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GLASS FORMATION IN BINARY AND TERNARY CHALCOGENIDE SYSTEMS

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Glass formation in the systems of chalcogenide materials with silicon, germanium, tin and lead are presented. The synthesis and growth of single crystals in the same systems AIVBVI and AIVBV2 are discussed. Glass formation in binary and ternary chalcogenide systems are presented and discussed in detail.

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1. Glass formation in A^{IV} B^{VI} binary chalcogenide systems

The glassy state of the solid matter, as opposite to the crystalline one, is a non-equilibrium state. From the thermodynamical point of view the glassy state can be characterized as the state that is not situated in the local minimum of free energy, and gradually suffer relaxation. The relaxation times, as opposite to non-glassy systems, could be very long, practically infinite. In spite of a great amount of various researches carried out for decades, the nature, mechanism and the criteria of the transition from the glass forming liquids (melts) to the solid glass with fixed structure are not completely understood. The accurate representation of the glassy phase and of the glass structure remains still challenging.

The glass formation by cooling the melts, as well as the deposition of amorphous films from gaseous phase, is firstly related to the choice of the special conditions for controlling the glass formation and amorphization processes. These must be the conditions for total or almost completely ended phase transitions of the first order, i.e. the crystallization, and, possibly, the conditions for previously occurring phenomena in liquids, related to the formation of stratification domains in the liquid phase (liquefaction or micro-phase separation). Now, there is accumulated a great amount of good experimental knowledge on the glass formation in binary chalcogenide systems. The study of the influence of the particularities of the phase diagrams on the glass formation processes has shown that the main role is played by the presence of glass forming chemical compounds [440], which remain stable up to high temperatures of the melt and determine in fact the extension (and shape) of the separated domains of glass formation. Such compounds are, e.g. As_2S_3, As_2Se_3, SiS_2, $SiSe_2$, GeS_2, $GeSe_2$, etc.

The glass formation is strongly related to the chemical nature of the atoms, to the character of the electron interaction between them and short-range order in the melt, which were insufficiently considered in the kinetic and thermodynamic theories of glass formation up to day. The elements that are able to take part in the glass formation in binary chalcogenide systems, consist in a limited number of members of the IV-th and V-th group of the Periodic Table: P, As, Si, Ge, and, also, of the III-rd group: B, Ga atoms, which have in the outer shell p-electrons. All these element are subjected to the Hume-Rothery rule [1], that is called, also, “the 8-N rule”: in the crystals of the element belonging to the 5-th – 7-th group, the number of nearest neighbours atoms is 8-N, where N is the number of the group in the Periodic Table. The difference 8-N represents the number of unpaired electrons in the valence shell and, consequently, it gives the number of possible covalent bonds. According to the fact that the binary glasses are formed from elements that satisfy the Hume-Rothery rule indicates that for glass formation it is necessary a concordance between the coordination numbers and valency of the atoms, i.e. the covalent bonding of the structure [2].

Nevertheless, not all materials whose structure is linked by covalent bonds show the tendency to transit in the glassy state.

Therefore, the presence of covalent bonds is a necessary but not sufficient condition for glass formation.

The second necessary condition for the transiton of the material in the glassy state is the polymer nature of the structure [2]. This condition was many years ago discussed by Zachariasen [3] in his theory of disordering in structural lattices. Myuller[4] and many other researchers considered the glass as a polymer network.

The results of the analysis of a large number of experimental data allowed to conclude on the following glass formation conditions [2]:

- the presence in the structure of localized electron-pair bonds of covalent nature;
- the construction of the fundamental structural network from long polymer complexes.
- the linking of the neighboring polymer complexes (group) only by bridging bonds, i.e. the presence in the fundamental structural network of bonds, which can be named joints.

The presence of covalent bonds gives flexibility (elasticity) to the structure that is a necessary factor for the topological disordering of the structure during glass formation [5]. The enough large flexibility that permits to the elementary components (atoms, cations, coordination polyhedra) to occupy different positions one relative to another, which fact does not create long range order and does not lead to the simultaneous appearance of strains, that destroy the structure, gives the ability to oxide and chalcogenide systems to form glasses.

Stoh [5] considers that the criterion of structural flexibility and the factors that prevent the ordering of the structure, include all the known partial criteria shown above, as necessary conditions for the existence of glass. This is a feature of the solid state and is related in the same time to the crystallo-chemical criterion of Goldschmidt and Zachariasen [3] for the existence of three-dimensional glass network, built from tetrahedral and triangles whose corners are linked by oxygen (chalcogen) bridges that are, indeed, necessary for the flexibility of the network. It is also important the so-called Smekal criterion [6] concerning the need of mixed chemical bonds: directional covalent bonds together with not directional ones (ionic or Van der Waals bonds), in order to ensure the freedom for the shifting of the structural elements, that makes the glass structure flexible.

A special role in the glass formation in binary and in more complex systems is played by the eutectics. The influence of the eutectic on the glass formation is explained by the significant decrease, in the non-stoichiometric materials, of the crystallization rates compared to the materials of stoichiometric compositions, as a consequence of reciprocal braking. The decrease of the crystallization ability and preferred formation of the glasses in materials based on eutectics have been named by Cornet [7] “the eutectic law”. In chalcogenide systems, the eutectics favor the glass formation and, in the absence of eutectics, in the partial eutectic systems, are favored the glass forming compounds. According to [8] [448], high glass formation ability of the eutectic melts is related mainly to the extreme increase in the domain of eutectic compositions, of viscosity and of the kinetical parameter $G_\eta (T_i)/RT_i$ for the liquidus temperature.

Funtikov [9] advanced the eutectoid hypothesis for glass formation, according to which the melts of all materials, with tendency to form glasses, must exhibit a quasi-eutectic structure. According to this model the glass of any composition, even elementary glass, can be considered as consisting from an eutectic with ultradispersed multi-components associated with frozen lyophillic colloidal solutions.

The eutectoid idea is based on the Smith idea regarding the pseudobinary systems and the understanding of the pseudo-phases, introduced by Porai-Koshits for glasses [10]. The pseudo-phases in glasses are fragments of simple materials and, also, stable and metastable compounds [9]. From the eutectoid model of the structure formation in glasses, it follows that the physico-chemical analysis of the glassy systems must be considered from the position of the physico-chemical analysis of micro-inhomogeneous systems that exhibit inhomogeneity at the level of medium-range order. According to this approach, the special points on the diagram “composition - property” must correspond both to the formation of chemically ordered structural elements and modification of the type of inhomogeneity.

Based on the above observations and on the experimental factors of the glass formation, bellow is analysed the ability of glass formation and are indicated the concentration boundaries of the glass formation domains in the known binary systems $A^{IV}B^{VI}$.

1.1. System Si-S

According to the position in the Periodic Table it is possible that both Si and Ge form with the chalcogens large domains of glass formation. During the transition from GeX_2 to SiX_2 (X = S, Se) takes place the formation of the crystalline structure, consisting exclusively from tetrahedral chains linked by edges [SiX_4]. In such structure it is impossible the rotation around the bridging bond of the chalcogen, and, as a consequence, starting from the general theoretical considerations, many structural configurations cannot be created and the glass formation in both binary systems Si-X becomes more difficult.

The glasses in the system Si-S have been firstly obtained by the method of heating in vacuum of impure SiS at 1323 K (red glass-like mass) [11]. Due to difficulty to get glassy SiS_2 the authors of [11] have limited the mass to 1÷2 g, and melt was quenched from the tekmperature of 1373 K in water. By DSC have been determined the glass temperature T_g = 726 K and crystallization temperature T_k = 815 K.

In the paper [12] are reported the results on preparation of non-stoichiometric Si_xS_{1-x}. In this case, too, the total mass was 1÷2 g. By quenching the melt in water, there were obtained non-stoichiometrical glasses, which contain from 5 to 35 at.% Si. Reports on the glass temperatures and crystallization temperatures in the non-stoichiometric Si_xS_{1-x} glasses are lacking.

1.2. System Si-Se

Weiss and Weiss [13] were the first to get glassy germanium di-selenide. By heating the crystalline SiS_2 in evacuated quartz ampoule up to 1333 K and rapid quenching of the melt it is formed yellowish transparent glass, which easily crystallizes. Tenhover et al. [12] report on the preparation of glassy $SiSe_2$, by melting the initial components at 1373 K along three days, followed by quenching the ampoule in water.The softening and crystallization temperatures, measured by DSC are: T_g = 733 K and T_{cryst} = 883 K.

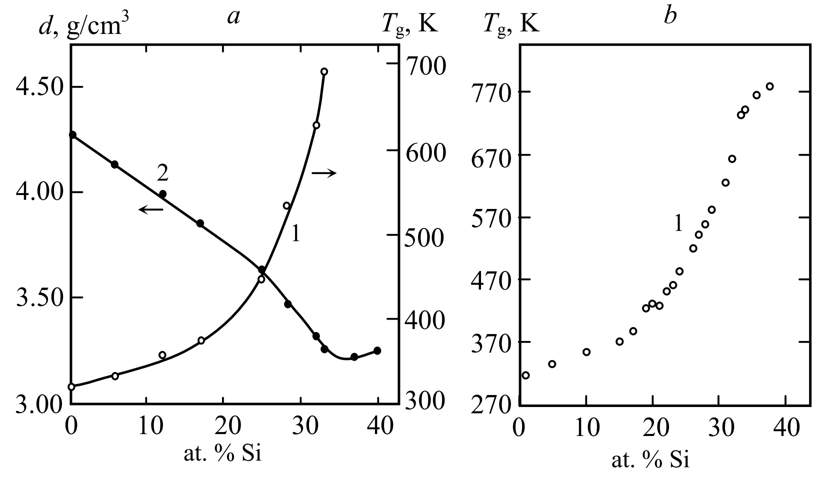

Fig. 6.1. The dependence on concentration of the softening temperature (1) and density (2) of the glasses in the system Si-Se a – [25]; b – [18].

Gherasimenko et al.[14] reported on the preparation of Si_xSe_{1-x} of non-stoichiometric glasses with Si content from 0.1 to 20 at.%. The glasses have been obtained from Se and powdered silicon, of semiconductor purity, by the method of vacuum synthesis at the temperatures 1173 ÷

1273 K, followed by the melt quenching in water. For more than 20 at.% Si the glass intensively decomposes.

The glass formation in the system Si-Se has been reported in the papers [15-18]. The glasses Si_xSe_{1-x} have been prepared by vacuum synthesis method from elements, at 1298 K, with the mass of 12 ÷13 g, followed by quenching in a mixture water + ice. During the preparation of the samples careful attention was paid to avoid the contact with water vapors. It was established that the glass formation domain in this system extends from 0 to 40 at.% Si. In the system Si-Se there are two eutectic compositions for $x = 0.12$ and 0.40 that facilitate the glass formation process [15, 16].

On Fig. 6.1 are represented the dependence on concentration of the density and glass temperature of the Si_xSe_{1-x} glasses. Similar to the case of the germanium selenide glasses, there are extremes and fractures corresponding to chemical compounds and eutectics in this system for $x = 0.33$ and $x \sim 0.22$.

