Journal of Optoelectronics and Advanced Materials Vol. 4, No. 4, December 2002, p. 843 - 855

ON THE POLYMERIC NANO-HETEROMORPHOUS GLASS STRUCTURE

V. S. Minaev

Research Institute of Material Science and Technology (RIMST)
124460, Moscow, Russia

According to the polymeric polymorphous-crystalloid concept of individual vitreous chemical substance structure, glass is a co-polymer of structural fragments (crystalloids) which are bearers of short-range and intermediate-range orders (SROs and IROs), of different crystal polymorphous modifications (PM), taking part in glass-formation, and having no a long-range order (LRO). When two-component systems are under consideration, the number and type of SROs and IROs in glass get changed, depending on concentration and chemical nature of the second component, to the point of the phenomenal occurrence – glass without IROs and SROs typical for crystalline PMs of initial chemical substances. Having based on the analysis of two-component glass-forming systems $GeSe_2$-Se, S-Se and SiO_2-GeO_2, the conclusion has been drawn that the glass consists of co-polymerized structural fragments of initial chemical substances that can be characterized by SROs and IROs of crystal PMs and/or by fragments without these orders. Such concurrent existence in glass of different structural fragments of the nanometric scale without LRO is called nano-heteromorphism. Nano-heteromorphism and nano-heteromorphous co-polymerization are necessary and sufficient conditions for glass-formation of mono- and multi-component glasses.

(Received September 17, 2002; accepted October 31, 2002)

Keywords: Glass, Polymeric structure, Nano-heteromorphous

1. Introduction

Beginning since thirties of the XX century till now a paradox situation can be observed in publications concerning glass: from one side, it is long ago and irrefutably proved that in well-prepared glass there are no even smallest crystals (crystallites) [1-3], but from the other side, that properties of a single-component glass, SiO_2 in particular, and its structure are related simultaneously with properties and structure of two, and even three (quartz, cristobalite, tridymite) crystalline polymorphous modifications (PM) [4-10, 3].

More than 60-years existence of the half-realized paradox "appearance of properties of crystalline polyforms in the glass without crystals" is explained, in our opinion, by the pagan fanatical affection of investigators (including the author) for the idea formed about a half-century ago: short-range orders (SRO) in vitreous and crystalline individual chemical substances (ICS) – for example, in SiO_2, P_2O_5, Se – are the same. This thesis was transmitted through well-known monographs of Mott and Devis [11], Feltz [12] and other works.

In this seemingly natural thesis a deadlock for solving the problem of glass structure has been laid down long ago.

During about twenty last years most investigators of non-crystalline substance structure have been already saying about an intermediate-range order (IRO) in non-crystalline structure 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 – fallaciousness, of the thesis of presence in an individual non-crystalline substance of a single short-range order and a single intermediate-range order.

2. The concept of polymeric polymorphous-crystalloid structure of individual vitreous chemical substance

The exit of the deadlock has been proposed in the concept of polymeric polymorphous-crystalloid structure of an individual vitreous chemical substance (CPPCSIVCS) [13-15]. This concept is supported by the following thesis:

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

2. The notion "crystalloid" is directly related with notions "short-range order" and "intermediate-range order" that are applicable to both non-crystalline and crystalline substance.

The short-range order is a stereometrically-determined composition of atoms including the atom taken as the origin point and surrounding atoms in the first coordination sphere. The SRO is characterized by the coordination number, type of constituent atoms, distance between atoms, and by inter-bond angles [16,17].

The intermediate-range order is a stereometrically-determined composition (a topology) of short-range orders in the limits of a crystalloid which is characterized by parameters of all SROs and by dihedral angles [14]. 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 – a smallest crystal in which the unit cells of the crystal lattice can be inter-translated.

Crystalloids in glass are bearers of IROs of different polymorphous modifications.

3. In every non-crystalline substance there are two or more SROs, two or more IROs (plurality of SROs and IROs), and there is no a long-range order (LRO). The number of IRO types is equal to the number of polymorphous modifications taking part in formation of the non-crystalline substance. For example, SiO_2 is characterized by SRO around an silicon atom and SRO around an oxygen atom. The latter SRO in cristobalite is different from those in quartz and other polymorphous modifications by the value of Si-O-Si angle that is the reason of difference of IROs in these polymorphous modifications.

4. Structure and properties of glass are determined by the concentration ratio of crystalloids of different PMs inherent to given glass and dependent on state of the initial material, conditions of formation and treatment of the vitreous material.

3. Some aspects of binary vitreous systems structure

3.1 Intermediate-range and short-range ordering in glass-forming system $GeSe_2$-Se

Glass-formation in individual chemical substances $GeSe_2$ and Se is caused by co-polymerization of crystalloids of different PMs of $GeSe_2$ and Se [14,15]. Minimal crystalloid $GeSe_2$ - the bearer of the intermediate-range order of one or another PM contains two joined tetrahedrons. The intermediate-range order of low-temperature PM (LTPM) is characterized by tetrahedrons joined by vertexes only. IRO of high-temperature PM (HTPM) is formed by tetrahedrons joined by both vertexes and edges [18].

Besides, there are different short-range orders in v-$GeSe_2$. Germanium atom surrounded by four selenium atoms forms two resembling but different SROs: $GeSe_{4/2}$. They are different in angles Se-Ge-Se and the length of the bond Ge-Se because in LTPM $GeSe_{4/2}$ tetrahedrons are joined by vertexes, and in HTPM – both vertexes and edges that in the latter case leads to distortion of tetrahedrons, and consequently SRO. Two different SROs exist around Se atoms connected with two Ge atoms (these

SROs ($SeGe_{2/4}$) are different in angles Ge-Se-Ge and the length of the bond Ge-Se due the same reason as SRO inside $GeSe_{4/2}$ tetrahedron).

