5), and the cooling rate at the glass synthesis were established in [30]. Relaxation enthalpy was expressed in terms of the dependence of the specific heat *vs*. temperature.

The preendothermic effect on the rapidly quenched glass (dash-dotted line) had not been set. Moreover, the experiment indicates a slight exothermic polymorphoid conversion of the HTPM into the LTPM that preceded of the endothermic effect at T_g (T_{w-rev}) and neutralized the pre-endoeffect [26].
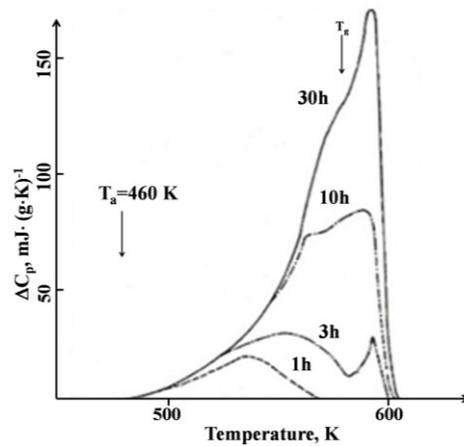

Fig. 4. Endothermic specific heat, ΔC_p, as a function of annealing time t_a, at $T_a = 460K$ [74].

On the glass, cooling at a rate of 20K / min (dashed line) there was a gradual increase of the endothermic peak. Finally, pre-endothermic effect which preceded the endothermic effect at T_g ($T_{w\,-rev}$) was detected on the annealed glass at 703 K during 27 hours.
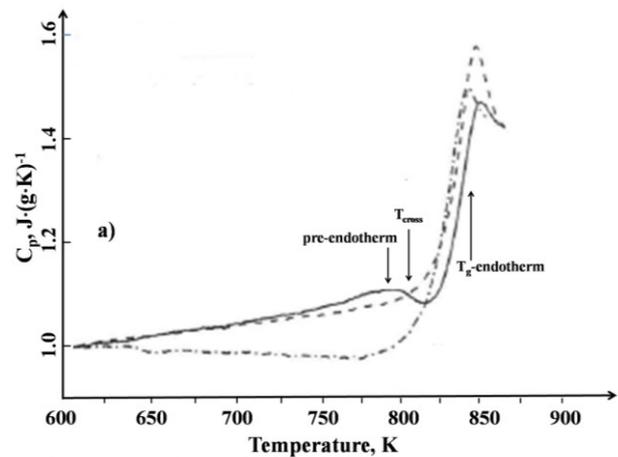

Fig. 5. The impact of annealing on the enthalpy relaxation of the hyperquenched calcium metaphosphate glass (HQ-CMP). (a) Heat capacities (C_p) as a function of temperature. Dot-dash curve: C_p of the HQ-CMP; solid curve: C_p of the HQ-CMP annealed for 27 h at 703 K; dash curve: C_p of the calcium metaphosphate glass (CMP) with a cooling history of 20 K/min. The glass cooled at 20 K/min is called a standard glass [30].

Thus, the process of glass devitrification by heating begins from Tammann's softening temperature, $T_{g\,(T)}$, - the transformation temperature of the solid brittle vitreous state to a viscous-flew liquid with a viscosity of 10^{14-16} Pa · s [55, 60]. The glass-forming substance above the $T_{g\,(T)}$ get into the stable region of the LTPM and the instable HTPM. This area was limited by the $T_{g(T)}$ and T_g (T_{w-rev}) temperatures where there was the polymorphoid transformation of the HTPM into the LTPM is observed, which is genetially related to the transformation of the

crystal HTPM into the crystal LTPM below the interconversion temperature of these polymorphic modifications. This transformation, as in the crystalline and in the glass state, was accompanied by an exothermic effect. This effect in the glass was the greater the faster it was cooled.

Ludwig [76] in his experiments demonstrated that the greater the cooling rate of the As_2Se_3 glass, i.e. the greater quantity of the HTPM polymorphoids rested after cooling of the HTPM, the larger the exothermic peak must to be. If there was the slow cooling of the glass, the exoeffect did not observe; most of the HTPM polymorphoids in this case has turned into LTPM polymorphoids [76, 54].

Ping Chen and Bulchand [65] found an exothermic effect under a heating of a glass of the same As_xSe_{1-x} system with the compositions x = 35; 37.5; 40; 47.5. Fig. 6 shows the curves of the modulated differential scanning calorimetry (MDC) of a rapidly quenched $As_{37.5}Se_{62.5}$ glass in water exposed to 8-year-old aging (presence of exsopeak) and the same " rejuvenated glass" heated above T_g and then cooled without quenching - absence of exsopeak.

