

POLYMORPHOUS-CRYSTALLOID STRUCTURE AND RELAXATION PROCESSES IN SOME CHALCOGENIDE GLASS-FORMING SUBSTANCES

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The processes related to the modification of glass and glass-forming liquid structure have been explained by the concept of polymeric polymorphous-crystalloid structure.

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1. Introduction

1.1. General remarks on relaxation of structure of substance in condensed state

The nature of vitreous state can not be perceived deeply without analysis of crystal and liquid states, without analysis of structure in these states, without understanding of ways and means of mutual transformations of these three states, as well as transformations inside them that take place under influence of such external influences as temperature, pressure, electromagnetic radiation, etc. As a matter of fact such transformations of various states (phase transformations) and transformations inside each of them (phase transformations – in crystal state, structural transformations – in liquid and vitreous states) represent relaxation* of substance, i.e. the process of establishment of thermodynamic equilibrium (complete or partial) in a physical system consisting of a large number of particles [1].

In this work phenomenological aspects of relaxation processes taking place, mainly, in individual chemical substances based on chalcogenides of IV and V main subgroups of the Periodic Table as well as in chalcogene Se are considered. Special attention is given to the most deeply investigated germanium diselenide GeSe_2 .

Our consideration is confined only structural relaxation above substances in crystalline, vitreous and, partially, liquid states, information on which is quite limited.

The largest experimental material in the field of chalcogenides is collected for the case of influence of temperature on substance, so in this work the relaxation of substance will be considered mainly as establishment of equilibrium in substance as a result of temperature influence, i.e. as a result of “placement” of substance from one temperature conditions to others. At that, as it will be shown later, for understanding of the nature of glass-formation the processes connected with relaxation of substance at placing it in higher temperature conditions (heating) are no less important than processes of cooling of substance to which a lion’s share of experimental materials is devoted that is evidenced, for example, such notions as “relaxation of glass-forming liquid” and “glass relaxation in region T_g ”.

Considering relaxation processes, it must be kept in mind that very frequently a substance does not achieve the equilibrium state due to not sufficient duration of conditions in which the system is kept. In the case conditions continuously change, the potential equilibrium state, to which the system aims at, changes as well.

Any alteration of state of a system leads to alteration of its properties. Substance properties in accordance with the main formula of physics-chemical analysis, the formula of Kurnakov-Tananaev [2], are functionally dependent on composition, structure and dispersion (the ratio of substance surface to its volume). At constant chemical composition and absence of significant dispersion, alteration of substance properties is directly related with alteration of its structure.

* In this work we do not consider the vapors state of substance, analysis of transformation of which in condensed non-crystalline state, in particular in ultra-dispersed and vitreous, is very important in obtaining non-crystalline films of chalcogenides.

Knowledge of substance structure is the most important condition of understanding of relaxation processes in it. As for individual chemical substances and, in particular, chalcogenides, there is a lack of data on structure of even “the most simple” crystal state, for example, crystallographic parameters of one of two polymorphous modifications (PM) as for GeSe₂ and AsSe. There is no confidence that all PM of individual chemical substances and chalcogenides, in particular, are discovered.

The situation is more complicated with structure of vitreous substances, and glass-forming liquids in particular.

For description of structure of liquid (melt) Tool, who founded the kinetic theory of glass-formation [3], introduced the notion of “the fictitious temperature” T_f that is frequently called “the structural temperature”. T_f (according to Tool) is the temperature of melt which structure coincides with the structure fixed in this glass. But although structures of glass and liquid at certain temperature in accordance with the kinetic theory of glass-formation are similar, it says nothing about their peculiar concrete stereometry of atom arrangement in glass or liquid.

1.2. Main concepts of glass structure

Analyzing and interpreting diffractometry and spectrometry data which evidence on structure and structure changes in glass and glass-forming liquid, investigators, consciously or unconsciously, are relied on a certain concept of glass structure or guided by some model of structure.

The most famous concepts of glass structure are the crystallite concept of Frankengeim (1835) – Lebedev (1921) [4, 5] in which for the first time a guess was given about connection of glass-formation and polymorphism, the concept of polymeric structure (Mendeleev – 1864 [6], Sosman – 1927 [7] and others), the concept of a continuous random network of Zachariasen – 1932 [8], the polymeric-crystallite concept of Poray-Koshits – 1959 [9] which relatively successfully combined three previous conceptions, the concept of clusters of structural-independent polyforms of Goodman [10] (actually developing ideas of Frankelgeim-Lebedev).

Each of above mentioned concepts reflects to certain extent an objective glass structure, but is distinctive either in excessive generality (the concept of polymeric structure and, to the certain extent, the Zachariasen’s concept) or contents theses contradicting to experimental data – modern diffractometric investigations show that in well synthesized glass there are no even smallest crystal inclusions.

We establish our interpretation of all processes related with alteration of glass and glass-forming liquid structure on the concept of polymeric polymorphous-crystalloid structure of glass and glass-forming liquid (CPPCSGL) produced from individual chemical substances [11-15] that we have been developing since the second half of eighties.

1.3. Main theses of the concept of polymeric polymorphous-crystalloid structure of glass

Basing on critical analysis of existing concepts of glass structure, a number of theses related with the structure of glass-forming liquid and glass expressed by Brukner (1970), Landa (1977), Balmakov, Blinov (1985), Gerber (1988) and others, Golubkov (1992), as well as on other data analyzed in [11-15], the following main theses of CPPCSGL have been established:

1. The process of formation of vitreous substance is the process of generation, mutual transformation and co-polymerization of structural fragments of various polymorphous modifications of a crystal substance without long-range order (crystalloids) in disordered polymeric polymorphous-crystalloid structure (network, tangle of chains, ribbons, etc.) of glass.

The term “crystalloid” was in the first time introduced by Graham and it meant particles of substance in the state of molecular fragmentation which are able to crystallize from solution [16]. It is evident that in our case this definition must be transformed to some extent and that has been done in [12].

2. The crystalloid is a fragment of the crystal structure consisting of a group of atoms connected by chemical bonds according to stereometric ordering rules inherent to one of crystal PMs of the substance and having no translational symmetry of the crystal. There is no even minimum long-

range order (LRO) in the crystalloid, i.e. two neighboring elementary cells of crystal structure which are able to intertranslate.

3. The notion “crystalloid” is directly connected with notions “short-range order” and “intermediate-range (medium) order” (SRO and IRO, MRO), "short-range ordering" and "medium-range ordering", applied both to non-crystalline and crystalline substances.

The short-range order is topologically determined composition of atoms including the atom taken as the origin point and surrounding atoms of the first coordination sphere. The SRO is characterized by the coordination number, by types (kinds) constituent atoms, by distances between atoms and interbond angles.

The intermediate (medium) order – is a stereometrically determined composition (topology) of short-range orders in the limits of a crystalloid characterized by parameters of all SROs (coordination numbers, distances between atoms, interbond angles) and dihedral angles.