The above said assertions agree with the glass model described by the chemically ordered continuous random network (COCRN) and based on the assumption that for all compositions heteropolar bonds having larger energy are more preferable than homopolar bonds [19,20]. In real glass $GeSe_2$ many authors (for example, Boolchand [21]) have observed Raman-spectra peaks which are characteristics of chemical bonds Ge-Ge (~ 170 cm^{-1}) with concentration up to 2% and Se-Se bonds (240-250 cm^{-1}).

It means that in real v-$GeSe_2$ two more SROs appear: 1) Ge atom surrounded by three Se atoms and one Ge atom - $Se_{3/2}\,GeGe_{1/4}$ and 2) Se atom connected with one Se atom and one Ge atom - $Se_{1/2}SeGe_{1/4}$. These SROs are formed from fragments of short-range orders of initial ICSs: $GeSe_2$ ($GeSe_{4/2}$) and Se ($SeSe_{2/2}$ – chains of three Se atoms). Therefore, these short-range orders can be called cmpound ones.

The minimum number of atoms necessary for creation of different IROs of selenium, in cis- and trans-configurations, typical for monoclinic and hexagonal PMs of selenium, is equal to 4 [14]. SRO of selenium is described above.

Now, let us consider intermediate compositions of the glass-forming system $GeSe_2$ – Se from the point of view of intermediate-range and short-range ordering.

When Se is added to $GeSe_2$, selenium atoms embed between $GeSe_{4/2}$ tetrahedrons forming at first two-fold and then three-fold, four-fold chains and so on. When selenium content of 80 at.% is achieved (at ideal mixing of $GeSe_2$ and Se), all tetrahedrons are isolated from each other by chemical bonds Se-Se, and in the result all crystalloids of high-temperature and low-temperature PMs, from which vitreous $GeSe_2$ (v-$GeSe_2$) is formed, turn out to be destroyed [15]. It means that in the composition $Ge_{20}Se_{80}$ IROs, typical for both PMs of $GeSe_2$, disappear (Fig.1,2). All germanium atoms at this composition are connected with each other by two-fold selenium chains which are not also typical for any selenium PM because they cannot form IRO of any selenium PM because, as it was described above, it is necessary to have no less than four Se atoms in the chain. The first chain of 4 selenium atoms appears in the composition when the ratio of selenium and germanium is greater than 6:1 ($Ge_{14.29}\,Se_{85.71}$).

Thus, whereas in ICS $GeSe_2$ and Se the glass-formation in the "ideal" case is provided for by different-structural, heteromorphous crystalloids – bearers of IRO of the nanometric scale inherent to different PMs of corresponding ICS, in the composition range of 80 > Se > 66,6(6) at.% there are, beside $GeSe_2$ crystalloids, nano-structural selenium fragments composed of two-fold chains which are not IRO bearers of any selenium PM. It means that, for this composition range, nano-heteromorphous structural fragments which form two IROs and all SROs of $GeSe_2$, and nano-heteromorphous structural fragments composed of two-fold chains of Se which unite $GeSe_2$ tetrahedrons and, as a result, organize the compound SRO $Se_{1/2}\,SeGe_{1/4}$, are typical (Fig.1).

Therefore, the nanoheteromorphism here - the assembly of nano-heteromorphous structural fragments – is presented by both structural nanofragments of different polymorphous modifications and nano-fragments which are not typical for any PM.

In the composition range of 80.00 ≤ Se ≤ 85.71 at.% there are neither structural fragments with IRO of $GeSe_2$ nor Se (Fig. 1).

In this range, nano-heteromorphous structural fragments are presented which are typical only for three different short-range orders: 1) the SRO reproducing $GeSe_2$ tetrahedrons, 2) the SRO organizing three-fold selenium chains and 3) the compound SRO $Se_{1/2}SeGe_{1/4}$.

For the composition range of 85.71 < Se < 100 at.%, IROs of two selenium PMs with inherent selenium SRO, SRO $GeSe_{4/2}$ and the compound SRO $Se_{1/2}SeGe_{1/4}$, are typical.

Thus, in the system $GeSe_2$-Se, which glass-formation region is characterized by concentration alteration of each element by 33.3(3) at.%, the nano-heteromorphism is not related with structural fragments of different polymorphous modifications in the range of 5.71 at.% only.

It follows from above considerations that the concentration of crystalloids – bearers of intermediate-range orders of polymorphous modifications of $GeSe_2$ – decreases from the maximum at 66.6(6) at.% Se to zero at 80.00 at.%. At selenium concentrations of 80.00-85.71 at.%, in glass at ideal homogenous distribution of components, crystalloids of any PMs are absent, and at further increase of selenium concentration from 85.71 at.% to 100% concentration of selenium crystalloids – bearers of its intermediate-range order – increases from zero to maximum. So, on the IRO bearers concentration vs. composition dependence we have two rectilinear sections: 66.6(6) – 80 at.% Se and 85.71 – 100 at.% Se divided by the section of 80.00–85.71 at.% Se with zero concentration of IRO bearers (Fig. 1).

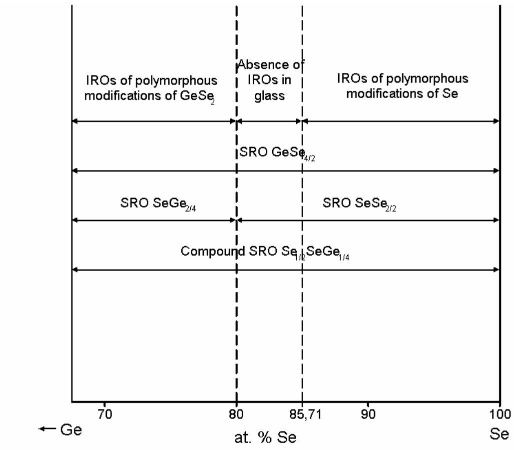

Fig. 1. The diagram of location of intermediate-range and short-range orders in the glass-forming system $GeSe_2$-Se at ideally homogeneous distribution of components.