1.3. System Si-Te

Firstly, in paper [81] was reported the possibility to glass formation in the system Si-Te. By comparing the domains of glass formation in the binary systems Ge-Te and Si-Te with the phase diagrams of these systems (Fig. 1.3 and Fig. 1.7, part I of this book) it is possible to conclude that in both systems the glass forms in the eutectic domain on the tellurium side. The eutectic between Te and Si_2Te_3 shows relatively low melting temperature (682 K) and corresponds to composition with 17÷18 at.% Si, that permits to relate it to the eutectic in the system Ge-Te. In this composition domain the viscosity of the melts is already enough large, and, therefore, in the given conditions it is possible the full solidification of the melt with the formation of glass in controlled conditions of quenching [7]. In the same time, the most glass formation ability is exhibited by $Si_{20}Te_{80}$ [19, 20] and not by the eutectic composition. According to [8], the experimentally observed concentration shift of the minima of critical cooling rate of the glass forming melt relative to the eutectic compositions is due to the fact that the compositions of the cooled compositions, where non-equilibrium processes of nucleation and growth of crystals of different phases are produced with the same velocities, do not coincide with the equilibrium eutectic compositions but with the formation during measuring of the critical speed of cooling, of metastable crystalline phases and eutectic structures.

The Si_xTe_{1-x} glass is usually synthesized by the method of direct melting of elementary components in evacuated, sealed quartz ampoules. During preparation of these glasses a special attention must be paid to the avoidance of the contact with the water vapors. The extension of the glass formation domain in the system Si-Te depends on the total mass and cooling speed of the melt. Thus, the composition $Si_{20}Te_{80}$ can be obtained as bulk glass in the amount up to 300 g by quenching the melt in water + ice [19, 21]. The total mass for the case of glass compositions close to the boundary of glass formation does not overcome 2 g. The speed of cooling not only predetermines the boundaries of the glass formation domains, but essentially influences the formation of the glass structure. As a result of various cooling regimes of the $Si_{20}Te_{80}$ melt, the formed glass by quenching in water + ice exhibits an amorphous structure, and for cooling in normal atmosphere does appear a system of Te nanocrystals with the size of ~100 Å [21] .

By using the quenching of the melt from 1273 K in liquid nitrogen, Altunian et al.[22] have found the glass formation domain in this system within the limits of composition from 15 to 25 at.% Si. A close glass formation domain (15÷23(25) at.% Si) has been obtained and reported in the papers [23-25]. There was used the quenching of the ampoule containing the melt in air and in water. For larger cooling speed of the melt (180 K/s) the glass formation domain in this system is situated in the concentration interval from 10 to 22 at.% Si [7]. By using thin wall ampoules and by performing the quenching of the melt from temperatures with 150÷200 K that overcome the liquidus temperature from the corresponding composition, in water + ice (cooling rate: ~250 K/s) it was possible to extend more the borders of the glass formation domain in the system Si-Te from 10 to 27.5 at.% Si [463, 467, 526]. These data support the results reported in [26-29], where glasses Si_xTe_{1-x} have been obtained by the usual method of rapid quenching.

By applying the method of sharp cooling of the melt on cold copper plate (melt spinning), it is possible to get Si_xTe_{1-x} glassy melts with a germanium content from 6 to 33.3 at.% after[30] and from 10 to 40 at.%, according to [31].

Thin amorphous films based on Si_xTe_{1-x} are obtained by various methods: thermal evaporation in vacuum of previously synthesized polycrystalline melts of composition 2 ÷ 40 at.% Si [23, 32]; by discrete thermal evaporation of polycrystals (5÷50 at.% Si) on not-heated substrates from polished glassy carbon [33]; by common evaporation of Si and Te in vacuum 133×10^{-6} Pa for substrate temperature 323 K (compositions with 0÷82 at.% Te) [34] and high frequency sputtering of polycrystalline melts in argon atmosphere on capton or mono-crystalline SiO_2 [35] substrate.

The investigation of the dependence of the temperature of the starting crystallization T_{cryst} from binary melts close to the eutectic composition $A^{IV}{}_{15}$ Te, where A^{IV} = Si, Ge, Sn, Pb, on the atomic number Z of the element A^{IV} has shown that T_{cryst} decreases linearly with the growth of Z [36].

This simple dependence is remarkable because the considered binary systems do not exhibit the properties of ideal solutions both in liquid and in solid state and indicates the existence of some dominant property determined by the element A^{IV} and does not depends on the nature and magnitude of the short-range order. The analysis of the thermodynamical data of these materials shows that the properties of the melt in the glassy state are determined by the properties of the dissociation products that appear in melt, and that T_{cryst} increases linearly with the growth of the melting entropy that appears on one atom of the element A^{IV} [36].

The crystallization of the glasses Si_xTe_{1-x} has been studied by DTA, DSK, XRD and Mössbauer spectroscopy [30, 26-29, 37]. On the curves of concentration dependence on glass temperature and temperature of crystallization (Fig. 6.2) were observed minima for x = 0.2 [26]. On the thermograms of the samples with x = 0.1 and 0.2, during heating it appears one endothermal peak related to the effect of glass formation, and two exothermal peaks related to two-steps crystallization. By cooling the melt after heating at the temperature situated between the two crystallization peaks, for the following heating was observed new endothermal peak, related to the effect of glass formation, and this indicates the stratification of the matrix in the first stage of crystallization. It was stated that the first stage of crystallization is related to the separation of Te crystals, and the second stage is related to the crystallization of the remaining amorphous matrix in the hexagonal phase $SiTe_2$ (c/a = 1.558). The glasses of composition $0.2<x\leq0.28$ exhibit one glass temperature (Fig. 6.2) and crystallize in one stage after an eutectic reaction with the formation of the hexagonal phases Te and Si_2Te_3.The crystallizing phases have a defect structure. By enhancing the silicon concentration the melting temperature increases, the temperature of the second crystallization stage and the second glass temperature decreases, but the temperature of the first crystallization stage and first glass temperature changes non-monotonously and reaches a maximum for x = 0.2.

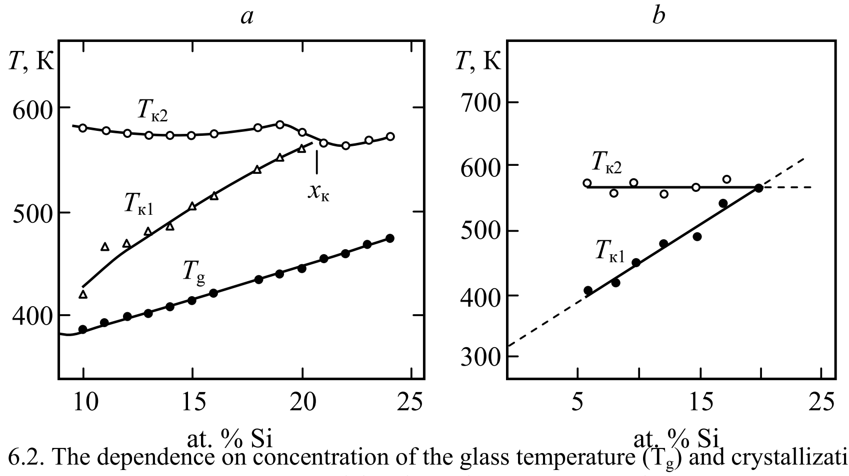

Fig. 6.2. The dependence on concentration of the glass temperature (T_g) and crystallization temperatures T_{k1}, T_{k2} of the Si-Te glasses. a - [476]; b – [30].

The polymorphous crystallization in the bulk glass $Si_{20}Te_{80}$ induced by pressure was reported in [38, 39]. In the temperature range 293 ÷ 640 K and pressures from atmospheric to 8.5 GPa, it was studied the influence of pressure on the electrical conductivity, crystallization and the transition semiconductor-metal in bulk glass $Si_{20}Te_{80}$ by DSC, electron microscopy, XRD and electro-conductivity. At room temperature and atmospheric pressure the resistivity is $\rho = 1.39\times10^6$ Ω.cm. With the increase of pressure ρ firstly decreases exponentially, and, thereafter, for 3 GPa the slope of lg(ρ) changes and for 7 GPa ρ sharply decreases by six orders of magnitude. The X-ray diffraction has shown that for this pressure occurs the polymorphous crystallization, the glass $Si_{20}Te_{80}$ transforms in crystal of hexagonal syngony with c/a = 1.5. The heating of this crystalline phase leads to its decomposition at 586 K in two crystalline phases stable to this temperature Te and $SiTe_2$. It must be observed that the transition glass-crystal induced by the pressure of 7 GPa is also a transition semiconductor-metal [39]. The $Si_{20}Te_{80}$ glass exhibits two softening temperatures and two stages of crystallization. During heating firstly crystallizes the excess tellurium and, then, the remained glass phase crystallizes as $SiTe_2$. It was shown the difference between crystallization, conditioned by the change of temperature (primary crystallization), and polymorphous or incongruent crystallization, induced by pressure.

1.4. Systems Ge-S(Se)

Glass formation in the binary systems Ge-S and Ge-Se has been investigated by many authors, but the conclusions regarding the boundaries of concentration for the glass formation are contradictory. Thus, in the paper [40] it is shown that in the system Ge-S, in general, has been not established the fact of glass formation as a result of melt quenching, while in other paper [41] glasses have been prepared with the quenching procedure for all compositions of the intermediary phases, that contain from 0 to 45 % Ge, including the stoichiometric composition GeS_2, obtained for the first time, as glass, by Nielsen [42]. Other researchers have evidenced in this system the existence of one limited domain of glass formation: from 15 to 30 at.% Ge [43], from 28 to 37 at.% Ge [44] and from 39.2 to 43.5 at.% Ge [45]. It is reported also the presence of two glass formation domains (from 10 to 33.3 and from 40 to 44 at.% Ge), according to the papers [46, 48].

By using enough high cooling velocities (~100 K/s), the authors of [49, 50] succeeded to extend somewhat the glass formation domain in the system Ge-S from 10 to ~50 % at.% Ge. For getting glassy GeS they used the method of blowing the melt in quartz capillary, cooled in water that sharply raised the stiffness of the quenched material.

The analogous situation of discordance in the estimations of the size of the glass formation domain has been found, also, in the system Ge-Se, where this domain, reported in [51], is limited by the compositions from elementary selenium to 25 at.% Ge [52, 53], and, finally, the domain was supplemented with the composition containing 40 at.% Ge, obtained in [54]. The investigation of the processes of glass formation for the eutectic and close to its melt between GeSe and $GeSe_2$, gradually led to the calculation of the second glass formation domain [45, 55]. Reports on the presence in the system Ge_xSe_{1-x} of two extended domains of glass formation, with the composition interval $0<x<0.33$ and $0.388<x<0.417$, have been given in paper [56]. These domains have been determined when the total mass was 20-30 g, and the average rate of cooling was ~ 2K/s.The results on the most complete investigation of the magnitude of the glass formation domain in the system Ge-Se are presented in the papers [57-60]. It was shown that if it is used the quenching in ice + water, then the domain extends continuously from elementary selenium to 43 ÷ 45 at.% Ge.

Such striking differences in the concentration boundaries of the glass formation domains in the binary systems Ge-S and Ge-Se, mainly must be related to the principial differences in the preparation conditions for these glasses: the initial temperature of the melt, the time of maintaining to this temperature, mass amount considered for melting, and purity of the initial components used and reported in various papers. As control factors of the process of getting glasses, firstly is the upper temperature from which the quenching is realized, the duration of maintaining to this temperature and the cooling rate through the interval of temperatures for glass formation. The difference in the stiffness of the quenched samples of the glass forming melts determines not only the position of the boundaries of the glass formation domain, but, also, the possibility to get glasses in general. Often the researchers do not consider the detailed conditions of maintaining and cooling, as well as the free volume of the ampoule, and, therefore, this explains the contradictory results.

As observed above, the glass formation in binary systems is achieved easily in the presence of one or several glass forming compounds. In every system Ge-S and Ge-Se are known two chemical compounds: GeX and GeX_2 (X = S, Se). In relation to the different appearance of these compounds to the phenomenon of glass formation it is of high interest to compare their structural differences in crystalline, liquid and amorphous phases. This was possible due to the publication of experimental data on the structure of the molten state in binary chalcogenide materials [61, 62]. It was established that $GeSe_2$ in liquid phase is stable and this has little influence even for long time heating at 1263 K, while GeSe in the melting state suddenly strongly dissociates.