The intermediate-range order, at least along one of crystallographic axes, has dimensions less than two periods of the crystal lattice. Otherwise, the crystalloid transforms in a crystallite.

The short-range ordering is a combination of various short-range orders (in crystalline and non-crystalline substances).

The intermediate-range ordering is a combination of various intermediate orders in a non-crystalline substance. In a crystalline substance the term “intermediate-range ordering” coincides with the term “intermediate-range order”.

4. In every non-crystalline substance there are two or more SROs, two or more IROs (plurality of SRO and IRO), and there is no LRO. The number of IRO types is equal to the number of polymorphous modifications taking part in formation of the non-crystalline substance. In a crystalline substance there may be one, two or more SROs and only one type of IRO and LRO.

5. Stereometrically ordered crystalloids of different PMs join together (polymorphous polymerization) also according to ordering rules of one of PMs (except for rules of translational symmetry, but because of statistical alternation of inherent to them IROs they form disordered polymeric polymorphous-crystalloid structure of vitreous substance in which the order (microlevel) and the disorder (macrolevel) organically co-exist.

6. Glass structure is not absolutely continuous, there are separate broken chemical bonds and other structural defects.

In accordance with above notions of the CPPCSGL glass structure and properties are determined by the concentration ratio of crystalloids of different PMs inherent to the given glass and depending on origin substance state, conditions of formation and treatment of the vitreous material.

In glas-forming liquid and glass substantial changes of structure and properties take place depending on concrete realization of the process of intertransformations of crystalloids of different PMs.

(T,P,Ph,E,H)

$$A_k + B_l + C_m + \dots + Z_x \quad ? \quad A_p + B_q + C_r + \dots + Z_y \quad (1)$$

where A, B, C ... Z – crystalloids of different PMs of substances which concentrations k, l, m ... p, q, n ... x, y are changed depending on conditions (temperature T, pressure P, irradiation Ph, electrical field E, magnetic field H, etc.) in the range from 0 to 100% [12, 17].

Actually, the expression (1) reflects physical-chemical essence of relaxation processes in crystal, vitreous and liquid states of substance.

2. Germanium diselenide GeSe₂

2.1. Crystalline polymorphous modifications and phase transitions

Germanium diselenide GeSe₂ exists at normal pressure in two polymorphous modifications – high-temperature (HTPM, β-modification) and low-temperature (LTPM, α-modification) [18, 19]. The HTPM has two-dimensional layered structure in which GeSe_{4/2} tetrahedrons, connected in vertexes (corner-shared tetrahedrons - CST), form chains connected by bridges from pairs of tetrahedrons, connected in edges (edge-shared tetrahedrons - EST). In HTPM there are equal numbers of CSTs and ESTs. The HTPM has yellow [20] (orange [21]) color and the melt temperature of

740 °C [20]. The LTPM is constructed of tetrahedron chains arranged along directions [001] and [101] and connected by only CST in the three-dimensional network [22]. LTPM can be obtained by photo-irradiation of thin vitreous samples by the He-Ne laser [23], by annealing at 325 °C of an amorphous film deposited by vacuum evaporation [22]. A comprehensive X-ray determination of LTPM structure is absent.

Azoulay in 1975 [21], heating glasses of Ge-Se system with 15-30 at.% Ge content up to temperatures of 280-300 °C, discovered in all cases inclusions of the same phase consisting of small crystals of red-brown color with approximate composition $\text{Ge}_{30}\text{Se}_{70}$. With further heating the orange phase GeSe_2 appears which co-exists with the red-brown phase. At heating to 400 °C and higher, the latter disappears while the orange phase GeSe_2 remains.

In accordance with the eutectic type of the phase diagram Ge-Se, in the range Se- GeSe_2 , at partial crystallization in the range of 15-30 at.% Ge only GeSe_2 phase can be formed. Therefore, Azoulay appears to be the first who discovered LTPM GeSe_2 and observed the phase transition LTPM \rightarrow HTPM which can be interpreted as the process of relaxation of crystalline GeSe_2 at temperature increase. The confirmation of the fact that Azoulay dealt with the phase transition in GeSe_2 is the Inoue's experiment [22] who at thermal annealing of amorphous film obtained LTPM at 325 °C and HTPM at 425 °C. The phase transition in the opposite direction HTPM \rightarrow LTPM is registered in the work [19] at increasing pressure to 7 GPa. The transition is realized via intermediate, completely disordered at 6.2 GPa, phase.

For GeSe_2 , two PMs obtained at high pressures are also known [24].

As it's seen from presented data the information on the crystal state of GeSe_2 is far from comprehensive. But the fact of existing of stable HTPM and LTPM at normal pressure in certain temperature intervals [18, 19, 23] says itself that GeSe_2 has the enantiotrope phase transition HTPM \rightarrow LTPM which is characterized by certain temperature of polymorphous transformation T_{tr} . Temperature of the enantiotrope transition T_{tr} is unknown. It is clear only that this transition is in the temperature range of 300-400 °C according to data [21] or 325-425 °C according to [22]. We didn't come across any facts of existing of HTPM \rightarrow LTPM transition at normal pressure. It appears that it is difficult to take place because of not sufficiently high temperatures. It is possible that it does take place, although slowly, at temperatures slightly less than the real T_{tr} . The transition HTPM \rightarrow LTPM can be activated by high pressure [19] that can be interpreted as a process of relaxation of crystalline GeSe_2 as a result of pressure increase or as a result of presence of structural fragments (crystalloids) LTPM which takes place in amorphous GeSe_2 film consisting, in accordance with CPPCSGL as well as [22, 23] data, from fragments of structure of both PMs. But in any case, one should not already say about the pure enantiotropic transition because, on definition, the enantiotropic transition must take place at normal pressure and in crystalline, but not in non-crystalline, substance. Nevertheless, the presented facts give evidence that LTPM is significantly more stable at temperatures below T_{tr} than HTPM that allows to state that the discussed phase polymorphous transformation is enantiotropic one. Some results of presented discussion are shown in Fig.1.