Naturally, we considered the ideally homogeneous distribution of components $GeSe_2$ and Se. But it is known that practically in any real glass, and glass-forming liquid as well, containing two or more components, a structural feature appears, so-called "concentration fluctuation" [22,23]. Therefore, in real glass in the whole glass-formation region of $GeSe_2$-Se system some amount of nano-heteromorphous formations characterizing IROs of different polymorphous modifications of $GeSe_2$ and Se will be present, and in this case the alteration of concentration of crystalloids – bearers of IRO of polymorphous modifications of $GeSe_2$ and Se - from maximum to minimum will deviate from the polyline composed of straight lines and will follow concave curves above points 80 and 85.71 at.% Se and asymptotically tending to zero in points 100 and 66.6(6) at.% Se, respectively. The summarized curve of the analyzed dependence will present a smooth concave curve with maximums at compositions of 66.6(6) and 100 at.% Se and the minimum above the zero line in the region of 80 - 85.71 at.% Se (Fig. 2).

It is interesting that the very same shape has been obtained for the dependence of endothermic non-reversing heat flow at heating of glasses of the $GeSe_2$-Se system in the softening region (T_g) by Temperature-Modulated Differential Scanning Calorimetry (TMDSC) in the work of Boolchand [21]. From the point of view of the concept of polymeric polymorphous-crystalloid glass structure [13-15] such dependence is quite natural. It is known [24] that the polymorphous transformation of low-temperature PMs in high-temperature PMs occurs with an endothermic effect. Both v-$GeSe_2$ and v-Se are formed of co-polymerized crystalloids of these PMs. And in the region T_g, where the transformation LTPM → HTPM is the most intensive, the endothermic effect is observed [18]. It has its maximum where concentration of crystalloids of these PMs is highest, i.e. for ICS $GeSe_2$ and Se. The minimum of the effect coincides with the minimum of concentration of crystalloids – bearers of intermediate-range order of polymorphous modifications. The Boolchand's experiment is one more evidence of correctness of the concept of polymeric polymorphous crystalloid glass structure.

It is necessary to note, however, that in the Boolchand's experiment [21] the minimum of the curve "the value of the endothermic effect vs. composition" corresponds to the glass in which the average coordination number **r** is equal to 2.46, i.e. the composition $Ge_{23}Se_{77}$. According to our calculations, this minimum should be located in the interval of compositions containing from 20 to 14.29 at.% of germanium and from 80 to 85.71 at.% of selenium, i.e. in the interval **r**=2.4÷2.29.

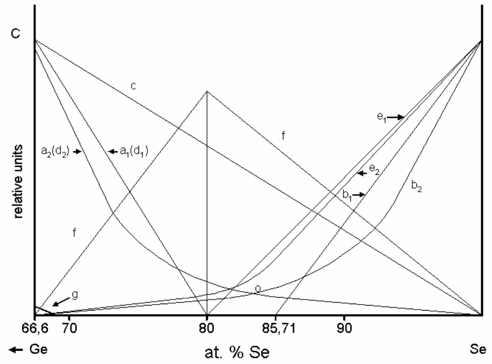

Fig. 2. The dependence of the concentration C (relative units) of crystalloids – bearers of intermediate-range orders of different polymorphous modifications of $GeSe_2$ (a_1 – for the case of ideally homogeneous distribution of components in glass, a_2 – for real glass) and Se (b_1 – "ideal" glass, b_2 – real glass), concentration of structural fragments – bearers of the short-range order in $GeSe_2$ (c - $GeSe_{4/2}$; d_1, d_2 - $SeGe_{2/4}$ in "ideal" and real glasses), in Se (e_1, e_2 - $SeSe_{2/2}$ in "ideal" and real glasses), the concentration of structural fragments – bearers of compound SRO (f - $Se_{1/2}SeGe_{1/4}$ in "ideal" glasses, g - $Ge_{1/4}GeSe_{3/2}$ in real glasses) in the glass-forming system $GeSe_2$-Se vs. composition. o – the point of intersection of curves a_2 and b_2.

Such shift of the minimum of the endothermic effect is likely determined by three factors.

Firstly. The presence of a number of bonds Ge-Ge (≈ 2% for $GeSe_2$ compound) decreasing the concentration of crystalloids of different PMs of $GeSe_2$ and, correspondingly, increasing the concentration of Se crystalloids.

Secondly. The appearance of 4-fold atomic chains of selenium, i.e. crystalloids of its polymorphous modifications, as the result of the non-ideal mixing of Ge and Se atoms in compositions containing more than 20 at.% of Ge.

Thirdly. The higher value of the endothermic effect of the polymorphous transformation in selenium than in $GeSe_2$, as is seen in Boolchand's Fig. 3.

It is interesting that the minimal endothermic effect in the Boolchand's experiment is quite distant from the zero level and equals to ≈ 0.1 cal/s.g while in systems $Ge_xAs_xSe_{1-2x}$ and $Ge_{0.25}S_{0\cdot75-x}I_x$ it practically equals to zero in the minimum point. In our opinion, it means that the in minimum point of the effect (r=2.46 in Fig. 3), i.e. in the composition $Ge_{23}Se_{77}$ both $GeSe_2$ and Se crystalloids present, and decreasing of their concentration at decreasing of $GeSe_2$ or Se concentrations takes place along curves continuing the right or left branches of the Boolchand's curve from the minimum point to the zero content of germanium in the zero point of the endothermic effect for $GeSe_2$, and, the second branch – from the minimum point to the composition $GeSe_2$ at the zero level of the endothermic effect for Se. In other words, it is completely similarly to curves of the concentration change of corresponding crystalloids (a_2 and b_2) in real glasses of Fig. 2.