Therefore, the germanium monochalcogenides cannot be obtained in bulk glassy state, but can be introduced as separate components in the composition of the liquid-forming glasses of the binary systems. Because the compounds of GeSe type decrease their co-ordination by transition from crystalline to the molten state, then one of the fundamental structural glass formation conditions is violated.

The germanium di-chalcogenides in the crystalline state exhibit several polymorphous modifications (see section 2.2). The glass formation is obtained only from high-temperature β-monoclinic phase. This is due to two causes. The first one, the strong quenching of the melt always starts from the temperatures that exceed the melting temperature of the high temperature β-modification (because the structure of the short-range order in melt corresponds to the structure of that monoclinic modification, which, also, satisfies one of the glass formation conditions). The second one, the keeping of the short range order during the transition from crystalline to glassy phase can be most easiest realized, if the crystals show van der Waals character of the bonds and there are groups of atoms, having ionic-covalent bonding with dominant covalent component. Such atomic groupings can form chains of tetrahedra in layered and chain crystals, and to these types of crystals belong β-GeS_2 and β-$GeSe_2$ [63]. For the study of the possibilities of the transition crystal-glass it is important the result of the analysis of the flexibility of these chains, or the layers formed from them. The analysis shows that the presence of two layers in the elementary cell and low symmetry of the crystal, on one hand, and, also, the "softness" of the coordination in the shell elements [GeX_4], on the other hand, favors the flexibility of the layers of chains and this correlates well with the tendency towards glass formation, e.g. for β-GeS_2 and β-$GeSe_2$ [63].

The GeS_2 and $GeSe_2$ melts are characterized by significant crystallization ability [64-67], which essentially depends on the impurities contained in melts, and, especially, on the presence of small amounts of structural units of germanium monochalcogenides that form for determined conditions of thermal processing. The critical speed of cooling for the GeS_2 melt in the interval of glass temperature is 17 K/s (for the quenching of a mass of 10 g in water) [68]. The kinetical crystallization parameters of the glasses GeS_2 and $GeSe_2$ are determined by the Kissinger method according to the position of the maxima in the TDA curves, recorded for different cooling rates 1.25 ÷ 40 K/min [69]. The effective activation energies of crystallization of germanium di-sulphide and di-selenide are equal to 219 and 298 kJ/mol, respectively.

One of the most important peculiarities of the glass formation in semiconductors is the freedom that they have, to destroy the stoichiometric proportions, by extending the glass formation domain of determined systems and permitting a significant distortion of the structure of the stoichiometric glasses. The destruction of the melt stoichiometry relative to GeS_2($GeSe_2$) both on the side of chalcogenide excess and on the side of germanium excess, permits the raising of the glass formation ability. Thus, the melt of composition $GeS_{2.06}$ can be transformed in glass state for a mass of 50 ÷200 g by cooling in air with the speed of roughly ~3 K/s [70]. The glassy state is most stable for glasses of non-stoichiometric compositions, with co-measured relation of different types of structural units, close to eutectic compositions, and for metastable compounds.

The high glass formation ability of the melt in the partial systems GeS-GeS$_2$ and GeSe-GeSe$_2$ is conditioned by the presence of an eutectic between glass forming and non-glass forming components, and, also, by the presence of metastable compounds Ge$_2$S$_3$ and Ge$_2$Se$_3$, which do not appear on the equilibrium diagram [45]. In the partial systems Se-GeSe$_2$ and S-GeS$_2$ the alloys of eutectic composition and materials close to eutectic, rich in chalcogen, are characterized by high ability to glass formation and stability against crystallization of the obtained glasses [67], which are related to the steric non-concordance of the chain structural units of the type Se(Se)$_{2/2}$ and structural units [GeS$_4$] and [GeSe$_4$], which form three-dimensional chain-like clusters. In particular, the minimum crystallization ability for long time heating is exhibited by eutectic selenide glasses that contain 8 at.% Ge, which differ from the glasses rich in germanium in an unique degree of homogeneous micro-nonhomogeneities construction, conditioned by specific backbone association of structural units [60].

Naturally, all the glasses rich in chalcogen are always micro-inhomogeneous, but especially for the composition 8÷10 at.% Ge in the glasses Ge-Se, the tetrahedral structural units [GeSe$_4$] terminate the formation of their fundamental three-dimensional backbone, and as a result, selenium has the possibility to enter into glassy materials, more rich in germanium, only in the form of microinclusions.

For the preparation of Ge$_x$Se$_{1-x}$ glasses without oxide traces the authors of [71] recommend to use pure (degased) Se and Ge powder, and the synthesis conditions to be chosen so that the traces formed as a result of the reaction (SeO$_2$, GeO, GeO$_2$) are eliminated by firing or evacuation in vacuum. The presence of oxides in the systems Ge-S(Se) is not desirable because even very small quantities of oxides favor the crystallization of the melts in these systems during cooling, playing the role of crystallization centers.

The systematical study of the dependence "composition-property" for glassy chalcogenide systems started more than 100 years ago [72]. But up to day the opinions are still not in agreement as to what the glass is from the point of view of the physico-chemical analysis and how are reflected the particularities of the corresponding phase diagrams on the dependences "composition-property", i.e. how the type of compound and character of its melting, and, also, the presence of solid solutions and eutectic are reflected on these dependences in the case of glassy phase formation. In this relation it appears necessary to follow the change with the concentration of the fundamental physico-chemical properties of the glasses in the binary systems Ge-S and Ge-Se.

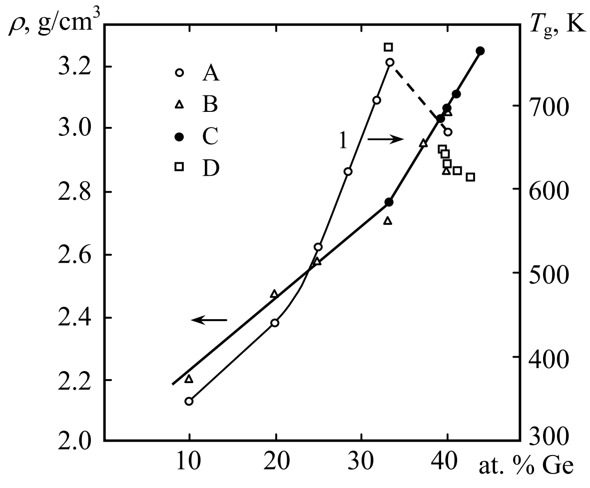

Fig. 6.3. The dependence on concentration of the density (1), glass temperature (2), and microhardness (3) of the glasses from the system Ge-S., A, B – [63], C, D – [45].

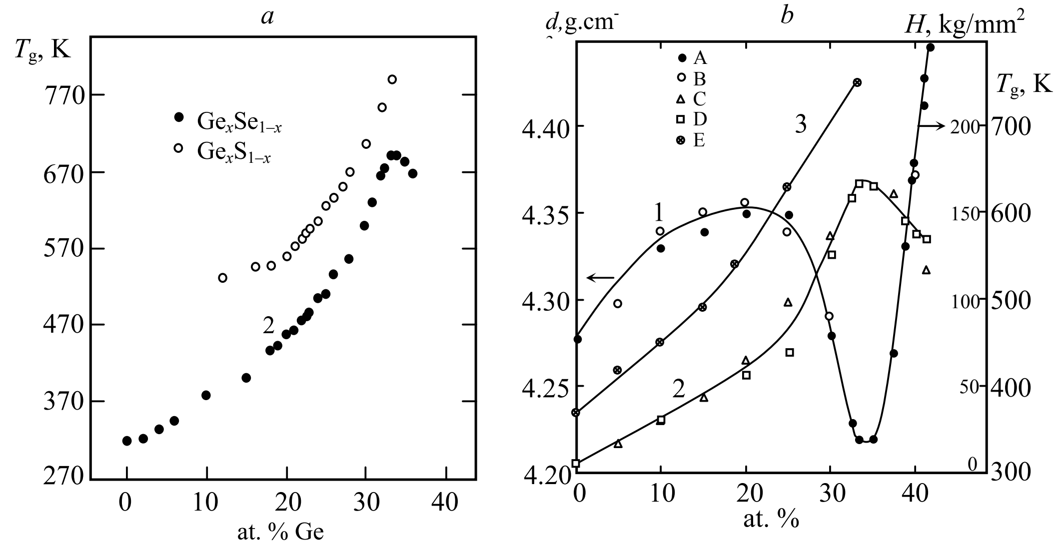

Fig. 6.4. The dependence on concentration of the density (1), glass temperature (2), and microhardness (3) of the glasses from the system Ge-Se, a – [58]; b – A, D - [56], B, C – [59], D – [57].

In Fig. 6.3 and 6.4 are given the dependences on concentration of the microhardness, density and the glass temperature of the glasses Ge_xS_{1-x} and Ge_xSe_{1-x}, respectively. From these figures it is evident that on the curves of dependency "composition-property" of the glasses from both systems one observes curvatures and fractures, which on the phase diagrams (Fig. 1.4 and 1.5) correspond to stoichiometric compositions or eutectics, the extrema on these dependences always correspond to to the compositions of the stoichiometric chemical compounds GeS_2 and $GeSe_2$. The density of the stoichiometric glass $GeSe_2$ is 4.26 g/cm^3 that is 2.1 % below the density of the corresponding crystalline state: 4.35 g/cm^3. Comparative investigations of the optical, electrical, photoelectrical and photoluminescent properties of the crystalline and glassy germanium dichalcogenides are reported in [47, 48, 53, 60, 73, 74, 76-78].

In the binary system Ge-Se, in the range of compositions rich in chalcogen ~80 at.% Se), on the curves of density as a function of concentration one observes still one maximum, while on the curves of glass temperature and microhardness vs. concentration are evidenced fractures, which, on the phase diagram correspond to the concentration close to the corresponding eutectic. The presence of the extrema on the curves of the physico-chemical properties vs concentration indicates structural changes in these systems. It was shown by the methods of oscillation spectroscopy [63, 79, 60] that in the range of the extrema takes place a substitution of different atoms or structural units in the glass network, which determines the transition from one dominant type of structural units to another. For the glasses Ge_xSe_{1-x} the temperature T_g is related to the average number of bonds on the atom *m*, by the relation $T_g = \exp(3.42\times\overline{m} - 3)$ [81].

On the diagrams "composition-property" of the glassy systems the special points correspond not only to the chemical ordering, but also to the change of the type of micro-inhomogeneities. The information on the micro-inhomogeneity structure of the glass can be obtained by equivalentometry [9, 80]. In the equivalentometry of the solid materials it is measured the value of the molar mass of the chemical equivalent of the solid body relative to the reaction of this material with determined chemical solvents. If the solid material contains macro and micro inhomogeneities down to the nanometric sizes, one predicts the selective dissolution of separate fragments of the material. By calculating the theoretical values of the molar mass of the chemical equivalent and by comparing them with the experimental values, it is possible to conclude on the structural-chemical composition of the glasses.

In the case of chemical inhomogeneities in the glass on the level of medium-range order, from glass it is possible to eliminate selectively the structural fragments that are frozen nuclei of the determined stable or unstable phases. By changing the type of aggressing solutions it is possible to get reciprocal supplementary information on the construction of the glass and on the composition of its fragments [9, 80].