The quick quenched glass contained a large amount HTPM polymorphoids, which under heating turned into the LTPM polymorphoids with an exothermic effect below T_g (Tw-rev). In Fig. 6 the exoeffect was pointing down and the endoeffect T_g - upgrade. The dotted line showed the MDSC curve of the "rejuvenated glass", which gave no exothermic peak due to the slow cooling, because the most of the HTPM polymorphoids have turned into the LTPM polymorphoids [26].
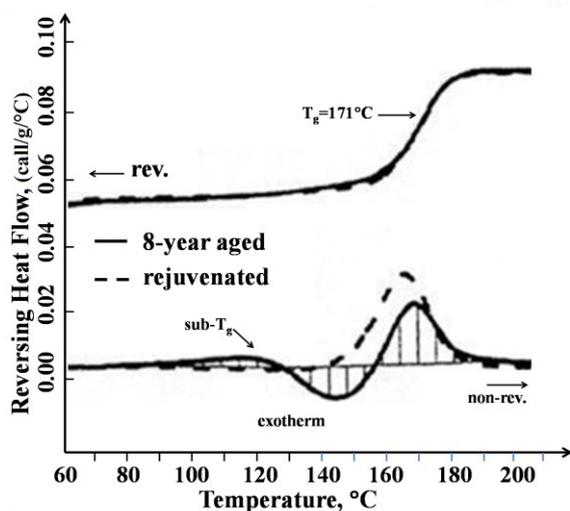

Fig. 6. MDSC scans of $As_{37.5}Se_{62.5}$ glass: water quenched – solid line and rejuvenated – dash line [65].

The pre-exoeffect also was observed in the rapidly-quenched glassy water (curve 1 in Fig. 7 [77]). This exoeffect was a conversion result of the HTPM polymorphoids (polyform of ice I), into the LTPM polymorphoids (polyform of ice II) [25]. At the same curve 1 was observed before an exoeffect the gradual elevation, which we refer to the predendotermic effect at Tamman's $T_{g(T)}$ temperature. The curve 2 shows the DSC

of the glass water aged at 130 K. In this case there was no any exoeffect since all HTPM polymorphoids have transformed into the LTPM polymorphoids. Curve 3 was the same water similar to the curve 2, showed the endothermic effect at $T_{g(Tw-rev)}$, fixing the polymorphoid conversion of the polymorphoids of the ice II into the polymorphoids of ice I.

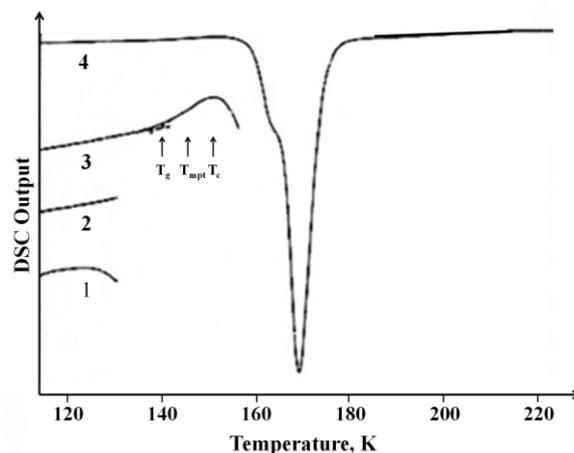*Fig. 7. The DSC scans of the hyperquenched glassy water taken during heating at 30 K·min^{-1}. Curve 1 is for 17.7 mg sample heated to 130 K. Curve 2 is for the same sample, but after annealing for 95 min at 130 K, cooled to 103 K and heated to 130 K. Curve 3 is for the same sample which was colled from 130 K to 103 K and again heated to 283 K. Curve 4 is the same as curve 3, but plotted on a reduced scale (1/8th) to slow the crystallization peak of glassy water to cubic ice. T_g is the glass transition temperature, T_{mdp} is the mid-point temperature, and T_c is the crystallization temperature, all corresponding to 30 K·min^{-1} heating rate [77].*

In all cited examples, the concept of polymer-polymorphoid structure accurately identified the exoeffect causes [58]. This exoeffect precedes endothermic effect when heated glass at T_g, which is actually a transformation temperature of the LTPM → HTPM polymorphoids at T_{w-rev} [27]. There was known only one attempt to explain the pre-exoeffect. Ping Chen and Bulchand in [65] suggest that the cause of this transformation in the As_xSe_{1-x} glass (0.35 <x <0.60) was a bundle frame of glass on the As_4Se_4 and As_4Se_3 molecules, or in other words: nanoscale phase separation (NSPS).

It is obvious that this debate cannot be applied to the vitreous substances as H_2O, Se, As_2Se_3, $GeSe_2$ [58], as well as any other one-component glass-forming substance. The pre-exoeffect during the devitrification of glass-forming substance under a subsequent heating was replaced by endoeffect of the LTPM into HTPM polymorphoids transformation at T_{w-rev}, which originated from T_w Tamman's temperature at the bending curve "property-temperature".