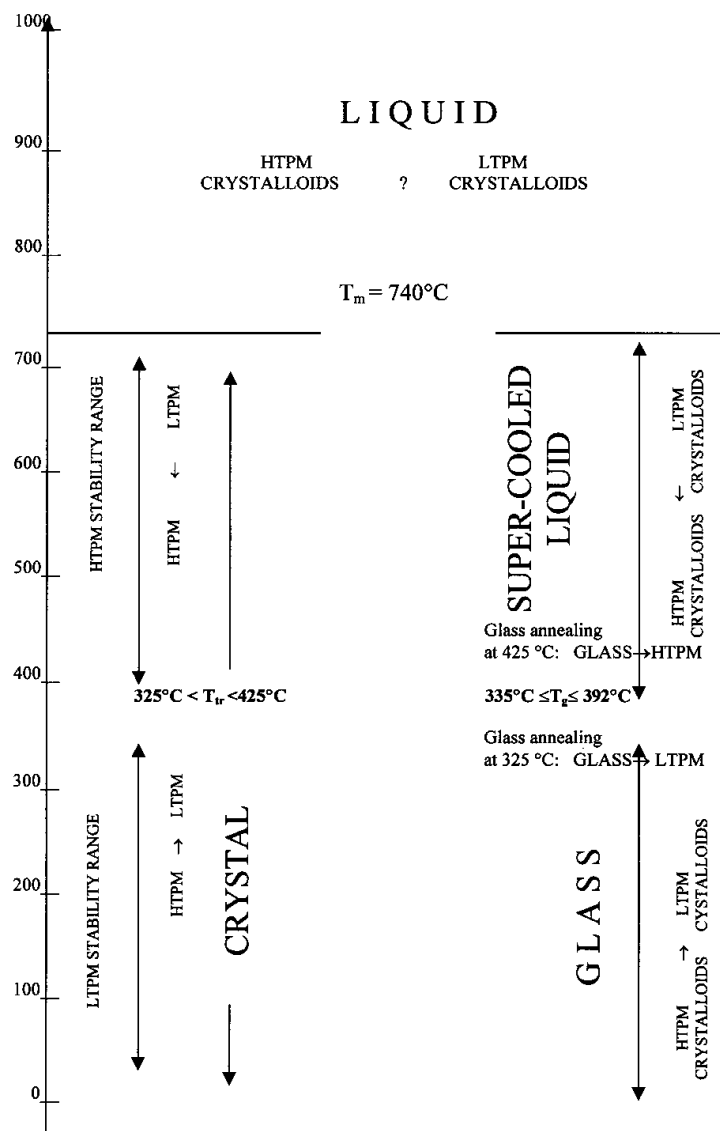
2.2. Structure of vitreous GeSe_2

Several structural models of vitreous GeSe_2 are known.

The model of a continuous random network (1973) of Poltavtsev and Pozdniakova [25] is practically not distinctive from Zachariazen's model – all $\text{GeSe}_{4/2}$ tetrahedrons are connected in vertexes through Se atoms.

In 1979 Bridenbaugh, Phillips, Griffiths and others [26] proposed a layered structure for v- GeSe_2 constructed from large ribbon-like structural units (clusters) called by the authors “outrigger-raft”. These structural units are obtained by extraction from the layer of HTPM. Along edges of ribbons the Se atoms are joined in pairs by Se-Se bonds.

In the beginning of eighties works of Lucovsky and others [27] and Nemanih and others [28] were published where authors proposed models of structure containing both tetrahedrons, connected along edges, and tetrahedrons, connected in vertexes that is the model of chemically ordered continuous random network.


 Fig. 1. Varieties of condensed state of GeSe₂.

In 1986-87 Sugai [23, 29] proposed a new stochastic random network model of germanium and silicon chalcogenides. The model is based on author's experiments who discovered existence of two different microcrystalline states (phases) – HTPM and LTPM obtained by photo-irradiation of vitreous GeSe₂ samples (and also obtained by vacuum deposition of amorphous films) by the beam of He-Ne laser (6328 Å) of various intensity – higher and lower than the threshold ($\approx 0.7 \text{ kW/cm}^2$). The stochastic random network model is characterized by one parameter P representing the probability of the ratio of chemical bonds of edge-shared tetrahedrons and chemical bonds of corner-shared tetrahedrons. P can be changed: it decreases at irradiation with intensity lower than the threshold and increases at irradiation with intensity higher than the threshold. The stochastic model gives, in the author's opinion, equal possibilities for photo-induced crystallization in two different crystalline phases while the "outrigger-raft" model – only one possibility.

Change of the ratio of chemical bonds of edge-shared tetrahedrons and corner-shared tetrahedrons (P) that was concluded basing on comparison of intensities of corresponding modes of Raman scattering A_1^c (219 cm^{-1}) and A_1 (202 cm^{-1}) was confirmed by other investigators as well. It is known [22-23] that Raman-spectra of HTPM are characterized by intensive bands 211 and 216 cm^{-1} , and LTPM is characterized by 201 cm^{-1} band. The works [22, 30-32] expand and make deeper investigations of problems studied by Sugai, confirming in the first place, presence of corner-shared

and edge-shared tetrahedrons in glass and glass-forming liquids, and, in the second place, fixing their different quantitative ratio.

2.3. Outdated ideas - the deadlock for solving problems of glass structure

Sugai has constructed his model from stochastically joined in three-dimensional network two types of “molecules”: tetrahedrons $\text{GeSe}_{4/2}$ and edge-shared tetrahedrons $\text{Se}_{2/2}\text{GeSe}_2\text{GeSe}_{2/2}$ [26] leaving aside the problem of short-range and intermediate-range ordering.

In works [22, 27, 28, 31, 32] the problem of the short-range and intermediate-range ordering has been mentioned directly or indirectly, but only the question of similarity of the intermediate-range order of glass and liquid to HTPM structure has been discussed. For example, in the work [32] it has been stated that at lesser liquid’s cooling rates the medium-range structure is topologically more similar to a crystal structure. At that, a layered crystal, i.e. HTPM, is meant. The short-range ordering, if mentioned, has been considered in passing, without any detailed analysis.

As we can see, one of the most important aspects in all considered models of structure of non-crystalline germanium diselenide is the aspect concerning conservation of similarity of its structure to the structure of crystalline germanium diselenide. Such approach is also typical for another non-crystalline substances (for example, for $v\text{-SiO}_2$) beginning from Lebedev [5] and Zachariassen [8]. For example, since Zachariassen’s times it is considered that the short-range order (SRO) in glass and crystal is the same. In this seemingly natural thesis a deadlock for solving the problem of glass structure has been made long ago.

During about 20 last years most investigators of non-crystalline substance structure have been already saying about the intermediate-range order in non-crystalline substance outside limits of the short-range order. The progress is evident. The situation has been lead out to the higher level of understanding. But the deadlock has not been broken yet. There is no a generally accepted definition of the IRO. There is no understanding of insufficiency, and moreover – falseness, of the concept of presence in an individual non-crystalline substance of a single short-range order and a single intermediate-range order.

The exit of the deadlock has been proposed in the CPPCSGL concept [11-15]. In the framework of this concept the definition of IRO has been formulated, the notion of multiplicity short- and intermediate-range orders in an individual non-crystalline substance has been introduced corresponding multiplicity of different polymorphous modifications taking part in formation of its structure. Therefore, the described deadlock situation has been liquidated and the way for further development of understanding of an individual non-crystalline, and particularly vitreous, substance structure has been opened.