It was shown that glasses in the system Ge-Se dissolves in alkaline solution (KOH) and in oxidizing solutions (potassium di-chromate, iron (III) chloride, copper nitrate, etc.) in principle, by different mechanisms, as a function of the composition belonging to the alloys close to eutectics [9, 80]. For germanium content up to 10 at.% it dominates the mechanism that leads to the dissolution of selenium, and for germanium content higher than 10 at.% dominates the mechanism according to which are destroyed firstly the fragments of $GeSe_2$ compound.

Thus, at around 10 at.% Ge in the glassy state appears the eutectic between selenium and germanium di-selenide. The fact that before and after the eutectic composition the components form different molecular compounds is supported by the change of the character the dependency on concentration of the chemical equivalent of the glasses. According to [9, 80], the obtained results indicate that the structural fragments of selenium and germanium di-selenides change their molecular forms (hypothetically low and high molecular forms) as a function of the composition of the melt and, correspondingly, determine the particularity of the medium range order of the glassy alloys, got from this melt.

These conclusions correspond well to the results of investigation of the dependence of the viscosity of the liquid solutions of the glass forming system Ge_xSe_{1-x} in the range $0<x<0.3$ and in the temperature domain 573÷873 K [53, 82, 83, 84]. On the viscosity isotherms one observes three domains. For $0<x<0.08$ the viscosity increases with of the increase of x. The dependencies are well described by the model where the germanium atoms serve as linking elements for the selenium chains. In the eutectic domain for $0.08<x<0.1$ on the isotherms appears a singularity, that increases with the increase of the temperature and this is related to the structural reconstruction of the system. In the range $0.1<x<0.3$, the activation energy of the viscous flow strongly increases with x. The structural elements in this domain, as well as in glassy state, are $[GeSe_4]$ tetrahedra, linked one to another to by selenium atoms. The number of chains and rings rapidly decreases with the increase of x. The viscosity properties of the liquid in this composition domain are determined by the formation in the solution of associates corresponding to the phase diagram.

Still one independent proof of the complex reconstruction of the structure of Ge_xSe_{1-x} glasses in the range of composition rich in selenium, is given by the results of relaxation processes [85].On the basis of the study on the shift of the glass temperature for changing the heating rate of the glass, the time of its aging can be determined by the corresponding activation energy of these processes (ΔE and $\Delta E'$). The application of this method to the glasses Ge_xSe_{1-x} has shown that they can be divided in two composition domains ($x = 0 \div 0.04$ and $0.04 \div 0.12$), which are not visible on the equilibrium phase diagram. In these domains the relaxation phenomena are linked with the mobility of the structural units $SeSe_{2/2}$ and $[GeSe_4]$ in the network that change their size by changing the composition. In the first domain the dimensionality of the network is decreased and the molecular mobility increases. In the second domain ($x = 0.04 – 0.12$) the dimensionality of the network is increased, and this leads to the gradual freezing of the mobility, so that the relaxation phenomena for compositions containing more than 12 mol.% Ge are not fixed by DSC.

Thus, the above given data indicate convincingly the complex reconstruction of the system of interatomic bonds during the formation of the glasses from the binary systems Ge-S and Ge-Se. This is accompanied by the change of the ratio of their structural components, a fact proved by the oscillation spectroscopy method.

The successive formation of the crystalline phases during heating of the amorphous films Ge_xSe_{1-x} ($0.1<x<0.4$), obtained by thermal evaporation, has been studied by the method of radiographic electron microscopy [86]. Starting with 673 K the film crystallization is accompanied by the separation of the high temperature equilibrium β-$GeSe_2$ phase, and, in the same time, the low temperature equilibrium α-phase, practically is absent, always, in all the investigated alloys. On the basis of experimental data, there was concluded that the local coordination of the atoms in the glassy state is close to that, which is achieved in the high temperature phase β-$GeSe_2$.

1.5. System Ge-Te

The glasses in the system Ge-Te have been obtained for the first time by strongly quenching the molten alloy on cold copper plate in a chamber filled by pure argon, using the splat-cooling method [87]. In this case the cooling rate of the melt reaches ~10^5 K/s. The extension of the glass formation domain in the system Ge-Te was established in [87]. The domain is situated in the composition range 10 ÷ 25 at.% Ge. A domain of glass formation of similar extension has been reported for quenched samples (~10^3 K/s) by spraying the molten alloy on a rotating wheel covered by silicon oil [88, 89].

The quenching regime in the domain of alloys with high tellurium content has a significant influence on the extent of the glass formation domain. In the quenching regime in iced-water, by casting the melt as a thin layer on the ampoule walls, there were obtained glassy Ge_xTe_{1-x} compositions with x = 0.15 ÷ 0.20 [90]. By using the method of quenching the alloys in iced water [91, 92] and liquid nitrogen [93], the glass formation domain extended from 10(12) up to 25 at. % Ge and from 15 up to 28 at.% Ge, respectively. The influence of the cooling rate of the melt on the position of the boundary of the glass formation domain in the system Ge-Te has been investigated in detail by Cornet, Psarev et al. [7, 94, 95]. In this system the glass with the composition $Ge_{18}Te_{82}$ is formed on the basis of the eutectic situated on the side of tellurium. The presence of this eutectic allows for the decrease of the crystallization ability of the non-stoichiometric alloys of the eutectic and close to eutectic compositions. For the increase of the cooling rate of the alloys up to 180 K/s the boundaries of glass formation domain extend, in this case, from 10 to 23 at.% Ge [7, 94], and the glass temperature of the glassy compositions formed in these conditions, reaches the values from 373 to 433 K.

The application of the spinning method for the preparation of the glasses in the system Ge-Te gave the possibility to extend the glass formation domain from 0 to 29 at.% Ge [96]. Above the limits of the glass formation domain the rapidly quenched alloys consists in a mixture of glass and crystallites. With this method the samples are obtained as bands of width 5÷6 mm and thickness of 20÷40 μm, The length of these bands is limited only by the charge of the quartz ampoule with molten alloy.

Using the magnetron method (sputtering) and the flash method of deposition one obtains amorphous films in the composition interval 5 ÷ 100 at.% Ge [88, 97].

In glasses and glass-crystals from the system Ge-Te there were revealed structural fragments of the metastable compound $GeTe_2$, which are lacking on the phase diagram of the stable equilibrium phases in the system Ge-Te [9, 80]. The presence of the compound $GeTe_2$ having the lattice isomorphous to the β-cristobalite, SiO_2, was demonstrated by X-ray diffraction in the annealed samples, at 473 K, of the amorphous films of analogous composition [98]. When the temperature increases up to 523 K, $GeTe_2$ decomposes in GeTe and Te. The macro-phase of the compound $GeTe_2$ does not permit its instability when prepared in usual conditions. Funtikov [9] obtained glass-crystal of composition $GeTe_3$, where the above compound, $GeTe_2$, is stable, being finely dispersed in the glassy matrix.

The bulk glasses and amorphous thin films of composition Ge_xTe_{1-x} exhibit poor stability and large crystallization ability during heating. The crystallization processes of the glassy alloys Ge_xTe_{1-x} were studied by DTA, XRD, electron microscopy and electron diffraction (SAED) by many authors [91, 95, 96, 99, 100-103]. On the example of the glassy alloy $Ge_{0.15}Te_{0.85}$ it was studied the influence of the heating rate (β) on the magnitude of the softening temperature (T_g), crystallization temperature (T_k), melting temperature (T_{melt}) and on the parameter $K_g = (T_k-T_g)/(T_{melt}-T_k)$ [102, 103]. It was established the increase of T_g and T_k with the increase of the heating rate, the change of the crystallization from the glassy phase, the shift of the maximum of the heat release, corresponding to these stages on the side of higher temperatures. Thus, during the modification from 1.25 to 80 K/ min. the parameters T_g and T_k changed by 27 and 42 K, but the melting temperature remained constant [102]. The glasses prepared by cooling with the rate that significantly overcomes β, are characterized by more abrupt dependence of T_g and T_k on β, than the glass prepared by slow cooling of the melt. For the comparison of the ability of the materials to form glasses, it was proposed in [102] to use the normalization parameter K_g, determined for β=1.

It is necessary to observe that although the parameter K_g is accepted for qualitative estimations, it does not have a defined physical meaning.

The investigation of the thermal crystallization process of the $Ge_{0.15}Te_{0.85}$ glass by electron microscopy has shown [101] that there exist many common things between crystallization from glass and from the liquid state. The process of transition from glassy state to the crystalline state is intermediary between crystallization from liquid state and the process of incoherent separation from saturated solid solution. For this, the energy of elastic deformations that appear during the transition from glassy phase in the crystalline phase, calculated for one atom gram Δg_a, is basically determined from the density ρ_c and ρ_k of these phases according to the law $\Delta g_a \sim \ln(\rho_c/\rho_k)$.

The study of the aging process of the glassy alloy $Ge_{-0.15}Te_{0.85}$ at temperatures somewhat lower than 451 K (minimum, down to 411 K) has shown that at its surface crystallizes pure Te [104]. The activation energy of the growth process of Te is 193 kJ/mol, which value corresponds to the energy of self-diffusion in tellurium, perpendicular to the hexagonal plane. Simultaneously, the formation of germanium rich phases and of the chemical compound GeTe prevents the free growth of the Te crystals, and as a result, the thickness of the films on the surface does not overcome 5 μm.

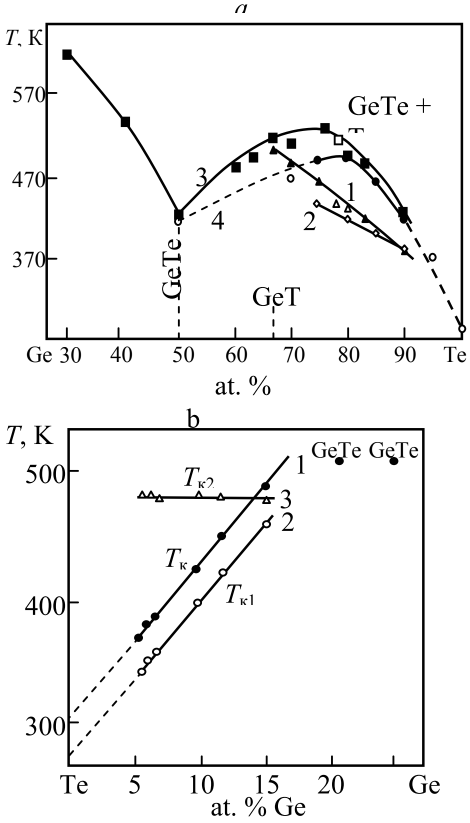

Fig. 6.5. a - The dependence on concentration of the glass temperature (1, 2), and crystallization temperature (3,4) of the glasses and amorphous alloys in the system Ge-Te (curves 1, 3 – [88]; curves 2, 4 – [91]); b. the dependency of the crystallization temperatures on the composition of the glassy alloys of the system Ge-Te. v_{heat}, K/min: 10(1) and 1 (2, 3) [96].

The character of the crystallization of the glasses Ge_xTe_{1-x} depends on composition, heating rate, rate of quenching from the melt and on the history of the processing. On the Fig. 6.5a are shown the dependencies on concentration of the T_g (curves 1, 2) and T_k (curve 3) of the glassy and amorphous phases of the binary system Ge-Te. With the increase of the tellurium content the glass formation decreases monotonously and T_k reaches a maximum at 80 at.% Te [91]. More detailed study of the crystallization process of the amorphous and glassy Ge_xTe_{1-x} alloy has shown that the character of their crystallization depends on the heating rate. By heating with ~10 K/min the crystallization takes place in one stage that is characterized by one peak on the DTA curve, whose temperature T_k in dependence on the concentration of the alloys is described by a linear dependence 1 (Fig. 6.5 b). The crystallization temperature for the compositions $GeTe_4$ and $GeTe_3$ does not superpose on this dependence. During heating with ~ 1 K/min the transformation process is a two-stage process with two peaks on the DTA curves, corresponding to the temperature T_{k1} and T_{k2}. T_{k1} is linearly dependent on the composition of the alloys, and T_{k2} does not depend on the composition of the alloys in the limit of the experimental error (Fig. 6.5 b).