We have already discussed this phenomenon on the example of the selenium [59] and basaltic glass [60] (Fig. 3.2), where the endothermic devitrification effect was

fixed at the heating of a glass-forming substance. The endoeffect under a heating was also being considered by Felz [47] for the glass-forming substances obtained with different cooling rates (Fig. 8). Unfortunately, Felz made a serious mistake. According to him, the heat capacities of glass (C_p) are equal in the case of different cooling rates. In fact, the heat capacity at a slow heating process of glass must be a greater value than the capacity of the rapidly cooled glass. A number of the LTPM polymorphoids which result from the HTPM →LTPM transformation were accumulated more in the slow cooling of the glass after a crossing of the T_g (T_{w-rev}) temperature. This is the major quantity of the LTPM heated polymorphoids, turning into HTPM polymorphoids, will provide a much greater quantity of heat, that we have designated as a dashed curve in Fig. 8 [47].
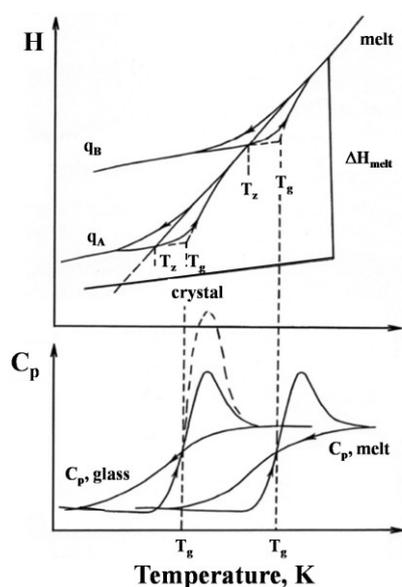

Fig. 8. The temperature dependence of the enthalpy H and heat capacity C_p in the forward and backward transition "melt – glassy state"; $q_B > q_A$ (q – speed of cooling and heating); T_g- is the glass transition temperature; T_z – the temperature of freezing [47].

Above T_{w-rev}, the LTPM → HTPM transformation process continues. This process as well as the preceding and the following T_{w-rev} conversion process of the polymorphoids (HTPM → LTPM), was recorded by Aleksandrovich et al. [78] for the vitreous GeSe₂ in the Raman spectroscopy. (Fig. 9). As seen in Fig. 9, there was an increasing of intensity for the line spectrum E (199sm-1) relating to the LTPM, and reduction of the intensity line A (216 cm-1) attributable to the HTPM with increasing of the annealing temperature of vitreous GeSe₂ in the range from room temperature to $T_{w-rev}(T_g)$ temperature, equal to 635 ± 2 K (sample b, c, d, e); so was the HTPM → LTPM polymorphoid conversion process.

Above T_{w-rev} (T_g) (f-m samples) there was an increasing of the intensity of A line (HTPM) and decreases of the intensity of E line (LTPM). There is a transformation process of the LTPM → HTPM polymorphoids, which ended during an annealing at ≈

750K by the HTPM crystallization. The glass during the heating at a speed above the critical speed (V_{cr}) [73], it was first transformed into a viscous-flow liquid, and then, without crystallization went into the equilibrium liquid (melt). Thus, the devitrification glass process was ended by the crystallization or transition into a molten state.
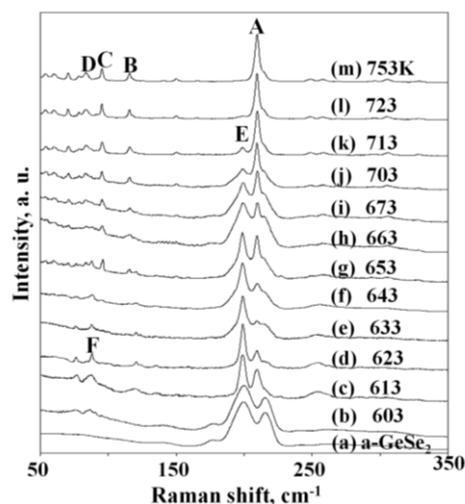

Fig. 9. Raman spectra of GeSe₂ glasses, annealed at various temperatures below (b – e) and higher (f – m) T_{w-rev} (T_g) =635±2K for 20 min, (a) - Raman spectrum of non-annealed glass. Annealing temperature is shown in figure. The lines A, B, C, D relate to high-temperature polymorph and the lines E and F relate to low-temperature polymorph of GeSe₂ [78].

The first of these options (V> V_{cr}) was presented in [78] on the basis of differential scanning calorimetry (DSC) of the GeSe₂ glass (Fig. 10). The DSC curve sequentially captured Tamman's $T_{g(T)}$ temperature (predendotermic effect) at 573 ± 2 K, then the T_{w-rev} temperature at 635 ± 2 K and, finally, an exothermic effect of crystallization at 754 ± 2 K, which ended the devitrification process.
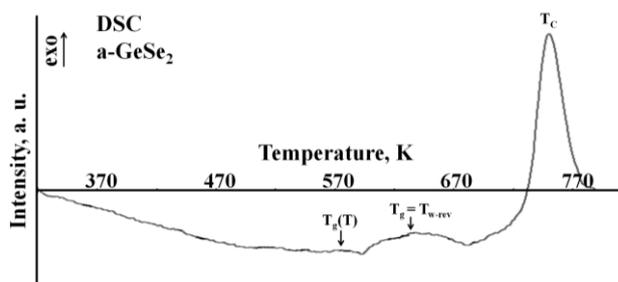

Fig. 10. The DSC curve of the GeSe2 glass recorded at a heating rate of 10K/min. T_g is the generally accepted glass-softening temperature (its beginning) at viscosity $\eta \sim 10^{12.3}$ Pa·s, which is the temperature of the reverse T_{w-rev} of the transformation of structural fragments of various (high- and low- temperature) polymorphic modifications (polymorphoids) of the substance that have no long-range order (HTPM→LTPM). $T_{g(T)}$ is Tamman's glass-softening temperature (viscosity $\eta \sim 10^{14-16}$ Pa·s). T_c is the crystallization temperature of a-GeSe₂ (glassy GeSe₂).