And, at last, in the Boolchand's figure the minimum of the endothermic effect for complicated systems $Ge_xAs_xSe_{1-2x}$ and $Ge_{0.25}S_{0\cdot75-x}I_x$ is located exactly in the middle of the interval of compositions containing in the system $GeSe_2$–Se 80–85.71 at.% Se (**r**=2.4÷2.29), i.e. it belongs to the composition $Ge_{17.15}Se_{82.85}$ (**r**=2.34) located in the center of the region in which, for the ideally mixed glass of the system $GeSe_2$ - Se, crystalloids – bearers of the intermediate-range order of PMs $GeSe_2$ and Se are absent (Fig. 2).

In this complicated systems there are apparently no bonds Ge-Ge and chalcogene's atoms are distributed more uniformly between Ge and As atoms in the former system and between Ge and I atoms in the latter system, and, as the result, the minimum of the endothermic effect is located in the place where it should be at the ideal mixing of components in systems $GeSe_2$-Se and GeS_2-S which are in the base of systems analyzed by Boolchand.

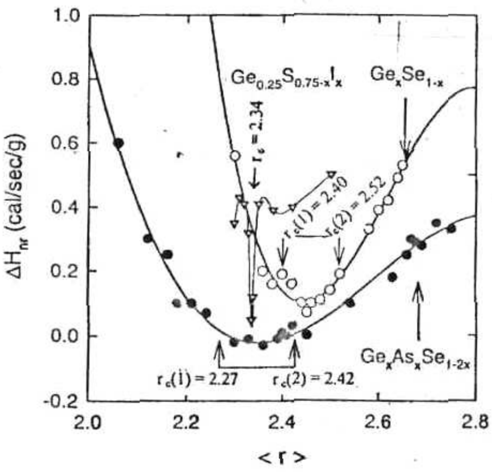

Fig. 3. ΔH_{nr} variation as a function of glass composition revealing thermally reversing windows in Ge_xSe_{1-x} (○), $Ge_xAs_xSe_{1-2x}$ (●) and $Ge_{0,25}S_{0,75}I_x$ (Δ) bulk glasses [21].

The correctness of our interpretation of Boolchand's data can be confirmed experimentally if selenium in the system $GeSe_2$-Se is replaced for the equi-atomic composition $S_{0.5}Se_{0.5}$ that does not contain structural fragments of any chalcogen PM because all atoms of one chalcogen form chemical bonds with atoms of another chalcogen in glass. In this case at increasing of the total concentration $S_{0.5}Se_{0.5}$> 80 at.% and up to 100% of $S_{0.5}Se_{0.5}$ (and in any other composition of the system $GeSe_2$-$S_{0.5}Se_{0.5}$, though) vitreous alloys will contain structural fragments of polymorphous modification neither sulfur nor selenium that will lead to the absence of such great endothermic effect, as for selenium, at T_g that is caused by the transformation of crystalloids of low-temperature (unstable) PMs in crystalloids of HTPMs. On the Boolchand's curve there will be no the branch reflecting the increase of the endothermic effect at increasing of the total chalcogen concentration from 85.71 at.% to 100 at.%. The dependence "the value of the endothermic effect vs. the total chalcogen's concentration" will resemble in real glass-forming alloys of the $GeSe_2$-$S_{0.5}Se_{0.5}$ system the curve of the concentration dependence of the content of crystalloids of different PMs $GeSe_2$ on the selenium's content in the system $GeSe_2$-Se (the curve a_2 in Fig. 2).

3.2 Intermediate-range and short-range ordering in glass-forming system S-Se

The two-component system S-Se is presented by the glass-formation region expanding on all compositions from sulfur to selenium [25].

Selenium is characterized by 3 monoclinic and 1 hexagonal modifications, sulfur – 19 polymorphous modifications [12]. At the present time there are no sufficient experimental data for a detailed analysis of glasses based on structures of all polymorphous modifications of chalcogens. Therefore, we will not go beyond reliable confirmed data on presence in vitreous sulfur and selenium of cis- and trans-fragments in arrangements of four chalcogen atoms characterizing different PMs. We take that chalcogen crystalloids of the minimum size contain 4 atoms and are in one of mentioned configurations (cis- and trans-) that in crystalline selenium form monoclinic and hexagonal modifications constructed from 8-fold rings and "endless" chains, correspondingly, in sulfur – the group of cis-modifications consisting of rings with different number of atoms (6,7,9,10,11,12,18,20, etc.) [12] and the trans-modification consisting of "endless" chains, correspondingly.

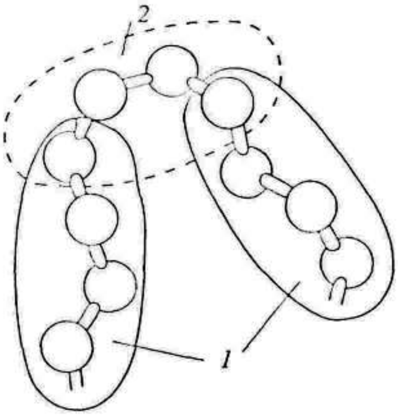

Fig. 4. Fragments (crystalloids) with *cis* and *trans* configurations (monoclinic and hexagonal polymorphic modifications, respectively) in the chain structure of vitreous selenium [26]. (1) Chain fragments (*trans configurations)* and (2) fragment of the Se_8 ring structure (*cis configurations).*