The crystallization of the pre-eutectic, eutectic and post-eutectic glassy alloys Ge_xTe_{1-x} are multi-stage processes and have in every case their own characteristic peculiarities. The first stage of crystallization of the post-eutectic glassy alloys is characterized by the separation of the monoclinic tellurium (whose formation is related to the dissolution of germanium in it), which transforms in hexagonal one only in the last stages of transformations that accompany the separation of germanium (at 623 K) and the formation of the compound GeTe. During crystallization of the glasses of the eutectic and pre-eutectic composition, in the first stage is formed firstly the hexagonal tellurium and, thereafter, the eutectic Te+GeTe [95]. The morphology of the formed crystalline phases depends on the concentration of the germanium in the alloy. The formation of the dendrite structure in the growth process of the crystalline phase was explained by Oleszak et al. [100] by the enrichment of the amorphous matrix with Te atoms and the approaching of the composition to the eutectic one.

The character of crystallization of the amorphous films Ge_xTe_{1-x} ($0.1<x<1$), obtained by discrete evaporation, also depends on the composition [97]. For the compositions with $x>2/3$ one observes one-stage transformation at 635 K with the formation of Ge and GeTe crystals having the structure of the high temperature modification with the NaCl-type lattice. For the compositions with $x<1/3$ one observes one-stage crystallization accompanied by the formation of a mixture of crystalline Te and rhombohedral GeTe at 443 K. In the intermediary domain of Ge concentration ($1/3<x<2/3$) there were observed two stages of crystallization. In the first stage, at 443 K, are separated GeTe crystals with rhombohedral lattice. In the second stage, at 653 K, takes place the separation of germanium crystals and the transformation of the GeTe lattice from rhombohedral to cubical one (NaCl type).

2. Ternary glass forming systems of chalcogenide elements with elements of the group IV

In these multi-component systems, in principle, it is possible to achieve a multitude of different, large number of parallel processes of structural transformations. As a result, in the complex alloy always exists (depending on temperature and pressure, and continuously changing in space and time) domains of nanometric size, enriched in structural elements of the possible crystals, although not coinciding with them. Practically, this speaks in favor of largely developed effects of micro-liquidation.

Different aspects of the structural transformation must influence the properties of the glasses that are formed, with different intensity. Thus, the freezing of the different changes of the structural configurations in multicomponent and multiphase materials must take place for essentially different temperatures. As a result, in the multicomponent glasses the liquidation is very strong, and the construction of the atom matrix of every member is more complex, than in binary glasses, considered in the previous section. Therefore, in the general case, for the phenomenon of glass formation in multicomponent systems it is necessary to consider during analysis the kinetic and structural criteria.

In this section are described only the most studied ternary chalcogenide systems, where glasses are formed. There are three groups:

1) in the system two components are chalcogens and the third one is a group IV element
2) the system contains one chalcogen and two elements of the group IV
3) the system contains the components of the group IV, V and VI.

The complication of the composition when one goes to the ternary systems, where it is possible the interaction of all three components with the formation of three-component structural units, or in which exist ternary eutectics, favors the glass formation. Because the detailed study on the considered systems is already achieved, the new papers in glass formation are very few, and, therefore, the shown particularities are based on traditional papers [105, 106].

The systems chosen by us can be divided according to their particular features, related to the interaction of the components in the process of glass formation:

1) systems where exist solid solutions based on glass forming component (in the system Ge-S-Se such solution is $GeS_{2x}Se_{2-2x}$ [107]);
2) systems which exhibit, in the limits of glass formation domain, one ternary compound (in the system Pb-Ge-S is $PbGeS_3$ [108]);
3) systems where the glass formation ability is significantly determined by the presence of double and triple eutectic (system Ge-Sb-Se [109]).

2.1 Glass formation in the system with two chalcogens.

2.1.1 System Si-S-Se

The glass formation in the system Si-S-Se has been studied in [110] along the quasi-binary section SiS_2-$SiSe_2$. The glassy solid solutions $SiS_{2x}Se_{2-2x}$ ($x = 0.00$, 0.12, 0.25, 0.37, 0.50, 0.70 and 1.00) have been obtained by vacuum synthesis, with total mass of $1 \div 2$ g, the maximum synthesis temperature 1370 K, time of annealing $40 \div 60$ h and final quenching in water. The glasses $SiS_{2x}Se_{2-2x}$ are unstable in air and show tendency to hydrolysis.

In the glassy solid solutions $SiS_{2x}Se_{2-2x}$ takes place the isoelectron substitution of sulphur by selenium with the change of composition and formation of mixed tetrahedral $Si(S_4$-NSeN).

2.1.2 System Si-Se-Te

The glass formation domain in the system Si-Se-Te has been not established. Malyj et al. [111] synthesized the glasses $Si_x(Se_{1-y}Te_y)_{1-x}$ with the compositions $0.333 \leq x \leq 0.43$ and $0 \leq y < 0.6$ and investigated their structure by oscillation Raman spectroscopy. The synthesis of ternary glasses has been carried out starting from elementary components (Si and Te of purity 99.999 % and selenium subjected to a special process of purification) in quartz ampoules evacuated at 133×10^{-3} Pa (the diameter of the ampoules was 6 mm and the length was 8 cm). The total mass of the components was $1 \div 2$ g. For the maximum synthesis temperature 1370 K the alloys were maintained for 60 h. Thereafter, the melts were quenched in water. The glasses enriched in selenium are hygroscopic.

On the basis of the oscillation spectroscopy data [111] it was proposed the chain-cluster model for the structure for the construction of the glasses $Si_x(Se_{1-y}Te_y)_{1-x}$. According to this model, for $y=0$ in the glass structure exist chains of tetrahedral $[SiSe_4]$, linked one to another by pair of selenium atoms (edge linking), as in the $SiSe_2$ crystal. By adding tellurium the glass structure is modified such as the neighbouring chains interlink and gives rise to tetrahedra $[Si(Se,Te)_4]$, which are bonded by their corners. For the compositions with $x \geq 0.35$ the added tellurium leads to the formation of structural units $Si(Se,Te)_{6/2}$, similar to the case of the crystal $SiSe_2$.

2.1.3. System Ge-S-Se

The investigation of the glass formation in this system has been carried out and reported in many papers [546, 549]. Alekseeva et al. [112] prepared Ge-S-Se alloys by vacuum synthesis from elementary components, and the heating temperature, established according to the content of germanium, was situated in the range $1023 \div 1273$ K. After maintaining at maximum temperature during 5 h, the cooling of the melt with the mass 5g, has been achieved by switching off the furnace or by quenching in normal atmosphere. The glass formation domain of the system Ge-S-Se (obtained in the above described conditions) is shown in Fig. 6.6 a.

It was established the existence of two separate glass domains. One of them (I) corresponds to selenium at the corners and in these glasses the increase of the sulphur concentration is accompanied by microstratification (the domain separated by dotted lines) in two glass phases, and also by microinhomogeneities. The second glass formation domain (II) is extended along the section $GeS_{1.5}$ – $GeSe_{1.5}$ (these glasses contain in average up to 40 at.% Ge).

The glasses are completely homogeneous, but small additions of germanium or chalcogen lead to their crystallization. The existence of the second domain of glass formation is conditioned by the formation of eutectic folds to the liquidus surface.

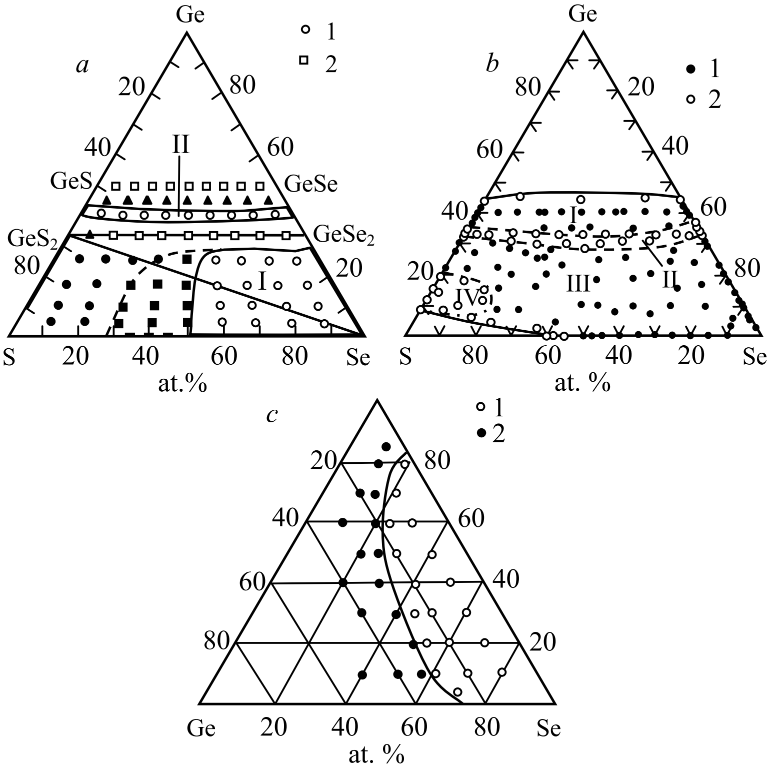

Fig. 6.6. Glass formation in the system Ge-S-Se after [112] (a) after [113], (b) and after [114] (c). 1- glassy alloys; 2 – crystalline alloys. a) I and II – domains of homogeneous glasses; with dotted line is evidenced the domain of glasses with crystalline inclusions, with black dots are shown the glasses showing stratifications; b) I and II - stable glasses that are obtaind by cooling in the regime of switched off the furnace; III – glasses that are obtained by sharp cooling; IV – glasse that exhibit stratification.

The boundaries of the domain stable glass formation and glass formation for sharp quenching of the melt, obtained for the system Ge-S-Se in the paper [113], are compared in Fig. 6.6 b. The alloys have been obtained by vacuum synthesis from elementary components, but the total mass was already 10÷12 g, and the maximum synthesis temperature overcame the liquidus temperature.

From the maximum temperature the melts were quenched in the regime of switching off the furnace or quenching in ice + water, or in liquid nitrogen. The increase of the cooling rate of the melt compared to the data from [112] lead to the extension of the borders of both domains of glass formation. Starting from the thermal criteria for getting glasses in the system Ge-S-Se the authors from [113] divided the whole domain of its glass formation in three superposed regions. The region I corresponds to compositions with the highest conditions of germanium: from 45 to 37 at. %; the glasses of this region are formed by cooling the melts in the regime of switching off the furnace (1÷2 K/min). The region II corresponds to the alloys with the germanium content of 38 ÷ 32 at.%. The glasses from this region can be obtained only in not too high amount, in the regime of sharp quenching of the melt in ice + water mixture or quenching in liquid nitrogen. The region III comprises the melts with the germanium content below 30÷32 at.% and are closely related to the partial double systems Ge-S and Ge-Se. Although the elementary selenium is the best glass forming element, with the exception of sulphur, the substitution of selenium by sulphur does not lead always to the difficulties in the achievement of the glass formation process.