According to the CPPCSGL concept, the feature of the short-range ordering in vitreous GeSe_2 is presence, mainly, of two types of SRO, with two different atoms taken as a reference point. In the first case it is a germanium atom surrounded by four selenium atoms $\text{GeSe}_{4/2}$, and, in the second case, it is a selenium atom surrounded by two germanium atoms $\text{SeGe}_{2/4}$. As we can see, both SROs are in agreement with the principle of the chemically ordered network [27, 28]. It must be noted straight away that each of these SROs has its own variations: differences in bond lengths Ge-Se and interbond angles Ge-Se-Ge and Se-Ge-Se in corner-shared and edge-shared $\text{GeSe}_{4/2}$ [28], i.e. SROs around Ge atoms and SROs around Se atoms in LTPM and HTPM are different.

The intermediate-range ordering in $v\text{-GeSe}_2$ is characterized mainly by two alternating intermediate-range orders: IRO inherent to HTPM (two-dimensional layered structure) and IRO adopted from LTPM (three-dimensional network structure). Each of these IROs includes variations of the short-range order corresponding to one or another PM.

On the base of mentioned works [22, 23, 27-29, 31, 32], from positions of the concept of polymeric polymorphous-crystalloid structure, the conclusion has been made [13, 15, 33] that the structure of vitreous GeSe_2 (and glass-forming liquid) is formed by co-polymerized (de-polymerized) crystalloids (structural fragments without a long-range order) of layered (two-dimensional) HTPM and three-dimensional LTPM which are joined in glass in a single three-dimensional network characterized by alternation of mainly two intermediate orders inherent to HTPM and LTPM.

2.4. Structure of GeSe₂ amorphous films and liquid

According to Sugai's data [29] Raman spectra of amorphous GeSe₂ films obtained by vacuum deposition show the structure similar to that of glass obtained by quenching from melt shows.

Data on viscosity of Ge-Se liquid [37] show that GeSe₂ in the liquid state starting from melt temperature ~740 °C to ~1000 °C behaves as a chemical compound, i.e. its short-range ordering is similar to that of the crystal substance. The structure of the glass-forming liquid is, according to the Tool's kinetic theory of glass-formation [3], a "precursor", and, taking into account fictitious, or structural temperature T_f , an analogue of glass structure.

Investigations of GaSe₂ melt at 771 °C by the neutron diffraction method have shown that its structure is mainly analogous to glass structure [30].

Authors of the work [31] assumed that similarity of liquid and glass structures is confirmed by similarity of Raman spectra of vitreous samples at 420 °C and melt at 730 °C.

Thus, there is no principal difference between structures of glass, deposited films and glass-forming liquid. So, the conclusion can be made about similarity of structures of glass, obtained by quenching from melt, films, obtained by vacuum deposition, and liquid. Difference of their structures, one can think, is concluded in the extent of co-polymerization of crystalloids which is the most in solid glass, some lesser in deposited films, and even lesser in liquid. As for structures of solid glass, obtained in different conditions, or liquids at different temperatures, they differ, in accordance with the CPPCSGL, in ratio of crystalloids of different PMs, and, seemingly, in their dimensions – the higher the temperature of tempering the lesser the dimensions.

2.5. Relaxation processes in vitreous GeSe₂ at heating. Physical-chemical essence of glass transition temperature T_g

In the temperature range of 250-350 °C which directly precedes the glass-transition temperature (T_g according to several authors lays in the range of 335-392 °C [20, 31, 38]) smooth exothermal rise is observed on the thermogram of differential scanning calorimetry (DSC) obtained at 10 K/min heating rate [38]. Raman-spectra at temperatures 250, 300 and 350 °C show some increase of relative intensity of A_1 band inherent to LTPM (201 cm⁻¹) and decrease of intensity of HTPM band (216 cm⁻¹) [31].

It is known that for individual substances the transition from HTPM to LTPM is followed by exothermal effect [39]. Therefore, data of DSC and Raman-spectra evidence that at heating of GeSe₂ glass in the temperature interval that precedes T_g a partial transformation of HTPM crystalloids in LTPM crystalloids takes place with concentration increase of the latter that is confirmed by annealing of non-crystalline GeSe₂ films at 325 °C leading to LTPM crystallization [22]. DSC and Raman-spectra in described experiments show transformation of a part of containing in glass HTPM crystalloids in LTPM crystalloids in the range "~250 °C – T_g " – the process that can be identified as the latent period preceding LTPM crystallization.

Higher T_g temperature on DSC thermogram [38] the endothermal effect is observed. The Raman-spectrum [31] shows decrease of A_1 band intensity that characterizes vibrations of corner-shared tetrahedrons, and increase of A_1^c band intensity that characterizes edge-shared tetrahedrons (HTPM). The ratio of band intensities $I(A_1^c):I(A_1)$ changes from 1:3 (below T_g) to 1:1 in the range $T_g - T_c$ (T_c – the crystallization temperature). The 1:1 ratio characterizes overcooled liquid just before the beginning of HTPM crystallization that coincides with the ratio of corner-shared and edge-shared tetrahedrons, also equal 1:1, for crystallized HTPM. This fact allows to evaluate quantity of corner-shared and edge-shared tetrahedrons from the ratio of band intensities of Raman-spectra, and this way a share of structural fragments (crystalloids) of HTPM and LTPM in glass and glass-forming liquid. In the interval " $T_g - T_c$ " the Raman-spectra, therefore, show disintegration of LTPM and growth of HTPM crystalloids concentration.

The polymorphous transition of LTPM in HTPM is followed, as it is known, by endothermal effect [39] that is just observed in DSC thermogram at temperatures higher T_g . The endothermal effect related with softening temperature of glass, formed from individual chemical substance with enantiotropic transformation in crystal state, represents energy (heat) absorbed by glass at structural transformation of LTPM crystalloids in HTPM crystalloids that is a part of polymorphous

transformation heat at enantiotropic transition LTPM \rightarrow HTPM in crystal substance. If the latter is known, it is possible, having measured energy absorbed at glass softening, to evaluate concentration of HTPM and LTPM crystalloids ratio in glass. It would be rather useful to compare such evaluation with evaluation of concentration ratio HTPM \rightarrow LTPM based on ratio of intensities of Raman-spectra bands. Thus, both DSC and Raman-spectra evidence that in the temperature range of T_g instability of LTPM structure fragments is observed that is also confirmed by annealing of non-crystalline GeSe₂ films at 425 °C (some lower than T_c in DSC thermograms) leading to HTPM crystallization [22].

If at crystallization of non-crystalline GeSe₂ films at 325 °C LTPM is formed and at 425 °C HTPM is formed, it means that in the interval of 325-425 °C the equilibrium temperature between these crystal modifications is located, i.e. the temperature of their enantiotropic transformation T_{tr} .