8. The relaxation and structure change of the glass-forming substance from exposure to a photo-irradiation

In this article, we will focus on the a photo-relaxation of the glass forming $GeSe_2$ [79, 80]. More extensive information on the photo-induced transformations of chalcogenide glass there is in [81].

In [79] the luminous flux of He-Ne-laser, less than 0.7 kW / cm^2 (Fig. 11 - «b», «c») changed the ratio of the intensity of the Raman spectrum bands of the vitreous $GeSe_2$. The intensity of the band responsible for the low temperature PM (~ 198 cm^{-1}) increased, and the intensity of the high-PM band (~ 210 cm^{-1}) decreased. The opposite effect was observed if a stream is more then 0.7kW / cm^2 (Fig. 11 - «d», «c», «f», «g»). The intensity of the HTPM band increased and the LTPM band decreased. In this experiment, it was possible to crystallize both the LTPM (luminous flux <0.7 kW/cm^2) having a color close to red and the HTPM (>0.7kW/cm^2) with a color close to yellow.

If we compare the experimental results in Fig. 9 [78] and 11 [79], we can make the conclusion about the identical influence of the heat (annealing) and light (laser irradiation) on the nature of the polymorphoids HTPM↔LTPM interconversion of the $GeSe_2$ glass

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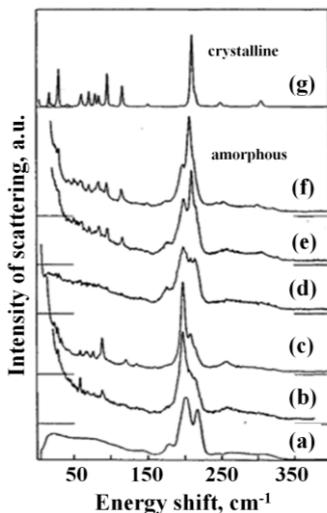*Fig. 11. Raman spectra of the sequence of photoinduced crystallization of $GeSe_2$ glass into two different structures according to the He-Ne laser (6328Å) intensity below (b), (c) and above (d) – (f) threshold (0.7 kW/sm^2) [79].*

The He-Ne-laser irradiation (λ = 633 nm) at T = 77 K of the freshly vitreous $GeSe_2$ film (sample 1) (Fig. 12) [80] has led to the photo-darkening of the sample 3 - the approach to the $GeSe_2$ red color form of the LTPM (transforming HTPM → LTPM polymorphoids). At a temperature of 300 K, the same exposure led to photo-bleaching of the sample 2 - approaching to the $GeSe_2$ yellow-orange color form of the HTPM (transforming LTPM → HTPM polymorphoids). This experiment demonstrated the synergistic effect of light and heat to the substance, leading to an increasing of the enthalpy (H) to a

level above the threshold (H$_{tr}$), where there was the interconversion of various PM, and clearly, in red and yellow colours, showed the physical and chemical nature of the glass relaxation processes: mutual transformation LTPM and HTPM polymorphoids.
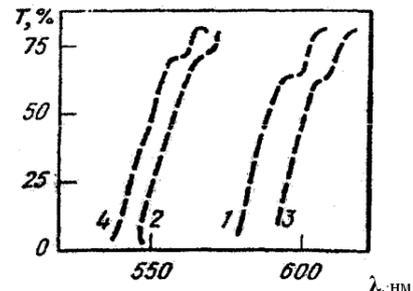

Fig. 12. The spectral characteristics of the transmittance T of films of the glassy $GeSe_2$:1) fresh; 2) irradiated at 300 K; 3) irradiated at 77 K; 4) annealed [80].

9. The quantitative nanodiagnostics of the structure of the glass-forming substance

The concentration ratio of polymorphoids (CRP) of different polymorphic modifications was continuously changing in the devitrification process of the glass-forming substance [13-15].

The aspect ratio of the spectral line intensities of the PM in the Raman spectra of glass-forming substance corresponded to the different concentration polymorphoids ratio of the PM. The calculation of this ratio was in practice nanodiagnostics of the structure of the glass-forming substance at different stages of synthesis or devitrification [82]. For the glass-forming $GeSe_2$, Raman spectra *vs.* the temperature [78] are shown in Fig. 9. The results of quantitative nanodiagnostics of the structure were shown in Fig.13.