Let's see the influence of the ability to the isomorphous substitution of the elements in the crystalline state on the glass formation process. Of course, it is not possible to explain the glass formation phenomenon with only the fact of formation of solid solutions in the crystalline state: for glass formation it is necessary the presence of glass formation components. Moreover, the existence of solid solutions based on glass forming compounds improves the glass formation effect. Thus, in the Ge-S-Se system that is at variance with other systems by the general domain of glass formation, it appears continuous rows of crystalline solid solutions along the sections GeS_2 – $GeSe_2$, GeS – GeSe and are known limited solid solutions with eutectic in the partial double system S-Se. In the glassy state are obtained only the $GeS_{2x}Se_{2-2x}$ solid solutions [115, 107]. The domain of stable glass formation of region I, with high germanium content (Fig. 6.6) extends also along the line of common separation of solid solution materials based on the system Ge_2S_3 – Ge_2Se_3 [116], close to the eutectic in the double systems Ge-S and Ge-Se.

As a conclusion, the ternary system Ge-S-Se is characterized by a significant glass domain due to multitude of causes (criteria), mainly structural: the presence of glassy elementary selenium, the presence of binary glass forming chemical compounds GeS_2 and $GeSe_2$, which form between them a continuous row of solid solutions, and, also, the presence of a binary eutectic.The magnitude of temperatures for glass formation in the system Ge-S-Se in the composition domain with high germanium concentration determined by DTA are 613 ÷ 633 K according to [112], or 599 ÷ 654 K, according to [113]. By decreasing the germanium concentration, this temperature decreases down to 378 ÷ 475 K (compositions with 5 and 10 at.% Ge, according to [113]). There was established that glasses from the region I, during the measurement process in DTA apparatus crystallize [546, 548], while the glasses enriched in selenium do not succeed to crystallize even after one month of annealing time [112].

2.1.4. System Ge-S-Te

For the first time the boundaries of the glass formation domain in the system Ge-S-Te have been studied in [117] by DTA, dilatometry, X-ray diffraction, metallography and electron spectroscopy. As a result, there were established the boundaries of seven sub-domains in the glass formation domain (Fig. 6.7 a), corresponding to the particularities of crystallization of the glasses, to the thermal and mechanical properties of the glasses (glass temperature, crystallization temperature, microhardness), there were determined the value of the broadening of the stratification domain in liquid state and the structure of several crystalline phases. The synthesis of the samples [117] has been performed from elementary components by vacuum method, using quartz ampoules and a total mass of 0.5 g. The heating was carried out in steps with isothermal annealing at 273 K, 673, 873 and 1273 K. At the maximum temperature the duration of annealing was 12 h. The cooling rate of the melts from this system, necessary to get glasses, depends on the composition. The melts of composition close to the borders of the glass formation domain need strong quenching in a mixture of hot salt mixed with lead, while the compositions of the internal parts of the glass formation domain forms at cooling rates of only 5 K/ min. The most stable glasses against crystallization where the glasses extended along the section that starts from the eutectic in the binary system Ge-Te and extends in the direction of the composition GeS. In the Fig. 6.7a that demonstrates the glass formation in the system Ge-S-Te, the domain, above mentioned, is hatched. The compositions of the most stable glasses (having the highest temperatures for the transition in the glassy state) are distributed on both sides of the quasi-binary section GeTe-$GeSe_2$ with minimum at the level of the eutectic e_1.The stratification in the liquid state leads to the separation of the samples, during melting, in two glass phases, one of which, enriched in tellurium, crystallizes during heating in the DTA process, while the second phase that contains poly-sulphide chains remains in the glassy state.

The glass formation in the system Ge-S-Te has been studied in [114, 118]. The alloys have been prepared by the method of vacuum synthesis from elementary components, the total mass was 5 g, the maximum synthesis temperature was 1023 ÷ 1273 K, as a function of germanium content. At the maximum temperature the duration of the heating was 5 h, thereafter a slow cooling of the melt was made in the regime of furnace switching off, with the rate of cooling 1÷2

K/min, or quenching in air (7÷10 K/min) [118]. For these regimes of synthesis and cooling in the system Ge-S-Te are observed two glass formation domains, as in the case of data reported in [119]. Nevertheless, their extension is somewhat less than the domains determined in [117], due to smaller cooling rates of the melt (Fig. 6.7 b).

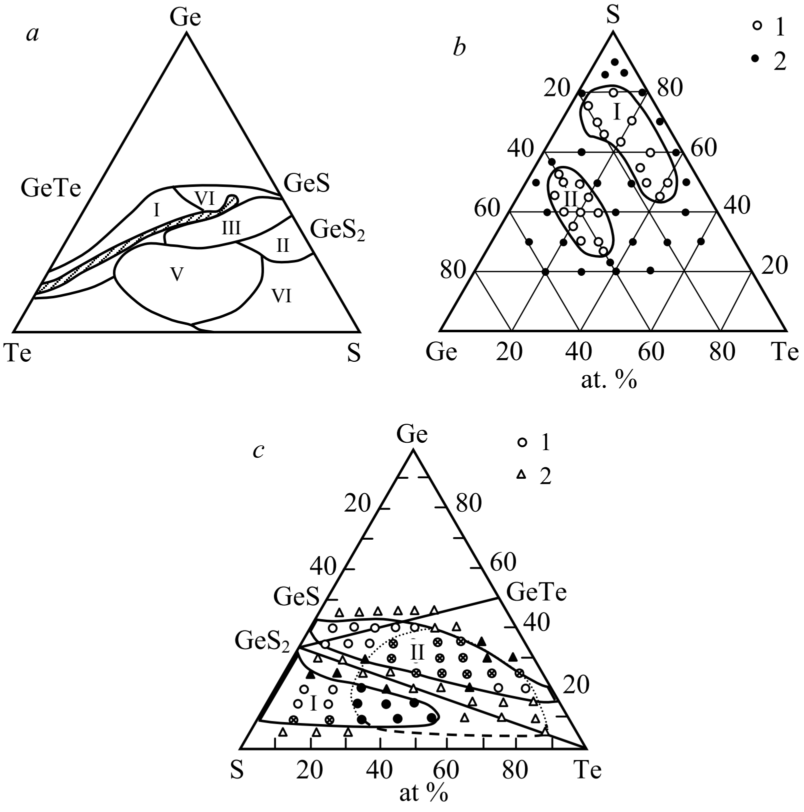

Fig. 6.7. The glass formation in the system Ge-S-Te after [117] (a), after [114] (b) and after [118] (c). 1 – glassy alloys 2 – crystalline alloys. a) I – V the domains of the glasses delimited by thick lines differ by their crystallization abilities. The domain of most stable glasses is hatched; b, c) I and II – the domains of stable glasses. By pointed lines are shown the boundaries of the stratification domains.

In the given system has been observed the stratification of the glass material in two glassy phases [117, 118]. In their domain is determined a co-node direction. It passes almost parallely to the quasi-binary section Te-GeS$_2$ and is somewhat developed in the counter-clockwise direction. The section GeS$_2$-Te is a quasi-binary section of the eutectic type [102]. On this section is situated the domain of stratification with the temperature of the monotectic process of 1058 K. The glasses from the system Ge-S-Te essentially differ from the point of view of their crystallization ability. The DTA data allowed to establish the size and the form of separated zones, whose materials are characterized by the same properties. In the region I the magnitude of the glass temperature increases with the increase of the germanium content from 369 to 604 K. Similarly behaves the crystallization temperature that increases from 401 K to 766 K. As a primary crystallization phase is separated pure tellurium. In the region II, is, also, produced a symbatic change of the glass temperature and crystallization temperature: from 573 to 673 K, and from 673 K to 713 K, respectively. The glasses from the region III do not crystallize in the process of DTA measurement, but they succeed to crystallize partially during a month of annealing at temperatures with 50 K higher than the glass temperature. The temperatures are changed from 623 to 673 K according to the compositions of the glasses in this region.The glass temperature of the glasses from the region IV is constant and is 523 K. They do not crystallize for the conditions of annealing described above. The papers [118, 120] report on the high stability of the glasses from this region. In the region V there was observed the stratification of the glassy materials in two separate phases, whose crystalline characteristics and properties strongly differ. Finally, the glasses from the region V are characterized by the presence of two exothermal effects on the thermograms, conditioned by the crystallization as primary phase of the compound GeTe, and as secondaries: GeS_2 or GeS materials.

In the system Ge-S-Te it was not observed the formation of ternary chemical compounds, but it exist two ternary eutectics and one ternary peritectic point [121]. The indicated points are situated at the limits of the most stable glasses (Fig. 6.7 a).

System Ge-Se-Te

The glass formation domain in the system Ge-Se-Te has been firstly determined in [122]. The alloys have been prepared by vacuum synthesis, and the maximum temperature reached 1173 K. After maintaining to this temperature for several hours, the melts were quenched in air. In the paper [123] the synthesis temperature was raised to 1223 K, and the process of quenching in air started only from the temperature of 1073 ÷1123 K. In both cases in the system have been observed two glass formation domains: one domain is situated in the selenium angle and the other is extended from the eutectic of the binary system Ge-Te in the direction of the composition GeSe (Fig. 6.8 a).

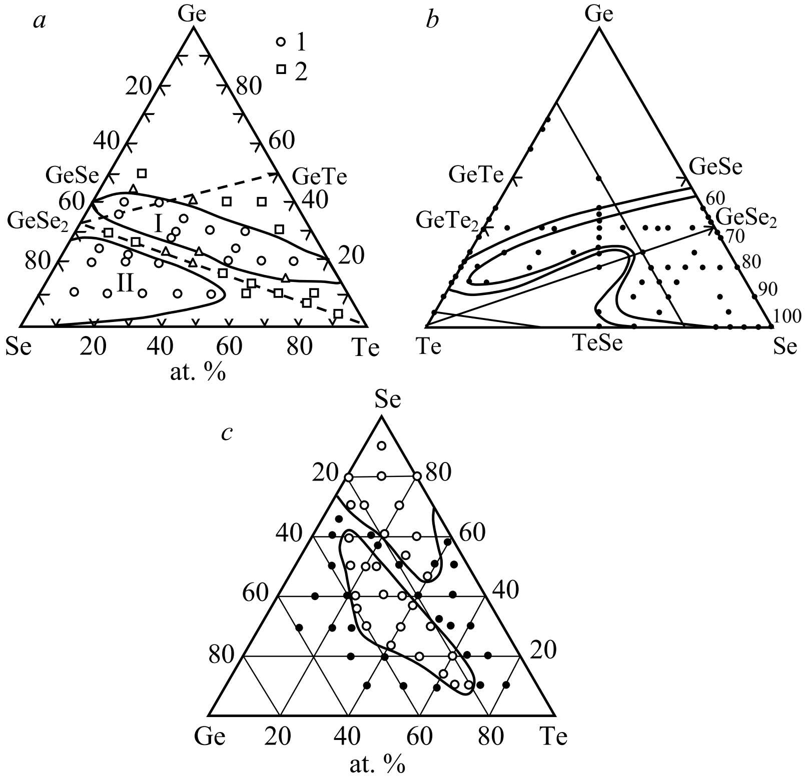

Fig. 8. Glass formation in the system Ge-Se-Te after [123] (a), after [509] (b) and after [114] (c). 1- glassy alloys; 2-crystalline alloys. A) I and II – the domains of homogeneous glasses; b) I – the domain of homogeneous glasses, II – the domain of single phase vacuum deposited amorphous films; c) I and II – the domains of homogeneous glasses.

Using the methods of DTA, scanning electron microscopy and X-ray diffraction, in the paper [124] has been built the phase diagram and was determined the glass formation domain of the pseudo-binary system $GeSe_2$-Te. It was observed a large liquidation domain, and it was demonstrated that the glass formation domain depends on the method of glass preparation. By using the method of vacuum synthesis from elements, the total mass of 10-12 g, quenching in water (cooling rate in the glass formation interval: 8 K/s), Bletskan et al. [125] have obtained glasses $(GeSe_2)_{100-x}Te_x$ of composition $0 \leq x \leq 30$ and their physical properties were investigated.