Therefore, at heating of glass in the range which directly precedes T_g , transformation of HTPM structure fragments (crystalloids) in LTPM crystalloids takes place. Higher T_g , in the T_g - T_c interval, a transformation process goes (and significantly more intensive due to higher temperature) in reverse direction. T_g expresses itself as a temperature point where inversion of inter-transformation of structural fragments of HTPM and LTPM takes place, as a temperature point separating stability regions of LTPM and HTPM crystalloids of GeSe₂, regions in which latent processes in glass take place preceding LTPM crystallization (lower T_g) and HTPM crystallization (higher T_g), and processes of glass softening, its de-polymerization and transformation in super-cooled liquid followed by increase of HTPM crystalloids concentration and their consequent crystallization. T_g is genetically related with temperature of enantiotropic transformation T_{tr} in crystal substance; T_g in glass is analogous to T_{tr} in crystal substance.

If glass is heated with the rate at which HTPM:LTPM crystalloids ratio do not reach a critical level for the beginning of crystallization during the time of passing the T_g - T_m interval (T_m – the melting temperature), the substance will pass the temperature interval of super-cooled liquid existence without crystallization and come to liquid state at T_m . At lesser heating rates, the substance crystallizes and then this crystalline HTPM phase melts.

2.6. Relaxation of glass-forming liquid

In the work [37] it is shown that just after melting (higher than 712 °C) of HTPM GeSe₂ films the intensity of A_1^c band (HTPM) decreases and intensity of A_1 band (LTPM) increases that evidences, in our opinion, on generation in liquid, along with HTPM structural fragments, of LTPM structural fragments. At increasing liquid temperature to 720-730 °C, as it was noted before, the band intensity ratio shifts to increase of LTPM crystalloid concentration.

The fact of generation of both HTPM and LTPM in melt along with mentioned data on polymorphous-crystalline structure of liquid is very important: cooling such melt below T_g will lead to co-polymerization of structural fragments (crystalloids) of different PMs that obstructs melt crystallization, increase viscosity of melt and promotes glass formation.

Liquid state at certain temperature is characterized by a certain concentration ratio of crystalloids of different PMs. At temperature changes the inverse reaction of crystalloids inter-transformation takes place: HTPM \rightarrow LTPM.

During cooling of liquid below the melting temperature there are two main processes take place. The first one is the process of co-polymerization of crystalloids of different PMs leading to viscosity increase and obstructing melt crystallization.

The second process is conditioned by the fact of passing of liquid of the HTPM stability range and LTPM instability range in the interval T_m - T_{tr} . It is naturally to expect that in these conditions crystalloids inter-transformation will be shifted in direction of HTPM fragments concentration increase and LTPM fragments disintegration is becoming apparent as the process of de-polymerization of super-cooled liquid going along with the main process of its polymerization.

At high cooling rate the first process (co-polymerization) prevails, overcooled liquid passes the LTPM instability range, having conserved, along with increasing HTPM crystalloids concentration which is sufficient for glass formation, LTPM crystalloids concentration. Then the substance is cooled being in glass state.

If the cooling rates is less than critical one, all LTPM crystalloids have enough time to transform in HTPM crystalloids before reaching the temperature range ($T < T_{tr}$) where LTPM is stable and HTPM is unstable. In this case super-cooled liquid crystallizes as HTPM.

Long aging of cooled substance at temperature directly under T_g in the high-temperature part of the LTPM stability range can lead to glass crystallization as LTPM, as it was shown for amorphous GeSe_2 films annealed at 325°C [22].

Thus, relaxation of GeSe_2 glass-forming liquid at cooling, depending on change of the temperature factor, can results in formation of glass, HTPM or LTPM.

2.7. Relaxation processes in vitreous GeSe_2 caused by photo-irradiation

Let us consider now relaxation processes taking place in the result of the other type of external influence – photo-irradiation, in particular He-Ne laser irradiation ($\lambda=6328 \text{ \AA}$).

In fresh vacuum deposited non-crystalline GeSe_2 films at He-Ne laser irradiation a shift of optical absorption edge is observed in the direction of shorter (the yellow region) wave lengths (photo-enlightenment) at 300 K and in the direction of longer (the red region) wave lengths (photo-darkening) at 77 K [40].

In the Sugai's experiment [23] the luminous flux of the He-Ne laser (less than 0.7 kW/cm^2) changed the intensities ratio $I(A_1^c):I(A_1)$ bands from 0.43 to 0.33 (the shift in the direction of LPTM concentration increase). At the flux more than 0.7 kW/cm^2 the intensities ratio $I(A_1^c):I(A_1)$ changed from 0.43 to 1.0. (the shift in the direction of HTPM, to the yellow region of the spectrum). In this experiment it was possible either to crystallize LTPM of red color (in the first case) or to crystallize HTPM of yellow color (in the second case).

The shift of the adsorption edge in the process of photo-irradiation (with corresponding change of the band intensities ratio responsible for LTPM and HTPM) visually, in color (yellow-red), demonstrates the physical-chemical nature of relaxation processes - mutual transformation of structural fragments of different PMs preceding photoinduced crystallization.

Photo(thermo)-darkening and photo(thermo)-enlightenment are photo(thermo)-indication of the latent pre-crystallization processes – the processes of transformation of HTPM crystalloids in LTPM crystalloids at darkening and LTPM crystalloids in HTPM crystalloids at enlightenment taking place during the latent periods which directly precede crystallization of LTPM and HTPM.

2.8. High pressure and relaxation processes in GeSe_2

The relaxation process of crystalline HTPM of GeSe_2 under influence of high pressure with phase identification by Raman-spectroscopy goes as follows [19]. Single crystal HTPM at pressure increase to 6,2 GPa loses its crystal structure completely and transforms in disordered non-crystalline substance, the color of the sample being changed from yellow to red. At further pressure increase to 7 GPa the transition from the disordered phase to the crystalline low-temperature polymorphous modification of GeSe_2 is observed. Further pressure increase (8-12.5 GPa) leads to transformation of LTPM in the disordered phase that becomes dark and nontransparent. If pressure was not higher than 10 GPa, the process turned out to be reversible: pressure removal caused GeSe_2 relaxation leading to recovering of HTPM. Correspondingly, the color reverse takes place to yellow color.

The character of Raman-spectra change, given in [19], as well as change of the sample color both at increase and removal of pressure, allow on the base of CPPCSGL to make the conclusion that relaxation of GeSe_2 at pressure increase present gradual transformation of HTPM in LTPM with formation of an intermediate phase consisting of crystalloids of both PMs which concentration ratio changes with pressure change: at its increase to 7 GPa LTPM crystalloids concentration increases and HTPM crystalloids concentration decreases. The reverse process takes place at pressure decrease (from 7 GPa).

Pressure increase higher 8 GPa leads to LTPM destruction and formation of crystalloids of some new, in our opinion, polymorphous modification and, as a result of that, the intermediate disordered phase is formed again. At further pressure increase higher 12.5 GPa the crystalloids concentration of the new PM can, finally, reach 100% and then a new crystalline phase of high

pressure will appear, possibly one of that mentioned in the beginning of this paper. We suggest this prognosis basing on main theses of CPPCSGG [11-15].