Vitreous selenium is constructed mainly from co-polymerized 4-atoms structural fragments consisting of cis- and trans-configurations (Fig.4 [26]), i.e. crystalloids monoclinic and hexagonal PMs [14]. When sulfur is added to selenium, its atoms embed between selenium atoms. At 10% of sulfur in the alloy in the case of its ‘ideal” dissolving and distribution, sulfur atoms will separate fragments of chains, consisting of 9 selenium atoms, at 20% of sulfur – of 4 selenium atoms, i.e. fragments which can still form both cis- and trans-configurations, i.e. represent crystalloids which are bearers of intermediate-range orders of two different PMs. At last, at 25 at.% S in Se all selenium chains consist of 3 atoms united by sulfur atoms in "endless" compound chains. In this case there are no already selenium crystalloids neither monoclinic nor hexagonal modifications, there are no intermediate-range orders characterizing these polyforms. And naturally, there is no IRO characterizing sulfur poly-forms. They are absent also in sulfur enriched compositions including $Se_{25}S_{75}$ composition (Fig. 5,6).

At further increasing sulfur content at alloys (again, in the "ideal" case), first four-fold sulfur chains appears which are able to organize cis- or trans-configuration of atoms and corresponding IRO characterizing ring-like or chain-like modifications.

So, in the range of $75 \geq Se(S) \geq 25$ at.% "ideal" glasses in the S-Se system do not have IRO of any PM. The intermediate-range-ordering in this system is proper only to $100 \geq Se(S) \geq 75$ at.% compositions (Fig. 5). It means that on the dependence "concentration of crystalloids – bearers of IRO of selenium and sulfur vs. composition", like the $GeSe_2$ - Se system, there will be two rectilinear section (100-75 at.% Se and 25-0 at.% Se) divided by the section of 75-25 at.% Se with zero concentration of IRO (Fig. 6). In real glass due to “concentration fluctuation” the summarized curve of the dependence will present, like the $GeSe_2$-Se system, a smooth concave curve with maximums at 100% S and Se and the minimum in the area of 50 at.% of each component above the zero level of the crystalloids concentration of S and Se. The dependence "endothermic effect vs. glass composition" must have the similar shape.

The short-range ordering in sulfur and selenium is characterized by the chain of three atoms in which the central atom is connected with two atoms of the same type: sulfur's SRO -S-S-S- and selenium's SRO -Se-Se-Se-, i.e. $SSe_{2/2}$ and $SeS_{2/2}$.

Short-range ordering in glasses of the S-Se system is characterized by nano-heteromorphous fragments consisting of three atoms of one element or both elements of the S-Se system.

In the "ideally" mixed alloy of sulfur and selenium chains –S-S-S- and -Se-Se-Se- can exist only at the sulfur or selenium concentration higher than 66.6(6) at.% of the given element. At the concentration of this element equal to 66,6(6) at.% all its chains consist of two atoms united in the "common" chain by individual atoms of another element.

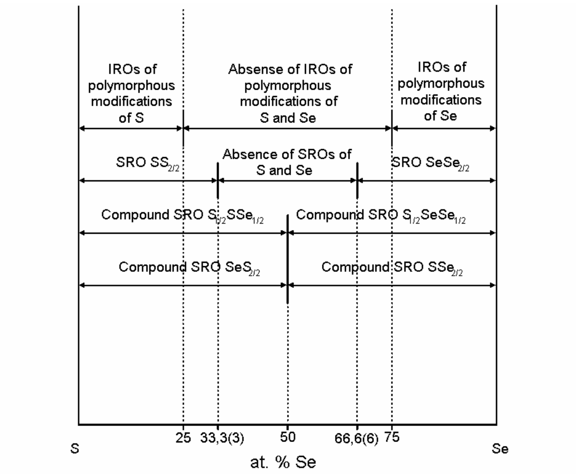

Fig. 5. The diagram of location of intermediate-range and short-range orders in the system S-Se at ideally homogenous distribution of components.

It means that the short-range order of initial components of the S-Se system takes place only at concentrations of $100 \geq Se(S) > 66.6(6)$ at.%. The range of 33.3(3) - 66.6(6) at.% Se(S) is characterized by absence of short-range orders of initial components of the binary system S-Se.

In the system S-Se there are, however, another short-range orders as well: SRO around the sulfur atom characterizing the chain -S-S-Se- ($S_{1/2}$ $SSe_{1/2}$) and SRO around the selenium atom characterizing the chain Se-Se-S-($Se_{1/2}SeS_{1/2}$), and also SROs characterizing chains -S-Se-S-($SeS_{2/2}$) and -Se-S-Se-($SSe_{2/2}$). The former two SROs are in the composition range of $100 > Se(S) > 50$ at.%, the latter two SROs are in the composition range of $100 > Se(S) \geq 50$ at.% (Fig. 5, 6).

Naturally, in real alloys the borders of the existence ranges of different intermediate-range and short-ranges orders get diffused, being greater at lower temperature and shorter time of the glass synthesis. Apparently, any of orders described can be revealed in the whole composition range 100 > at.% S(Se) > 0 but the main part of structural fragments corresponding to all orders listed are in the indicated above ranges (Fig. 5).

3.3 Intermediate-range and short-range ordering in SiO_2-GeO_2 system

The two-component system SiO_2-GeO_2 is the glass-forming system in the whole range of compositions [27]. Vitreous SiO_2 (v-SiO_2) is constructed from co-polymerized crystalloids of mainly LTPM-quartz and HTPM-cristobalite [14], v-GeO_2 – from crystalloids of LTPM-cristobalite and HTPM-quartz [15].