Sections 6, 8 on the basis of thermal analysis, Raman spectroscopy parameters and other techniques for a number of glass-forming substance H_2O, B_2O_3, SiO_2, Se,$GeSe_2$, As_2Se_3, $BeCl_2$, and basaltic glass showed that in devitrification process (at the heating) in the range of $T_{g(T)}$- T_{w-rev} the concentration of the LTPM polymorphoids increased and concentration of the HTPM polymorphoid decreased. This phenomenon was due to the conversion HTPM → LTPM polymorphoids. The reverse process LTPM → HTPM occurs in the interval T_{w-rev} − T_m (T_m is the melting temperature).

These processes are clearly fixed on the Raman spectra, taken with increasing of the annealing temperature of the glass-forming substance. So, for $GeSe_2$, the increasing of the spectral intensity of line E (typical for crystalline LTPM) and the simultaneous reducing of the spectral intensity of line A (typical for crystalline HTPM) corresponded to the increasing of the concentration of LTPM polymorphoids and reducing of the concentration of HTPM polymorphoids (Fig. 9). [78] The reverse process was fixed in the range of T_{w-rev} − T_m.

Thus, the ratio of the intensities of the spectral lines E and A corresponded the concentration ratio of the LTPM and HTPM polymorphoids in the structure of the glass-

forming substance. The calculation results of the concentration ratio of polymorphoids (CRP) of different polymorphic modifications coincided with the nanodiagnostic structure of the glass-forming substance.

The structure nanodiagnostics of the $GeSe_2$ glass (Fig. 13 [78]) was given as the ratio of the integrated intensities of the Raman spectrum of modes E (LTPM) and A (HTPM) equivalent to the ratio (CRP). The calculation of the ratio of the intensities of the modes is made on the basis of Raman spectra shown in Fig. 9. The concentration ratio of the LTPM and HTPM polymorphoids in the $GeSe_2$ glass at 600K is approximately equal to 1. At T>600 K. Where the substance was already in the viscous-flow state CRP of the relation LTPM and HTPM increased to a maximum of ~ 2.5. There are about ~70% of the LTPM polymorphoids at T_{w-rev}, equal to ~ 635K [78]).
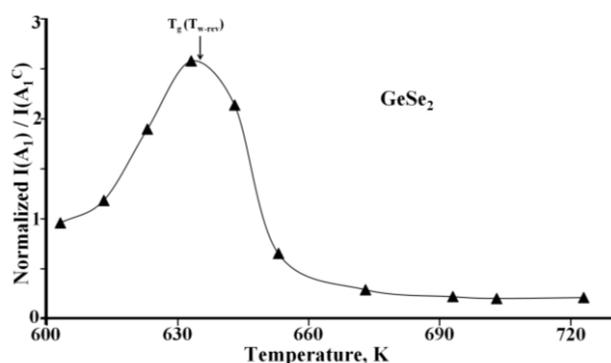

Fig. 13. Ratio of the integrated intensity of modes E (LTPM) and A (HTPM) as a function of temperature. The data were taken from the Raman spectra of the $GeSe_2$ glass

Above T_{w-rev} there was the reverse process - the number of the LTPM polymorphoid was reduced and the number of polymorphoid HTPM was growing to ~ 80% at about 720 K. At temperatures of 663K and above the diffraction patterns of the $GeSe_2$ glass gave the reflection line from the crystal lattice HTPM [78] prior to the subsequent crystallization of the total glass into the HTPM. Nanodiagnostics structure glass-forming substances may be carried out in both the solid and liquid states. The Raman spectrum of the liquid $BeCl_2$ at 470°C was shown in Fig. 14, in accordance with Pavlotou and Papateodorou [42]. The temperature dependence of the ratio of intensities band I^E/I^B of the high temperature «α» (328 cm^{-1}) and the low temperature «β» (274 cm^{-1}) for the polymorphous modifications of glass and glass-forming liquids was shown in the inset A. This dependence from the liquid nitrogen temperature to the beginning of devitrification temperature (~ 200°C) did not change significantly. The ratio of intensities of the bands almost immediately became 3, under a melting of the crystallized under the heating of the high-temperature PM. Consequently, about a quarter of the substance was transformed into the LTPM polymorphoids and ¾ rested in the state of the HTPM polymorphoids. The ratio HTPM and LTPM increased to ~ 4 at the temperature increasing

of the melt. A similar phenomenon was observed in the melting of the H_2O-ice polymorphic modification and when, according to Pauling [35], in the range from 0˚C to 4˚C, up to 50% of the ice (I) structure fragments turned into the structure fragments of ice II (33%) and ice III (17%).

From the standpoint of polymer polymorphoid structure, the polymorphoids of different polymorphic modifications with different structures were formed and coexist in glass-forming liquids, of the glass-forming substance during of the HTPM melting. Rapid cooling of such liquid led to of the nano-geteromorphic copolymerization of the heterogeneous nanofragments (polymorphoids) of the different structure non having of the long-range order, which prevents crystallization of the substance and bring into the vitreous state formation [14, 15]. Thus, the quantitative nanodiagnostic of the $BeCl_2$ and H_2O liquid structures was first carried out by means of Raman spectroscopy [42] and X-ray analysis [35].