Due to the "eutectic effect" that represents the extremal appearance "of the effect of liquidus temperature", the most expressed tendency to the formation of ternary glasses exhibit the compositions situated on the curves of crystallization of double eutectic and also the triple eutectic alloys. Because these monovariant curves come from the points of the double eutectic, the glass formation domains, situated close to them must cross the lines of thinning of the double eutectic [126]. As a matter of fact the position and form of the second glass formation domain in the system Ge-S-Se corresponds to the presence of the binary eutectics in the partial systems $GeSe_2$-GeSe and GeTe-Te, and also with the composition of the ternary eutectic. In this part of the ternary system, there are obtained in glassy state only the alloys with the minimum liquidus temperature. The study of glass formation in the system Ge-Se-Te has been continued in the papers [88, 114, 127, 128, 129]. The alloys were synthesized from elementary components in vacuum, and the maximum temperature reached 1223 K. After maintaining at this temperature for 16 h, the mass of 1 g was quenched in water + ice or by dropping small drops in a recipient with silicon oil. In both cases was produced the raising of the cooling rate of the melt, the enlargement of the boundaries of both glass formation domains and their reciprocal coverage (Fig. 6.8 b). Nevertheless, the use of the method of slow cooling (1-2 K/min) always leads to the formation of two glassy domains (Fig. 6.8 b).

In the glasses situated close to selenium corner the glass temperature practically does not depend on the relations of concentrations of chalcogen atoms of different kind. In the glasses rich in germanium, the value of the glass temperature increases from 362 K to 609 K symbatically with the increase of the concentration of this element.

The crystallization of the glasses in the system Ge-Se-Te has been studied by DTA, DSC, and XRD [88, 130]. The glasses close to two-components Ge-Se glasses (5÷20 at.% Ge) exhibit the lowest crystallization ability. For ternary glasses, in the domain of the composition $Ge_{20}Se_{20}Te_{40}$ there exist two T_g effects, which indicate the liquid phase decomposition. One phase is enriched in $GeSe_2$, the second one is tellurium. The phase decomposition has been explained in [88] by the strength of the Ge-Se bonds and its high degree of ionicity if compared to the other bonds. For the composition $Ge_{20}Se_5Te_{75}$ have been observed exothermal peaks of crystallization at temperatures 492, 556, 591 and 601 K. It was evidenced the formation of crystalline tellurium after heating at 513 K and mixture of Te + GeTe after heat treatment at 573, 598, 608 K. It was studied the crystallization kinetics of the given glasses at various temperatures, which is described by the Avrami equation. With the help of the Avrami equation have been determined the kinetic parameters of crystallization. The value of the activation energy of the crystal growth for the temperatures 560 ÷640 K is 1.02 ± 0.12 eV. It was established that the crystallization of the glass of composition $Ge_{20}Se_5Te_{75}$ is a double-measure process.

In the paper [131] has been studied by DSC the glass formation along the section $GeSe_2$ – $GeTe_2$ and it was shown the possibility to get bulk glasses by quenching the melt in cold water. The stable glasses $GeSe_{2x}Te_{2-2x}$ are obtained in the concentration interval $0.4 \leq x \leq 1.0$.

2.2. Germanium chalcogenide glasses, containing Si, Sn and Pb

2.2.1. System Ge-Si-S

Firstly the boundaries of the glass formation domain in the system Ge-Si-S have been established by Stepanek and Hruby [132, 133]. They studied the glass formation in the composition domain $Si_xGe_{1-x}S_y$, where x = 0.05; 0.1; 0.2 or 0.3, and y changed in the limits: 1.28 ÷ 3.6. The synthesis of the alloys in this system is very difficult from technological point of view. That is why the authors of [132, 133] synthesized preliminarily the polycrystalline materials from elementary components in evacuated quartz ampoules in a two-zone horizontal furnace. One end of the ampoule, containing sulphur has been positioned in the "cold" zone (623 K) of the furnace, and the second end with silicon and germanium has been placed in the "hot" zone (1173 K). The synthesis in this regime has been carried out for 48 h, then the temperatures of both zones were balanced at 1173 K and the product of the reaction has been homogenized at this temperature for 24 h. After that the temperature has been decreased at 723 K and the ampoule has been taken off the furnace.

The polycrystalline alloys prepared by the described method have been introduced in thin wall quartz ampoules with the internal diameter of 3 mm, have been melted and the melt was quenched in water. In this way have been studied the compositions $Si_xGe_{1-x}S_y$, where $0.05 \leq x \leq 0.3$; $1.28 \leq y \leq 3.6$.

If more than 30 at.% of germanium is substituted by silicon, then the reaction temperature is raised above 1400 K. In these conditions the free silicon comes already in chemical interactions with the quartz ampoules, and the high elasticity of the sulphur vapors, as normally, lead to the explosion of the ampoule. In Fig. 6.9 are given the concentration domains of glass formation in the system Ge-Si-S. Comparatively easy are obtained glasses with the silicon content up to 4 at.% for sulphur content up to 60÷66 at.% (domain III). Much higher quenching rates are necessary for getting glasses, that contain 4÷10 at.% Si (domain II). In the domain I always are obtained crystals.

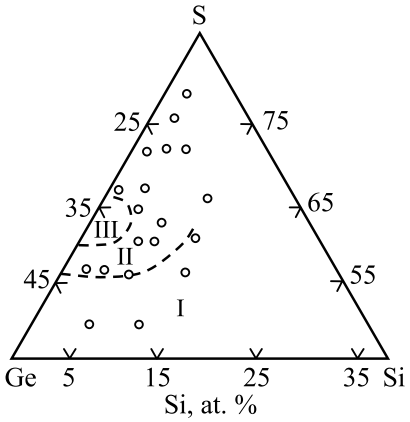

Fig. 6.9. The glass formation in the system Ge-Si-S [132, 133]. I – domain of crystalline materials; II – domain of hardly forming glasess; III – domain of easily forming glasses.

The substitution of germanium by silicon is not accompanied by the increase of the glass formation ability of the material. Together with this, the substitution of germanium by silicon is not accompanied by significant change of the glass temperatures and crystallization temperatures of the glasses.

It is necessary to observe that in the glass formation domains presented in Fig. 6.9, it was not reflected the existence of the glasses along the quasi-binary section SiS_2-GeS_2, established in paper [134] for all the values $0<x<1$ ($Si_xGe_{1-x}S_2$). It was shown by the method of combined scattering of the light that the structure of the ternary glasses $Si_xGe_{1-x}S_2$ is formed by molecular clusters [SiS_4] and [GeS_4] that are characteristic for limit binary glasses SiS_2 and GeS_2. During the formation of the mixed glassy alloys the short and medium range order of these clusters do not change and does not occur the isoelectron substitution Si(Ge) by Ge(Si) correspondingly, and, as a consequence, in glasses coexist network of separated tetrahedral [SiS_4] and [GeS_4]. The following study with the help of combined scattering of the effect of isoelectron substitution in the glasses Si-Ge-S, has been performed by Tenhover et al. [135] for non-stoichiometric glasses $(Si_xGe_{1-x})S_{1-y}$ for $0 \leq x \leq 1$; $0.30 \leq y \leq 0.36$, i.e. the compositions are extended on both sides of the quasi-binary section SiS_2-GeS_2.

2.2.2. System Ge-Si-Te

The glass formation in the system Ge-Si-Te has been studied in [24, 136-138]. The alloys have been synthesized by the method of direct melting of the elementary components at 1273 ÷ 1473 K for 24 h in evacuated ampoules, with application of vibrational mixing. After the end of synthesis the ampoule with the melt of 10÷20 g has been quenched in water. The domain of glass formation in the system Ge-Si-Te (Fig. 6.10) is situated between two domains of glass formation in the partial double systems Si-Te and Ge-Te.

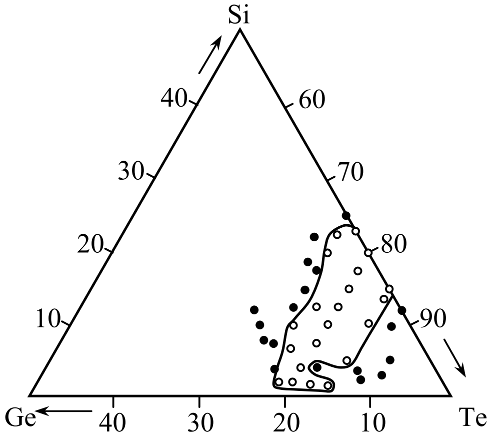

Fig. 6. 10 Glass formation in the system Ge-Si-Te [24].

Starting from the eutectic properties of the alloys containing tellurium in the domain with ~80 mol.% Te, it is possible to suppose that glass formation here is obtained for relative low temperatures of liquidus along the eutectic line, that links both double eutectics.

In the paper [138] has been studied the glass formation in the partial section $Ge_{20}Te_{80}$-$Si_{20}Te_{80}$. The alloys have been obtained by vacuum synthesis followed by quenching in ice + water. By using the compressed shape of the ampoule, it was possible to reach the cooling rate of 200 ÷ 250 K/s. As a result, there were obtained glasses for all compositions of the section $Ge_{20}Te_{80}$-$Si_{20}Te_{80}$

In [24, 138] has been measured by TDA, the glass temperature in the system Ge-Si-Te. By adding germanium in the binary glasses of the system Si-Te the glass temperature diminishes. The diminishing of tellurium content is accompanied by the increase of glass temperature from 373 ÷389 K (85 at.% Te) up to 427 ÷ 435 K (75 at.% Te). Its maximum value in this system reaches 443 K for the glass of composition $Ge_{16}Si_7Te_{77}$.

System Ge-Sn-S

Glass formation in the system Ge-Sn-S has been studied by TDA, XRD and Mössbauer spectroscopy [139-141]. The domain of existence for the glasses in the partial system GeS_2-GeS-SnS is enough narrow and is limited, mainly by the GeS content (Fig. 6.11).

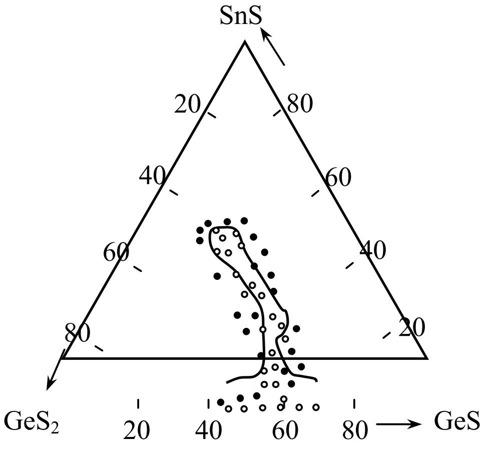

Fig. 6. 11. Glass formation in the system GeS$_2$-GeS-SnS [139, 140].

The alloys have been prepared by vacuum synthesis from the elementary components, the total mass was 10 g, the maximum synthesis temperature overcame the liquidus temperature. The cooling rate of the melt reached 70 K/min. From Fig. 6.11 it is obvious that the domain of glass formation is extended in the given system along the line that links two eutectics in the partial double systems: the eutectic between SnS and SnS$_2$ (its melting temperature is 1011 K) and the eutectic between GeS and GeS$_2$ (870 K). In the glass it is possible to introduce up to 47.5 mol. % SnS (20 at.% Sn). After TDA data the glass formation temperature weakly depends on composition: during increase of the SnS content from 10 to 47.5 mol. % the value T_g decreases from 548 to 508 K. The molar volume of the glasses decreases by isomorphous substitution of GeS by SnS up to ~20 mol.% SnS, and, thereafter remains constant. The maximum density has been observed in the glasses of composition $(SnS)_{0.46}(GeS)_{0.24}(GeS_2)_{0.30}$ [573].