At adding GeO_2 in SiO_2, the concentration of SiO_2 crystalloids of both PMs decreases and at "ideal" mixing of $SiO_{4/2}$ and $GeO_{4/2}$ tetrahedrons becomes equal to zero in the composition with equal content of these oxides. In this case, each SiO_2 tetrahedron is connected with four GeO_2 tetrahedrons and vice versa, i.e. there is no connection (in the "ideal" case) of two tetrahedrons of the same type (for example, SiO_2) which is the smallest bearer of the intermediate-range order which is intrinsic for one of PMs of SiO_2. Therefore, the concentration of SiO_2 IRO bearers decreases following the straight line from maximum in pure v-SiO_2 to zero in the composition $(SiO_2)_{0,5}.(GeO_2)_{0,5}$ (Fig. 7, 8). At further increase of the GeO_2 concentration in glass, crystalloids appear – the bearers of IRO of polymorphous modifications GeO_2 which concentration increases to maximum in pure GeO_2. The composition $(SiO_2)_{0,5}.(GeO_2)_{0,5}$ does not have an intermediate-range order of any initial component.

The real concentration dependence curve of IRO vs. composition will have, like in the case of S-Se system, a concave shape with the minimum in the range of 50 at.% each of components above the zero concentration line. The same shape (it's just an assumption!) will have the dependence of the endothermic effect vs. composition in the range of the softening temperature T_g.

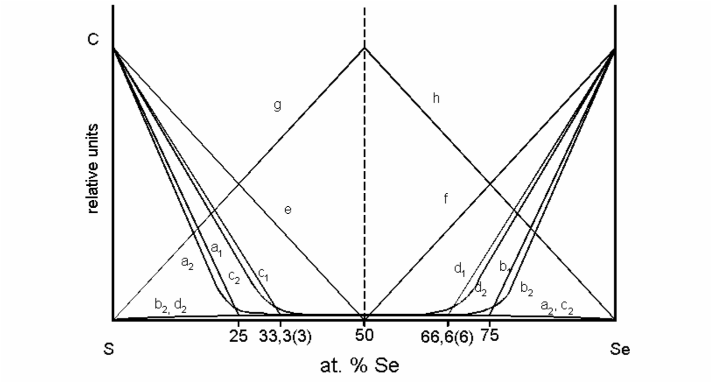

Fig. 6. The dependence of the concentration C (relative units) of crystalloids – bearers of intermediate-range orders of different polymorphous modifications of S (a_1 – for the case of ideally homogenous distribution of components in glass, a_2 – for real glass) and Se (b_1 – "ideal" glass, b_2 – real glass), the concentration of structural fragments – bearers of the short-range order in sulfur $SS_{2/2}$ (c_1 and c_2 for "ideal" and real glass, respectively), selenium SRO $SeSe_{2/2}$ (d_1 and d_2 - for "ideal" and real glass, respectively), the concentration of structural fragments – bearers of compound SRO $S_{1/2}SSe_{1/2}$ (e), $S_{1/2}SeSe_{1/2}$ (f), $SeS_{2/2}$ (g), $SSe_{2/2}$ (h) – for the case of ideally homogenous distribution of components in glass vs. composition.

As for short-range orders which are characteristic for SiO_2 and GeO_2, the following can be said about them.

In each of the oxides there are SRO around cation atoms (Si, Ge) and around oxygen atoms. And while the former SRO (SRO-1), characterized by tetrahedrons $SiO_{4/2}$ or $GeO_{4/2}$, is practically the same for both PMs of each these oxides, the latter SRO (SRO-2) around the oxygen atom - $OSi_{2/4}$ ($OGe_{2/4}$) – is different for quartz and cristobalite – for each PM its own inter-bond angle Si-O-Si or Ge-O-Ge is intrinsic.

The concentration of tetrahedrons - the bearers of SRO-1 of one of the components of the system SiO_2-GeO_2 - decreases from maximum for pure substance to zero at approaching 100% content of the second component (Fig. 7, 8).

At adding germanium oxide to silicon oxide (and visa versa), the compound SRO-2 appears around the oxygen atom $Si_{1/4}OGe_{1/4}$. Its concentration increases from zero in the individual oxide to the maximum in the composition $(SiO_2)_{0.5}(GeO_2)_{0.5}$ (Fig. 7,8).

3.4 Some general regularities of glass structure in binary glass-forming systems $GeSe_2$-Se, S-Se and SiO_2-GeO_2

The analysis of structure of three binary glass-forming systems shows that for a non-single component vitreous substance the nanoheteromorphism is typical – concurrent existence of different structural fragments of the nanometric scale without a long-range order.

These fragments can be divided in three types:

1) crystalloids – bearers of intermediate-range orders of PMs of initial components of glass-forming systems,
2) structural fragment – bearers of short-range orders of initial components, and
3) structural fragments – bearers of short-range of orders compound formed from atoms of both initial components.

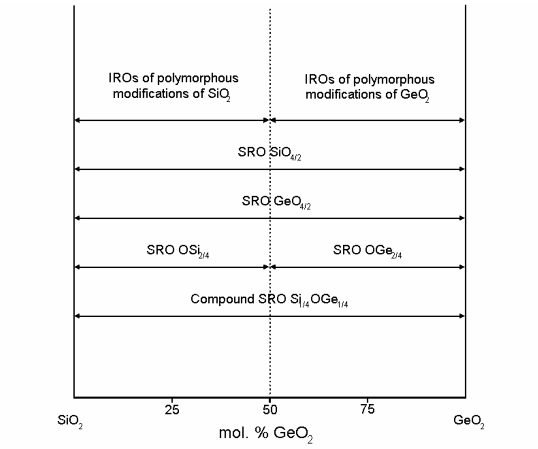

Fig. 7. The diagram of location of intermediate range and short-range orders in the glass-forming system SiO_2-GeO_2 at ideally homogenous distribution of components.