3. Chalcogenides GeS_2 , SiSe_2 , SiS_2 . Relaxation processes in glass under influence of photo-irradiation

GeS_2 , like GeSe_2 , exists at normal pressure as high-temperature and low-temperature polymorphous modifications (HTPM and LTPM). The former forms a layered structure from tetrahedrons $\text{GeSe}_{4/2}$, one half of which are corner-shared and the other - edge-shared. The latter presents a three-dimensional network of corner-shared tetrahedrons. GeS_2 glass, according to interpretation of Raman-spectra and diffractometry data, built of corner-shared and edge-shared tetrahedrons, the average distance between atoms Ge-S corresponds with good approximation to bond lengths of both crystal PMs [20] that evidences in favor of the concept of polymorphous-crystalloid structure of glass according to which glass consists of co-polymerized fragments of structure of different PMs without a long-range order (crystalloids) [18]. T_g of $v\text{-GeS}_2$ is equal to 495 °C that practically coincides with the phase equilibrium temperature of HTPM and LTPM (with S excess) in the Ge-S phase diagram [20], i.e. here also, like the case of GeSe_2 , a genetic relation is observed between T_g and the temperature of enantiotropic polymorphous transformation [33-36].

Photoinduced crystallization of vitreous GeS_2 according to Sugai's data [29] causes, depending on radiation intensity, crystallization of LTPM or HTPM that shows complete analogy of relaxation processes taking place in GeS_2 and GeSe_2 at photo irradiation.

Unlike germanium chalcogenides, SiS_2 and SiSe_2 have HTPM where all tetrahedrons are edge-shared.

Glass structures SiS_2 , SiSe_2 , GeS_2 , GeSe_2 , according to Sugai [29], can be characterized by one parameter P representing a ratio of probabilities of existence of edge-shared and corner-shared bonds between tetrahedrons. Value of P can be changed by photo-irradiation. P decreases after irradiation with intensity lesser than the threshold and increases if intensity is higher than the threshold. For example, at irradiation of SiSe_2 glass by Ar-ion laser (4579 Å) with 15 mW power during 310 min the intensity ratio $I(A_1^c): I(A_1)$ decreases from 2.3 (P=1.05) to 1.8 (P=0.8) while irradiation with 30 mW power during just 10 min increases $I(A_1^c): I(A_1)$ to 3.0 (P=1.41). Sugai's experiments are in complete compliance with our polymorphous-crystalloid concept of structure of these glasses and show that physical-chemical essence of processes taking place in vitreous disulfides and diselenides of germanium and silicon effected by photo-irradiation is mutual transformation of structural fragments of edge-shared and corner-shared tetrahedrons $\text{AX}_{4/2}$, i.e. mutual transformation of HTPM and LTPM crystalloids: $\text{HTPM} \rightarrow \text{LTPM}$. If intensity of the external impact changes and exceeds a threshold, the direction of crystalloids transformation changes to the opposite direction that reflects ability of given substances to undergo enantiotropic polymorphous transformation in crystal state.

4. Arsenic selenide $\text{As}_{50}\text{Se}_{50}$. Relaxation processes.

Crystalline arsenic selenide $\text{As}_{50}\text{Se}_{50}$ exists in two polymorphous modifications. LTPM is isomorphic to molecular modification As_4Se_4 . HTPM is not identified comprehensively by X-ray analysis. In works [41, 42] diffractograms of both PM are presented.

Annealing of amorphous films $\text{As}_{50}\text{Se}_{50}$ obtained by vacuum deposition at temperatures less than T_g (~180 °C) leads to crystallization of LTPM, and at temperatures higher than T_g - to crystallization of HTPM [42]. This situation is similar to situation with GeSe_2 films behavior described earlier and evidences that amorphous $\text{As}_{50}\text{Se}_{50}$ is apparently formed by crystalloids of both PMs. At $T < T_g$ the process of transformation of crystalloids $\text{HTPM} \rightarrow \text{LTPM}$ and crystallization of the latter take place. At $T > T_g$ the relaxation takes place in direction of HTPM concentration increase. Like the case of $v\text{-GeSe}_2$ the softening temperature is in this case a point where the reverse of mutual transformation direction $\text{HTPM} \rightarrow \text{LTPM}$ takes place that is the analog of the enantiotropic transformation in crystalline substance. Thus, the relaxation of amorphous $\text{As}_{50}\text{Se}_{50}$ also goes by two ways determined by heating temperature of films and results in two-variant crystallization depending on annealing temperature: as LTPM or as HTPM. The additional confirmation of this relaxation

model are data of differential scanning calorimetry of $As_{50}Se_{50}$ films [42] that show two exothermal peaks one of which is lower T_g and another is higher T_g . This model is well blended with the experiment on photo-amorphization of crystallized as LTPM $As_{50}Se_{50}$ films [42, 43]. From the CPPCSGL point of view the process of transformation of LTPM in HTPM is taking place (but not finishing) here. The result is the formation of a structure containing crystalloids of both PMs with the concentration ratio depending on time and intensity of radiation. Increase of duration or intensity of these two factors must lead to crystallization of amorphous films as HTPM. Authors [42] have interpreted described relaxation processes differently in some respects, although they are close enough to our point of view. They consider that $As_{50}Se_{50}$ glass has two structural modifications related correspondingly to low- and high temperature forms of crystal. Irradiation and annealing can move glass from one modification to another.

Assumptions of existence of different modifications of non-crystalline, including vitreous, substance have been proposed during more than 20 last years. Some data on that are presented in [11, page 50]. It has been also shown there, based on the concept of polymorphous-crystalloid structure of non-crystalline substance making first steps that time and being a general case of CPPCSGL, that "poly-amorphism" does not exist in the nature, and "polyforms" of non-crystalline substance represent a composition of structural fragments of different PMs without long-range order, having different concentration ratios which are able to change from 0 to 1 depending on time and intensity of external influence. During the last 20 years, neither proofs of existence of amorphous polyforms nor a strict definition of this notion have appeared. The "relationship" sign [42] is evidently not enough for such definition.

5. Selenium

5.1. Structure of crystalline and vitreous selenium

Selenium forms three types (α -, β - and γ -) of monoclinic PM [20] which structures are constructed from molecules Se_8 . For Se_8 molecules the cis-configuration in arrangement of four consecutive linked atoms is inherent. α -monoclinic Se melts at 144 °C and spontaneously transforms in hexagonal Se; β -modification behaves similarly but at temperatures higher than 100 °C [20] (Fig.2).

Rhombohedral selenium constructed from Se_6 molecules is also known [44]. The thermodynamically stable Se modification is hexagonal PM consisting of spiral chains of atoms [20] with trans-configuration atom arrangement in four-fold fragments of the chain.

Analysis of IR- and Raman-spectroscopy, X-ray diffractometry, UV-photoelectron spectroscopy data as well as structural models proposed by Lukovsky [45] and other authors [20] allows to make the conclusion based on CPPCSGL [11-15] that vitreous selenium is constructed from a tangle of chains consisting of fragments of 8-fold rings of monoclinic PM, fragments of 6-fold rings of rhombohedral PM (in smaller amount) and fragments of chains of hexagonal selenium [46].