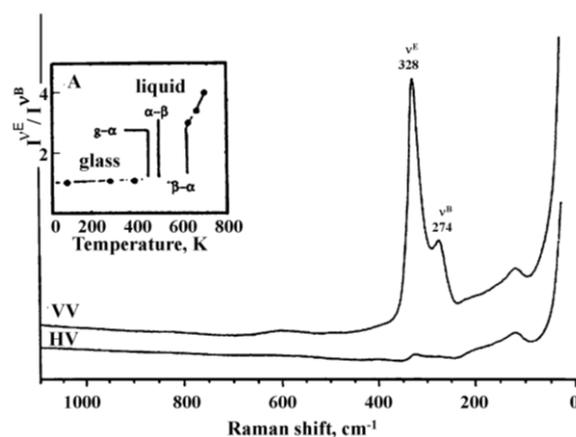*Fig. 14. Raman spectra (Ar-laser, =514.5nm) of liquid $BeCl_2$ at 470°C. Inset A: temperature variation of the relative intensities of the stretching vibrational modes of pure $BeCl_2$ (v^E - α-PM and v^B – β-PM) in temperature range from liquid N_2 temperature to 520°C [42].*

In the near future, apparently, we can expect the distribution of nanodiagnostics of the glass forming substance (both solid and liquid) at most one-component compounds. Then, the process should extend to multi-component glass, considering the features contained in the models of the glass structure [18], [19] and [20].

10. Conclusion

The concept of a polymer nano-heteromorphic structure and the relaxation of a glass-forming substance, and the special case of the concept of the polymer-polymorphoid structure and relaxation of one-component glass-forming material has been presented.

One-component glass and glass-forming components of multi-component glass have been built from crystal lattices of nano-fragments (polymorphoids) of different polymorphs having no translational symmetry (long-range order), but having short and middle (intermediate-range) orders.

The multi-component glass is the copolymer of glass-former polymorphoids presented in various polymorphic modifications and polymorphoids of modificators, which represent one polymorph modification. Changes in the structure of a one-component glass-forming substance in the process of relaxation during the cooling of the melt, glass heating, and under the action photo-irradiation have been traced. The changing of the concentration ratio of polymorphoids (CRP) of various PMs is the physico-chemical essence of the processes observed in the glass.

Proposed by Tamman, the hence forgotten temperature of glass softening (today glass transition), T_g, has been restored. The T_g temperature is situated below the T_w temperature of bending on the "property vs temperature" curve. The physico-chemical sense of the T_w temperature (wrongly renamed T_g) has been revealed. It is a fixed temperature for the reversing of direction for the polymorphoid transformation of the high- and low-temperature polymorph modifications. The new temperature designation T_{w-rev} (instead of T_g and T_w) has been introduced. It reinstates the Tamman temperature T_w and opens the physico-chemical essence of the reverse phenomenon that occurs at this temperature.

The quantitative structural nano-diagnostics of the solid ($GeSe_2$, $BeCl_2$) and liquid (**$BeCl_2$**, H_2O) glass-forming substances has been carried out. It is an experimental determination by Raman spectroscopy ($GeSe_2$, $BeCl_2$) and X-ray phase analysis (H_2O) of the CRP for different polymorphic modifications of the studied compounds.

The nano-diagnostics of most one-component glass-forming substances, as well as multi-component glasses based on the determination of all components CRP, including glass-forming components represented by polymorphoids of different polymorph modifications, have been predicted.

The structural features of nano-heteromorphic glass-forming substances (polymorphism, nano-fragmentation (polymorphoids), polymerization, covalent and non-covalent (H_2O) chemical bonds) are close to the peculiarities of the matter structure studied in the framework of supramolecular chemistry. This suggests that the concept of polymer nano-heteromorphous structure of glass-forming substances and supramolecular chemistry are related areas of material science.

Acknowledgements

References

[1] N. S. Kurnakov, Vvedenie w phisico-chemicheskiy analiz, Moskwa-Leningrad. Izd. AN SSSR (1940).

[2] U. B. Tananaev, Vestnik AN SSSR, № 2, 212 (1972).

[3] M. L. Frankenheim, J. Prakt. Chem. **54** (7-8), 430 (1851).

[4] A. A. Lebedev, Proc. State Opt. Inst. (Russian), **3** (4), 1 (1924).

[5] D. I. Mendeleev, Glass Production, Sankt-Peterburg (1864).

[6] R. B. Sosman, Properties of silica. American Chem. Soc. Monograph series № 37. Chemical Catalog Co. Inc, New-York (1927).

[7] V. V. Tarasov, Problems of Glass Physics, Stroiizdat Publishers, Moscow (1979).

[8] W. H. Zachariasen, J. Am. Chem Soc., **54**, 3841 (1932).