Glass-formation is realized due to co-polymerization of fragments of different structure – nano-heteromorphous fragments without a long-range order which are not able to form a crystalline substance because of their heteromorphous character. For one-component substances (individual chemical substances) such fragments are fragments of the first type: crystalloids – bearers of intermediate-range orders of different PMs.

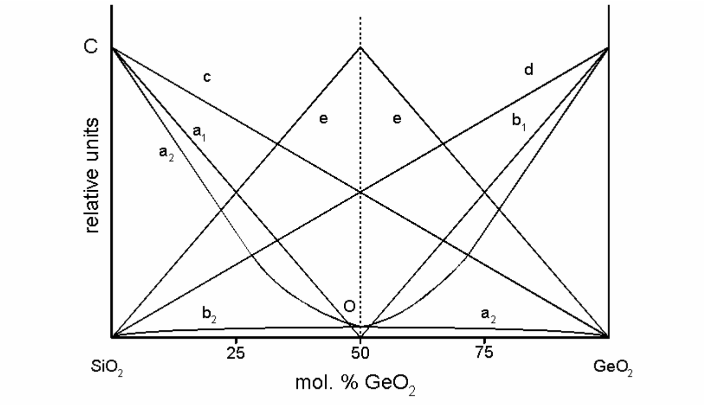

Fig. 8. The dependence of the concentration C (relative units) of crystalloids – bearers of intermediate-range orders of different polymorphous modifications of SiO_2 and SRO $OSi_{2/4}$ (a_1 – for the case of ideally homogenous distribution of components in glass, a_2 – for real glass), IROs of different PMs of GeO_2 and SRO $OGe_{2/4}$ (b_1 – "ideal" glass, b_2 – real glass), the concentration of structural fragments – bearers of SRO $SiO_{4/2}$ (c) and SRO $GeO_{4/2}$ (d), the concentration of structural fragments – bearers of compound SRO $Si_{1/4}OGe_{1/4}$ of "ideal" (e) glass vs. composition.

Two-component glasses can be formed (depending on their composition):

- the first case – from fragments of all three above mentioned types, for example compositions $Ge_{30}Se_{70}$, $S_{20}Se_{80}$, $(SiO_2)_{40}(GeO_2)_{60}$ and others – see Fig. 1,5,7),
- the second case – from fragments of second and third types (for, example, compositions $Ge_{17}Se_{83}$, $S_{30}Se_{70}$, $(SiO_2)_{50}(GeO_2)_{50}$),

the third case – from fragments of the third type (for example, the composition $S_{50}Se_{50}$).

Thus, in binary systems there are some glass compositions in which intermediate-range ordering is absent, in which there are no intermediate-range orders characterizing initial components. In the system S-Se we meet the case where in some glass compositions both intermediate-range and short-range orders typical for initial components are absent. In these cases there are only SROs of compound.

All above mentioned is related with glasses having ideally homogeneous distribution of components. In real glasses there are always "concentration fluctuations" of components which lead to the situation where in any two-component glass all three analyzed structural fragments are present. But in the second case (glass formation from structural fragments of 2nd and 3rd types – see above) there is very insignificant amount (fractions of percent or several percents in the case of poorly synthesized glass) fragments – bearers of IRO, and in the third case – bearers of IRO and SRO of initial components.

Any concept of structure of multi-component glass-forming substances (binary, in particular) has the right to exist in the case it naturally includes a certain concept of structure of vitreous individual chemical substance, a concept of structure of one-component glass-forming system.

The systems analyzed above show genetic relation between the concept of polymeric polymorphous-crystalloid glass structure applicable to individual chemical substances [3,5] and the more general concept, coming into being, of polymeric nanoheteromorphous glass structure (PNHGS) applicable to multi-component systems as well.

Some features of these concepts as well as differences between them, connected with the fact that the former is the special case of the latter, are shown above. Other differences as well as generalized theses of the PNHGS concept will be stated later, after analysis of other binary and multi-component systems. But it appears that the main thesis of the new concept can already be stated now: nano-heteromorphism and nano-heteromorphous co-polymerization are necessary and sufficient conditions of glass-formation in any substance.

4. Conclusions

The new notion is suggested for description of non-crystalline substance structure – nano-heteromorphism.

Nano-heteromorphism is a concurrent existence in non-crystalline substance of structurally different fragments of nanometric dimensions without a long-range order.

Nano-heteromorphous fragments of a glass-forming structure are:

- crystalloids – bearers of intermediate-range orders of different polymorphous modifications of individual chemical substances,
- fragments – bearers of short-range orders of different ICS, and
- fragments – bearers of compound short-range orders formed from atoms of different ICS.

Nano-heteromorphism and nano-heteromorphous co-polymerization are necessary and sufficient conditions for glass-formation in any substance.

Genetic relation between the concept of polymeric polymorphous-crystalloid structure of individual vitreous chemical substance [13-15] and the generalized concept of nano-heteromorphous glass structure, proposed for the first time and applicable to multi-component compositions as well, has been shown by the example of glass-forming systems $GeSe_2$-Se, S-Se and SiO_2-GeO_2.

For glasses of binary systems in the case of ideally homogeneous distribution of components, the presence of intermediate-range orders inherent to different polymorphous modifications of initial components is typical in composition ranges:

- in the $GeSe_2$-Se system: 66.6(6)-80 at.% Se and 85.71-100 at.% Se
- in the S-Se system: 0-25 at.% and 75-100 at.% S (Se)
- in the SiO_2-GeO_2 system: $100 \geq$ mol.% SiO_2 (GeO_2) > 50

The intermediate-range ordering is absent:

- in $GeSe_2$-Se system in the composition range of $80 \leq$ at.% Se ≤ 85.71,
- in S-Se system – in the composition range of $25 \leq$ at.% Se ≤ 75,
- in SiO_2-GeO_2 system – in the single composition $(SiO_2)_{50}(GeO_2)_{50}$.