5.2. Structural relaxation in crystalline and vitreous selenium under temperature influence

Relaxation processes in metastable PMs (MSPM) at temperature influence manifest themselves on phenomenological level as polymorphous transformations "monoclinic PM \rightarrow hexagonal PM" (in single crystal samples the beginning of transformation is fixed after heating during 630 min at 70 °C [47]) and "rhombohedral PM \rightarrow hexagonal PM" at temperature higher 105 °C [44]. Both transformations are characterized by irreversibility that shows monotropic character of the performing phase transition.

Investigations of viscosity-elastic properties and strain relaxation in vitreous selenium, carried out by Bomer and Angel [47], have shown that at heating of glass in the temperature range of 27-42 °C the fraction of ring-like conformations sharply decreases and the fraction of chain-like conformations sharply increases in softening glass structure ($T_g \approx 37 \pm 10$ °C). Such change of "ring-chain" ratio is identified by authors as a phase transition between ring and chain structures. From CPPCSGL positions the presented facts are considered as structural transformation in glass Se phase of crystalloids of monoclinic MSPM in crystalloids of stable hexagonal PM (SPM), as the latent pre-

crystallization period preceding crystallization of hexagonal SPM. The beginning of this crystallization is fixed at 50 °C [48].

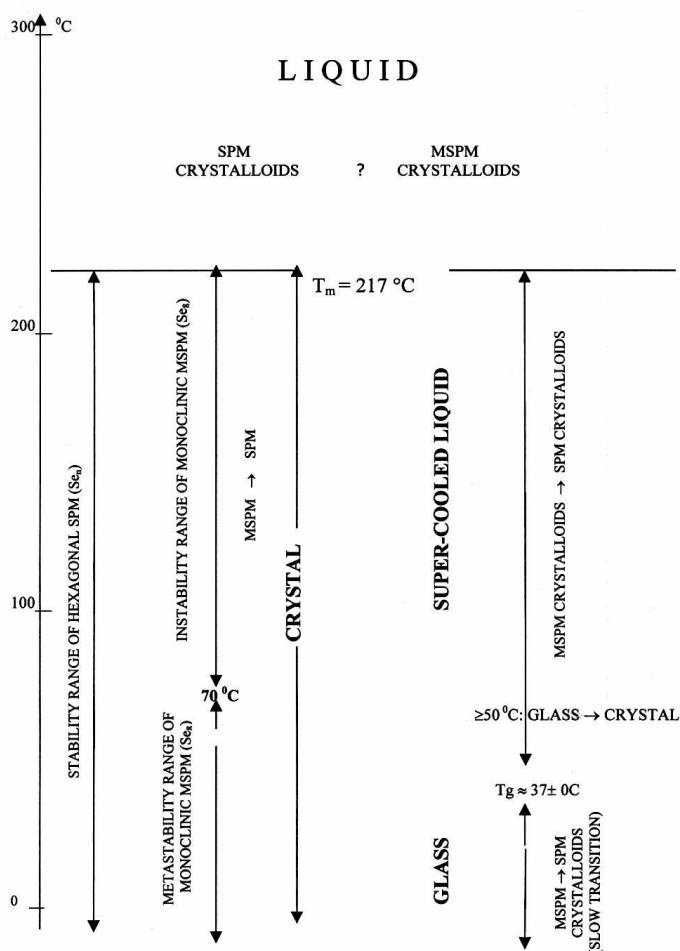


Fig. 2. Varieties of condensed state of Se.

As it can be seen from presented data, relaxation processes in vitreous selenium taking place at heating are similar to that in crystal substance (transformation of MSPM crystalloids in SPM crystalloids – “MSPM→ SPM”), but they begin at lower temperatures that is related, in our opinion, with greater energy of the disordered glass network, with heterogeneity of glass structure and the activation role of presented structural fragments of hexagonal SPM.

5.3. Phenomenological aspects of liquid selenium relaxation at cooling

Heating of crystallized hexagonal PM leads to its melting at 217 °C. Diffractometry data, as well as data on the viscosity temperature dependence [20, 48], give evidence that the melt structure is very similar to glass structure and there is also a statistical distribution of cis- and trans- configuration of selenium that is characteristic for ring and chain structures. Formation in melt of fragments of SPM and MSPM, change their ratio with temperature change [48] evidences that the main physical-chemical feature of liquid selenium relaxation is mutual transformation of SPM and MSPM crystalloids “MSPM → SPM”, unlike to the one-directional transformation "MSPM→ SPM",- in crystal and glass states.

Mutual transformation of crystalloids “SPM → MSPM” and their growing polymorphous copolymerization at melt cooling is the main cause hindering melt crystallization and increasing its viscosity right up to solid glass state. However, if the melt cooling rate is less than the critical cooling

rate (CCR), equal to 20 K/min [20], all crystalloids of MSPM will have enough time during cooling to transform in crystalloids of stable hexagonal PM and super-cooled liquid will crystallize. This observed fact evidences that CCR is a function of concentration and crystalloids transformation rate MSPM → SPM.

5.4. Photo-irradiation and relaxation processes in vitreous selenium

Sugai [29] investigated the process of photo-crystallization in vitreous selenium at irradiation by the He-Ne laser ($\lambda=6328$ Å) of different effective incident power (4 W/cm², 8 W/cm² and 8kW/cm²). Raman spectra of monoclinic selenium is characterized by the peak at 251.5 cm⁻¹ attributed to the A₁ mode of Se rings, hexagonal selenium chains are characterized by the 234 cm⁻¹ peak. In glass spectra bands corresponding to modes of both PM are observed. At irradiation by the laser beam with increasing effective power the intensity of 251.5 cm⁻¹ band decreases to almost complete disappearance at 0.8 kW/cm² power and the intensity of 234 cm⁻¹ band increases that evidences on transformation of monoclinic modification crystalloids (cis-configuration of atom arrangement) in hexagonal modification crystalloids (trans-configuration). The same structural changes are observed at thermal annealing.

As these facts show, relaxation processes in vitreous Se and v-GeSe₂ under temperature influence and He-Ne laser irradiation are principally different. The relaxation in GeSe₂ follows two-variant LTPM- and HTPM-crystallization that is characteristic for substances with enantiotropic polymorphous transformation.

For selenium with its monotropic polymorphous transformations in crystal state, influence of temperature and photo-irradiation leads to the single way of structural relaxation in glass - increase of concentration of crystalloids of thermodynamically stable hexagonal PM at the expense of decrease of concentration of structural fragments of metastable monoclinic and, possibly, rhombohedral modifications. As the result, only single-variant crystallization is characteristic for v-Se.