[9] E. A. Porai-Koshits. Glass structure. In: M. A. Bezborodov, N. N. Bobkova et al Politeckh. Inst. Minsk, 13 (1959).

[10] I. Krogh-Moe, Phys. Chem. Glasses **6** (2), 46 (1965).

[11] C. H. L. Goodman, Nature, **241**, 370 (1975).

[12] G. Lucovsky, T. M. Hayes. In: «Amorphous Semiconductors, Ed. M. H. Brodsky. Springer-Verlag, Berlin, Heidelberg, New-York, pp. 268-310 (Russian Translation) (1979).

[13] V. S. Minaev, Stekloobraznye Poluprovodnikovye Splavy (Vitreous semiconductor alloys). Metallurgy Publishers, Moscow (1991).

[14] V. S. Minaev, In: Semiconducting Chacogenide Glass I, Eds R. Fairman and B. Ushkov, **78** Elsevier Academic Press, Amsterdam, New-York, 139 (2004).

[15] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin, (in Russian). Moscow, MIET, 144 (2010).

[16] I. T. Randall, H. P. Rooksby, B. S. Cooper. I. Soc. Glass Techn. **14,** 219 (1930).

[17] B. E. Warren, J. Appl. Phys., **8**, 645 (1937).

[18] N. M. Vedishcheva, B. A. Shahmatkin, A. C. Wright, Advanced Materials Research. **39-40**, 103 (2008).

[19] L. Apakova, O. Yanush, O. Derkacheva, T. Markova et al. J. Non-Cryst. Solids. **357**, 2675 (2011).

[20] K.B. Aleinikova, E.N. Zinchenko, R.S. Bubnova et al, Phizika i khimiya stekla (Russia) **35**(3), 365 (2009).

[21] V. S. Minaev, Proc. Int. Conf. V. 1, 190, Uzhgorod, USSR (1989).

[22] V. S. Minaev, Fiz. K'him. Stekla **18,** 175 (Sov. J. Glass Phys. Chem. (Engl. Transl) **18**, 95 (1992)).

[23] V. S. Minaev, Fiz. K'him. Stekla **22**, 314 (Sov. J. Glass Phys. Chem. (Engl. Transl) **22**, 235 (1996)).

[24] V. S. Minaev, J. Optoelectron. Adv. M. **4**, 843 (2002).

[25] V. S. Minaev, S. P. Timoshenkov, S. P. Chernykh, J. Optoelectron. Adv. M. **6**(1), 103 (2004).

[26] V. S. Minaev, N. M. Parfenov, S. P. Timoshenkov, V. P. Vassiliev, V. V. Kalugin, L. P. Batyunya, D. Z. Mukimov, J. Non-Cryst. Solids **404**, 174 (2014).

[27] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin, J. Optoelectron. Adv. M. **13**(11-12), 1393 (2011).

[28] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin,

Phys. Status Solid **8** (9), 2701 (2011).

[29] G. A.Tamman, Der Glaszustand, Leipzig (1933).

[30] Y. Yue, Phys. Chem. Glasses. **46**, 354 (2005).

[31] A. R. Cooper, In: Non-Crystalline solids. Aedermannsdorf, Switzerland, p. 384 (1977).

[32] O. V. Mazurin. Steclovanie (in Russian) (Glass transition – in Engl) «Nauka», Leningrad (1986).

[33] J. W. Steed, J. L. Atwood, Supramolecular Chemistry. –John Willy & Sons, Ltd (2009).

[34] J. M. Lehn, Supramolecular Chemistry: Concepts and perspectives, Weinhein, VCH (1995).

[35] L. Pauling, General Chemistry, W. A. Freeman and Co., San Francisco (1970).

[36] M. V. Alphimov, Rossiiskie nanotechnoligii **8**(3-4), 1 (2013).

[37] A. Eisenberg, A. V. Tobolsky, J. Polym. Sci **46**, 19 (1960).

[38] Y. Wang, M. Nakamura, O. Matsuda et al. J. Non-Cryst. Solids. **198-200**, 753 (1996).

[39] H. Rawson, Inorganic glass forming systems. Academic Press, London and New York (1967).

[40] Th. Gerber, B. Himmel, H. Lorenz, D. Stachel. Cryst. Res. Technol. **23**, 1293 (1988).

[41] V. S. Minaev, J. Optoelectron. Adv. M. **11**(12), 1946 (2009).

[42] E. A. Pavlatou, G. N. Papatheodorou, Phys. Chem. Chem. Phys. **2**, 1035 (2000).

[43] M. Ya. Gamarnic. Physics of Firm Body (in Russian) **30**(5), 1399 (1988).

[44] Y. I. Vesnin, J. Struct. Chem (in Russian) **36** (4), 24 (1995).

[45] V. S. Minaev, I. M. Terashkevich, S. P. Timoshenkov, V. V. Kalugin, S. N. Novikov J. Optoelectron. Adv. Materials. **9**(10), 3253 (2007).

[46] V. D. Aleksandrov, Barannikov (J. Phys. Chem. – in Russian) 74 (2000).