In real glasses, due to fluctuations of homogenous distribution of components, in mentioned composition ranges there are some quantity of crystalloids of different polymorphous modifications that are bearers of intermediate-range orders.

In the glass-forming system S-Se in the composition range of 33.3(3)-66.6(6) at.% Se for the case of ideal mixing of component, structural fragments – bearers of short-range orders (three-fold chains of one-type atoms) – are absent. In real glasses, some quantity of SRO's bearers of initial components is present due to fluctuations of the chemical composition.

In glass forming systems $GeSe_2$-Se, S-Se and SiO_2-GeO_2, beside nano-heteromorphous structural fragments – bearers of short-range orders typical for initial ICS, there are fragments – bearers of compound short-range orders (-Se-Se-Ge≡), (-S-S-Se-), (-Se-Se-S-), (-S-Se-S-), (-Se-S-Se-) and (≡Si-O-Ge≡), or $Se_{1/2}SeGe_{1/4}$, $S_{1/2}SSe_{1/2}$, $Se_{1/2}SeS_{1/2}$, $SeS_{2/2}$, $SSe_{2/2}$, $Si_{1/4}$ $OGe_{1/4}$, respectively.

References

[1] B. E. Warren, J. Appl. Phys. **8**, 645 (1937).
[2] O. V. Mazurin, B. A. Porai-Koshits, M. M. Shul'ts, Glass: Nature and Structure. "Znanie" Publishers, Leningrad: 32 (1985).
[3] V. V. Golubkov, Fiz. Khim. Stekla. 1992, **18**, 1, 57 [Sov. J. Glass Phys. Chem. (Engl. Transl.). 1992, **18**, 1, 28].
[4] A. A. Lebedev, Gos. Opt. Inst. Proceedings **3**, 4, 1 (1924).
[5] E. Deeg, Naturwissenschaften. **44**, 10, 303 (1957).
[6] J. D. Mackenzie, J. Am. Ceram. Soc. **43**, 12, 615 (1960).
[7] R. Bruckner, J. Non-Cryst. Solids **5**, 2, 123 (1970); J. Non-Cryst. Solids **5**, 3, 177 (1971).
[8] C. H. I. Goodman, Nature (London) **257**, 5525, 370 (1975).
[9] E. A. Porai-Koshits, Fiz. Khim. Stekla **18**, 6, 3 (1992) [Sov. J. Glass Phys. Chem. (Engl. Transl.) **18**, 6, 408 (1992)].
[10] Th. Gerber, B. Himmel, H. Lorenz, D. Stachel, Cryst. Res. Technol. **23**, 10/11, 1293 (1988).
[11] N. F. Mott, E. A. Davis, Electron processes in non-crystalline materials, Clarenden Press. Oxford, 1979.
[12] A. Feltz, Amorphe und glasartige anorganische festkorper., Akademik-verlag, Berlin, 1983
[13] V. S. Minaev, Stekloobraznie Poluprovodnikovie Splavy (Glass-forming Semiconductor Alloys), Metallurgy Publishing House. Moscow, Russia, 407 pp., 1991
[14] V. S. Minaev, Glass Physics and Chemistry (official English translation of Fizika i Khimia Stekla) **22**, 3, 235 (1996).
[15] V. S. Minaev, Glastech. Ber. Glass Sci. Technol. **71C**, 416 (1998).
[16] A. P. Ioffe, A. R. Regel Non-Crystalline Amorphous and Liquid Electronic Semiconductors. Progress in Semiconductors. V.4. London-Heywood & Company Ltd., 237, 1960.
[17] A. R. Regel, V. M. Glazov, Periodic Law and Physical Properties of Electronic Melts. Moscow. "Nauka" Publishers, 399 pp., 1978.
[18] V. S. Minaev, J. Optoelectron. Adv. Mater. **3**, 2, 233 (2001).
[19] G. Lucovsky, T. M. Hayes, In: Amorphous Semiconductors. Ed. Brodsky M.H. Springer Varlag Berlin Heidelberg New York. 1979.
[20] R. J. Nemanich, F. L. Galeener, J. C. Mikkelsen, G. A. N. Connell, G. Etherington, A. C. Wright, R. N. Sinclair, Physica **117B-118B**, 959 (1983).
[21] P. Boolchand, W. J. Bresser, D. G. Georgiev, Y. Wang, J. Wells, In: Phase Transitions and Self-Organization in Electronic and Molecular Networks. Eds. Phillips J. S., Thorpe M. F. Kluwer Academic / Plenum Publishers, 65, 2001.
[22] O. V. Mazurin, Steklovanie (Glass Transition). Leningrad: "Nauka" Publishing House. Russia. 159 (1986).
[23] E. A. Porai-Koshits. In: Stekloobraznoe sostojanie (The Glassy State). Leningrad: "Nauka" Publishing House. (Russia), 5 (1983).
[24] V. I. Lihtman, In: "Brief Chemical Encyclopedia". Moscow: "Soviet Encyclopedia" Publishing

House. (Russia) **4**, 194 (1965).
[25] V. P. Shilo, Ph. D. Thesis. Moscow: Institute of General and Non-Organic Chemistry of Academy of Sciences of the USSR. 1967. 199 pp.
[26] G. Lucovsky In: The Physics of Selenium and Tellurium. Eds. Gerlach E., Grosse P. Springer-Series in Solid-State Science 13. Springer-Verlag., 178, 1979
[27] M. Imaoka In: "Advances in glass technology. Techn. papers of VI Intern. Congress on Glass, Plenum Press., New-York, Pt.1, 149, 1962.