6. Nanoheteromorphism and Ge-Se glass-forming system

The main cause and physical-chemical essence of glass formation is co-polymerization of different fragments of structure without long-range order. Difference in fragment's structures do not allow co-polymerizing substance to organize translational symmetry (a long-range order), i.e. to be crystallized.

Nanoheteromorphism in non-crystalline substance is co-existence of different structural fragments (structural inhomogeneities) having no long-range order. Nanoheteromorphism and nanoheteromorphous co-polymerization are the necessary and sufficient conditions for glass-formation.

In the case of individual chemical substances which are able to exist in non-crystalline, vitreous in particular, state, such structural fragments are crystalloids of different polymorphous modifications. If glass contains more than one component, i.e. it is formed of two and more individual chemical substances (ICS), presence of structural fragments of these ICS is sufficient for glass formation irrespective of existence or non-existence of their different PMs.

An intermediate variant is possible: presence in glass of crystalloids of different PMs modifications of one of ICS and structural fragments of the other (others) ICS irrespective of its (theirs) ability to form polymorphous modifications.

Let us consider from this point of view the glass-forming system Ge-Se. The glass-formation region in this system ranges from 100 at.% to ~ 45 at.% Se [20]. As it has been shown before, glass-formation in individual chemical substances GeSe₂ and Se is caused by co-polymerization of crystalloids of different PMs of GeSe₂ and Se. At adding Se to GeSe₂, Se atoms are built in between GeSe_{4/2} tetrahedrons forming at first two- and then three-, four-fold chains, etc. When reaching Se content of 80%, all tetrahedrons turn to be isolated from each other by chemical bonds Se-Se and, as a result, all crystalloids belonging to HTPM and LTPM of GeSe₂ turn to be destructed. (The smallest crystalloid of GeSe₂ - the carrier of the intermediate-range order of this or that PM - contains two united tetrahedrons having common Se atom (atoms)). It means that in the composition Ge₂₀Se₈₀ the

intermediate-range order (IRO), which is characteristic for both GeSe_2 PMs, vanishes away. All Ge atoms in this composition are connected to each other by selenium's two-fold chains which are also not characteristic for any of selenium PMs because they cannot form an intermediate-range order for any of selenium PMs. The minimum quantity of atoms necessary for formation of selenium IRO, with cis- or trans-configuration of atom arrangement, is four. The first chain of 4 selenium atoms appears (theoretically) in the composition where Se:Ge ratio is more than 6:1 ($\text{Ge}_{14.886}\text{Se}_{85.714}$).

Thus, glass-formation in ICS GeSe_2 and Se is ensured by nanoheteromorphism based on crystalloids inherent to different PMs. For the range of compositions where $80.0 > \text{Se} > 66.6(6)$ at.%, nanoheteromorphism is based on presence of crystalloids of different PMs of GeSe_2 and structural fragments of Se composed of two- and three-fold chains and not being IRO carriers of any PM. In the range of compositions where $80.0 < \text{Se} < 85.714$ at.%, there are no structural fragments with IRO of GeSe_2 or Se. Here, nanoheteromorphism is presented by structural fragments with three types of the short-range order: SRO, which is typical for GeSe_4 , SRO, which is characteristic for three-fold Se chains, and SRO, which is typical for structural fragments consisting from a selenium atom connected by one bond (Ge-Se) with a germanium atom and by one bond (Se-Se) with a selenium atom. For the range of compositions $85.714 < \text{Se} < 100$ at.%, IROs of both selenium PMs, SRO of $\text{GeSe}_{4/2}$, and SRO, where selenium atom is connected with germanium atom and other selenium atom, are typical. From above, the conclusion can be made that in Ge-Se system the glass-formation region, which is characterized by concentration change of each elements of more than 40 at.%, only in the range of ~5.7% nanoheteromorphism is not related with structural fragments of different polymorphous modifications.

Thus, in pure GeSe_2 and Se the basis of relaxation processes is the transformation of crystalloids of one PM to crystalloids of another PM, being reversible in GeSe_2 and irreversible in Se. In the rest compositions relaxation processes are related with structural polymorphous transformations either partially, or (in compositions $80.0 < \text{Se} < 85.714$ at.%) not related completely and follow to the classical relaxation theory [49].

7. Conclusion

1. Chalcogenides of Ge-Se system, individual chalcogenides GeS_2 , SiSe_2 , SiS_2 , AsSe and chalcogen Se being as examples, it has been shown that glass represents a co-polymer of structurally different nanoheteromorphous fragments of crystal lattices without a long-range order. Nanoheteromorphism and co-polymerization of fragments with different structures is the main cause hindering crystallization of substance when liquid is cooled. In the case of individual chemical substance, nanoheteromorphous fragments are exclusively structural fragments of different PMs of given substance without a long-range order (crystalloids), having medium-range order inherent to one or another PM. A combination of different medium-range orders is the main feature of structure of individual chemical substances in vitreous state.

2. Glass-forming melt of individual chemical substances is also built of HTPM and LTPM crystalloids in the case of substances with enantiotropic polymorphous transformation in crystal state (GeSe_2 , GeS_2 , SiSe_2 , SiS_2 , AsSe), or it is built of SPM and MSPM crystalloids in the case of substances with monotropic transformation (Se). One in two physical-chemical essence of relaxation of cooled glass-forming liquid is as follows:

- a) the process of co-polymerization of crystalloids of HTPM and LTPM (or SPM and MSPM), and
- b) the process of disintegration of LTPM (or MSPM) crystalloids in the range of their instability lower T_m followed by partial de-polymerization and transformation in HTPM (SPM) crystalloids which are stable in this temperature region.

At cooling rates less than critical one, the latter process prevails, and glass crystallization in the form of HTPM (or SPM) takes place. At cooling rates higher than critical one, the former process prevails, and glass - co-polymer of HTPM and LTPM (or SPM and MSPM) crystalloids - is formed.

3. Relaxation of individual vitreous substance at heating is determined by relaxation behavior of its crystal analog which, at heating, undergoes: a) enantiotropic or b) monotropic polymorphous transformation.

In the a) case, at slow heating or annealing lower $T_g \approx T_{tr}$ glass crystallizes in the form of LTPM, and at slow heating or annealing in the $T_g - T_m$ interval glass crystallizes in the form of HTPM (two-variant crystallization). T_g represents the temperature separating stability temperature regions of LTPM and HTPM crystalloids, the temperature where inversion of mutual transformation direction of LTPM and HTPM structural fragments takes place, the temperature which is the analog of the enantiotropic transformation temperature T_{tr} of crystal substance.

In the b) case at slow heating or annealing, glass crystallizes exclusively in the form of SPM (one-variant crystallization). T_g is the temperature of the beginning of the active stage of transformation of MSPM crystalloids in SPM crystalloids.

4. The main physical-chemical essence of relaxation processes in glass at photo-irradiation is mutual transformation of LTPM and HTPM crystalloids or transformation of MSPM crystalloids in SPM crystalloids.

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