[47] Adalber Feltz, Amorphe und Glasartige Anorganische Festkörper. Akademik - Verlag. Berlin (1983).

[48] K. Inoue, O. Matsuda, K. Murase, Solid State Commun, **79**, 905 (1991).

[49] M. Afifi, Phys. Rev. B, **48**, 1634 (1993).

[50] D. M. Chizhikov, V. P. Schastlivyi, Selen I Selenidy (in Russian), Izd. «Nauka», Moskva, (1964).

[51] A. Eisenberg, Polym. Letters, **1**, 177 (1963).

[52] V. S. Minaev, J. Optoelectron. Adv. M. **3**(27), 233 (2001).

[53] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin, J. Optoelectron. Adv. M. **7**(4), 1717 (2005).

[54] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin, S. N. Novikov, S. I. Kovalev, Moldavian J. of Physical Sciences **8** (2), 151 (2009).

[55] A. Winter-Klein, Verres et refractaires (4), 217 (1953).

[56] S. V. Nemilov, in: Vitreous state (in Russian). Trudy 4th Vsesoyuzogo Soveshchaniya. Moskwa-Leningrad: «Nauka», 64 (1965).

[57] V. I. Lihtman, Brief Chemical Encyclopedia, **4** (Soviet. Enc. Publ) Moscow, 194 (1965).

[58] V. S. Minaev, S. P. Timoshenkov, V. V. Kalugin, V. P. Vassiliev, J. Optoelectron. Adv. M. **11**(12), 1950 (2009).

[59] S. O. Kasap, B. Polischuk, V. Aiyah, S. Yannacopoulos, J. Non-Cryst. Solids **114**, 49 (1989).

[60] Y. Yue, J. Non-Cryst. Solids. **345-346**, 523 (2004).

[61] S. V. Nemilov, Glass. Sci. Technol. **78**(6), 269 (2005).

[62] S. V. Nemilov, Glass. Phys. Chem. **36**(3), 315 (2010).

[63] P. Boolchand, W. J. Bresser, D. G. Georgiev, J. Wang, J. Wells, Kluwer Academic Plenum Publishers, 65 (2001).

[64] P. Boolchand, D. G. Georgiev, M. Micolaat. J. Optoelectron. Adv. M. **4**(4), 823 (2002).

[65] Ping Chen, P. Boolchand, D. G. Georgiev, J. Phys: Condens. Matter **22**, 065104 (2010).

[66] P. Boolchand, S. Bhosle, K. Ganasekera, K. Vignarooban, S. Charcraborty, J. Optoelectron. Adv. Material. **13**(11-12), 1353 (2011).

[67] R. Golovchak, H. Yaim, O. Spotyuk, A. Kozdras, A. Saiter, J.-M. Saiter, Phys. Rev. B **78** (014202-1-014202-6) (2008).

[68] O. Shpotyuk, M. Hyla, V. Boyko, R. Golovchak, Physica B **403**, 3830 (2008).

[69] R. Golovchak, A. Kozdras, O. Spotyuk, S. Kozykhin, J. Mater. Sci. **44**, 3962 (2009).

[70] D. G. Georgiev, P. Boolchand, M. Micolaut. Phys. Rev. B **62** (14), R9228 (2000).

[71] Y. P. Youle, in: The Scientific Papers of Y.P.Youle. – London: Taylor and Francies, **1**, 558 (1887).

[72] S. V. Nemilov, Thermodynamic and kinetic aspects of the vitreous state. –Boca Raton (USA); Ann Arbor (USA); London; Tokio: CRC Press (1995).

[73] Yu. K. Lapin, M. D. Mikhailov, Phisica I khimia stekla (in Russian) **18**(4), 16 (1992).

[74] H. S. Chen, C. R. Kurkijan, J. Am. Ceram. Soc. **66**, 613 (1983).

[75] L. Landa, K. Landa, S. Tomson, Yanus Publishing House. St. Petersburg (2004).

[76] W. Ludwig. J. Therm. Anal. **8**, 75 (1975).

[77] C. P. Johari, A. Hallbracker, E. Mayer. Nature **330**, 552 (1987).

[78] E. V. Aleksandrovich, V. S. Minaev, S. P. Timoshenkov, J. Techn. Phys. (in Russian) **8**(4), 32 (2015).

[79] S. Sugai. Phys. Rev. Lett. **57,** 456 (1986).

[80] A. V. Kolobov, B. T. Kolomiets, V. M. Lubin, N. Sebastian, M. A. Tagirjanov, Solid State Phys. (in Russian) **24**, 1062 (1982).

[81] Mihai Popescu, in: Semiconducting Chalcogenide Glass 1; Eds: R. Fairman, B.Ushkov, Semiconductors and Semimetals, V. **78**. - Elsevier Academic Press, 181 (2004).

[82] V. S. Minaev, Radioteckhnicheskii universitet, fisico-technich. inst. im. A.F. Ioffe Rossiiskoi Academii nauk, Ryazan', Russia, Tom. **1**, Ss. 107 (2011).

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