The study of the Mössbauer spectra of the glasses from the system SnS-GeS-GeS$_2$ of various composition [140, 2141] indicates an unique chemical neighbouring of the Sn atoms in all the samples, and, also, in the ternary compound SnGeS$_3$, and confirms that the degree of oxidation of Sn atoms in all the compositions is +2, because for the atoms Sn(4+) the value of the isomer shift is significantly lower.

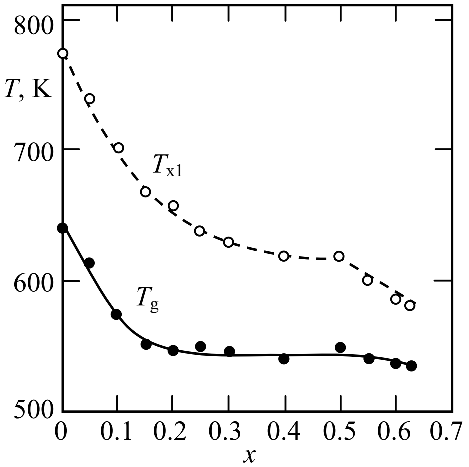

Fig. 6.12. The glass temperature (T_g) and crystallization temperature (T_{cryst1}) versus concentration for the glasses $Ge_{2-2x}Sn_{2x}S_3$ [142].

Although, in the papers [139-140] has been not established the glass formation processes along the section GeS_2-SnS, according to [143] the authors succeeded to get tin thio-germanate ($SnGeS_3$) in the glassy state and its physical properties have been investigated. It was shown by oscillation spectroscopy method [291] that during crystal-glass transition in $SnGeS_3$ the short range order is preserved. The density decreases from 3.71 g/cm^3 for crystal to 3.56 g/cm^3 for glass, and the glass temperature is $T_g = 599$ K.

It was not found glass formation along the section Ge_2S_3 – Sn_2S_3 studied in [142, 144] (Fig. 6.11). By DSC there was studied the glass temperature and isothermal crystallization of the ternary glasses $Ge_{2-2x}Sn_{2x}S_3$ ($0<x<0.62$) (Fig. 6.12). According to [144] the structural network of the glasses with $x<0.25$ consists in two molecular phases: metastable ethane-like phase of the type Ge_2S_3 and the GeS phase with distorted NaCl lattice. For $x>0.25$ the structural network is formed by zig-zag chains based on crystalline $SnGeS_3$. The crystallization behaviour is correlated with the molecular structure of the glasses $Ge_{2-2x}Sn_{2x}S_3$: in the domain of compositions $x<0.25$ the crystallization is controlled by the nuclei formation and by the crystal growth process. For $x>0.25$ the growth phenomena dominate [144].

By crystallization of the other compositions of the glasses in the system Ge-Sn-S, the primary separated phase is formed by crystals of the compound $SnGeS_3$, and the secondary phase is GeS. In the domain rich in in GeS_2 takes place the diminishing of the high temperature crystalline modification β-GeS_2.

2.2.3. System Ge-Sn-Se

The boundaries of the glass formation domain in the system Ge-Sn-Se are studied in the papers [145-147] and are shown in the Fig. 6.13. The authors of [145] have obtained glasses in the system Ge-Sn-Se from elementary components of high purity by the usual method of vacuum synthesis, whose maximum temperature is 1223 K, followed by quenching of the melt in air. The glass formation domain is extended on the selenium side. The glasses can contain up to 13 at.% Sn. By using the same synthesis conditions as in [145], and total mass of components 10 g, Fukunaga et al. [146] defined the glass formation domain in the system Ge-Sn-Se (Fig. 6.13 a). The extension of the glass formation domain was possible by using stronger quenching of the melt in water [147] (Fig. 6.13 b). In this case, too, the glass formation domain does not include glasses along two pseudobinary sectionsGeSe$_2$ – $SnSe_2$ and Ge_2Se_3-Sn_2Se_3, obtained and studied in [112-114, 117, 120]. The glass temperature of the compositions from the glass formation domain, represented in the Fig. 6.13 b is 399÷591 K. Using the Mössbauer method it was shown [145] that in these glasses tin has four valencies and is bonded only to selenium. The most stable glasses against crystallization are obtained in the case of the alloys with a content of 70÷80 at.% Se. The glass formation in the system Ge-Sn-Se allows for the presence of the ternary eutectics in this system with the co-ordinates: composition $GeSe_2$-$SnSe_2$ - 0.75 SnSe and melting temperature 829 K [148].

By quenching the melts in ternary system $Ge_{2-2x}Sn_{2x}Se_3$ the authors of [142, 150] have obtained homogeneous glasses in a large domain of compositions ($0<x<0.72$). The formation of the glasses along the section Ge_2Se_3 – Sn_2Se_3 is a surprising result, because the cations Sn^{2+} are not good glass formers. By DSC and NMR have been measured the local molecular structure of these glasses. The microscopic nature of the unusual behaviour of the system $Ge_{2-2x}Sn_{2x}Se_3$ relative to the glass formation, has been related by the authors [149] with the existence of the molecular fragments as zig-zag chains of [$GeSe_4$] tetrahedra, linked by side bonds through the Sn^{2+} ions, that remember by their structure the crystalline analogue $GeSnS_3$. Analogous structural fragments are observed in glassy $GeSnS_3$. In the same time the crystalline material of composition $GeSnSe_3$ exhibits completely other structure, i.e. it is not a structural analogue of the glass $GeSnS_3$. Thus, the short-range order of the crystalline $GeSnSe_3$, as opposite to $GeSnS_3$ is not preserved during the transition crystal-glass, and this is considered by the authors of [150] as a violation of the so-called Joffe-Regel rule. The absence of the glass formation in the studied system at $x>0.72$ is conditioned by the formation of microcrystalline fragments SnSe and $SnSe_2$, having hard ionic shell.

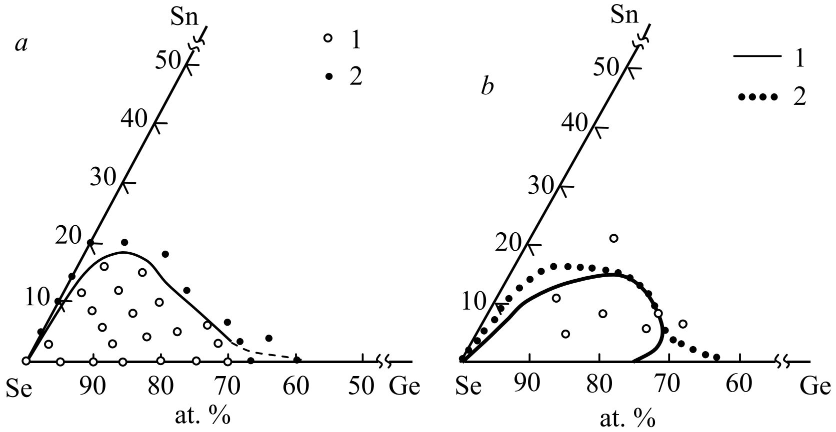

Fig. 6.13. The boundaries of the glass formation domain in the system Ge-Sn-Se: a – after [579], 1 – homogeneous glasses, 2 – crystals; b – after [149], 1 – quenching of the melt in air, 2 – quenching of the melt in ice + water.

Ternary glasses of the variable composition $Ge_{1-x}Sn_xSe_{2.5}$ ($0<x\leq0.6$) have synthesized by Griffiths et al. [151] and Ksendzov et al. [152]. They studied their glass temperatures, optical absorption edge and red spectra. It was shown that the curvature of the Urbach tail of the fundamental absorption edge (σ) and T_g show practically identical functions on the glass composition. On the basis of analysis of the experimental data has been discussed the topological peculiarities of the structure of valency bonds in this system.

2.2.4. System Ge-Pb-S

The study of the glass formation in the ternary systems with Pb: Ge-Pb-S and Ge-Pb-Se [153-162] has shown, surprisingly, the presence of enough large domains of stable glasses. This surprise is conditioned by the fact that in the majority of other chalcogenide systems, Pb always exhibits low ability of interaction with chalcogens and binary chalcogenides. The boundaries of the glass formation domain in the system Ge-Pb-S are shown in Fig. 6.14.

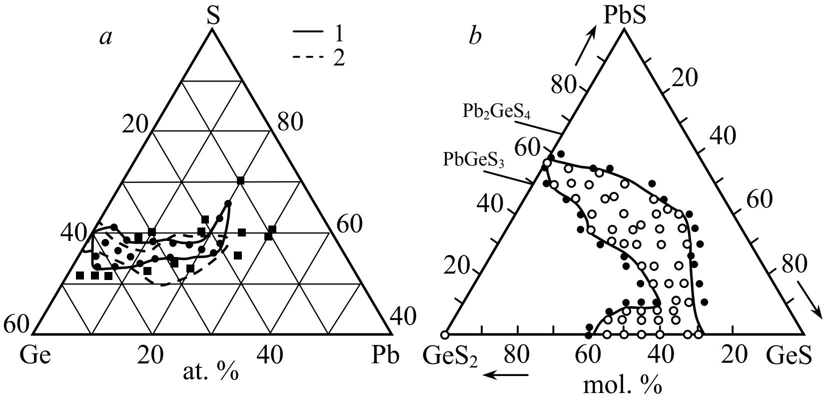

Fig. 6.14. a – Glass formation in the system Ge-Pb-S after [156] (thick line), after [154] (dashed line); with squares are evidenced the crystallized melts; b – domains of glass formation in the system PbS-GeS-GeS_2 [154].

The attention is paid to similar extension and shape of the glass formation domains, obtained by two groups of authors [153-156]. The authors of [154] report that on the boundaries of the glass formation domain it is possible to make glasses of 10-20 g by quenching the melt in water. For the melts situated in the concentration interval 30 ÷ 47 mol.% PbS, 20 ÷45 mol.% GeS, 26 ÷ 45 and 25 ÷ 35 mol. % GeS_2, in the glassy state can be obtained up to 50÷100 g material by the method of air quenching. Both groups of authors [154, 156] have studied mainly the glass formation in the partial system PbS-GeS-GeS_2.

Although in the double system PbS-GeS_2 exist two ternary compounds (Pb_2GeS_4 and $PbGeS_3$) in no one of the cited papers is reported the preparation of the two compositions in the glassy state. Only in the paper [108], published much later, it is indicated on the possibility to prepare glassy $PbGeS_3$ by quenching the melt from the temperature of 1123 ÷ 1173 K, in water. For this, the total mass of material can be 10 ÷ 12 g. The glass temperature of $PbGeS_3$ determined by TDA, is 525 K, and the density 4.90 g/cm^3. The electronic and oscillation properties of the glassy $PbGeS_3$ have been studied in [163, 108, 157].

The density of the non-stoichiometric Ge-Pb-S glasses increases monotonously with the increase of Pb content. Microhardness and T_g temperature sharply decrease by transition from the glass without Pb to the glass with 11 at.% Pb. The glass temperature in the system PbS-GeS-GeS_2 is 533÷563 K [154].

2.2.5. System Ge-Pb-Se

The glass formation in the system Ge-Pb-Se has been studied in [158-163]. In the triangle diagram of the Fig. 6.15 a is presented the glass formation domain for the partial system PbSe-GeSe-$GeSe_2$ for the concentration of the components $GeSe_2$: 24 ÷ 38, GeSe: 30 ÷55 and PbSe: 15 ÷ 46 mol.%. From this figure results that for the use of normal cooling rates (quenching in water) in the composition of the glasses in the double system Ge-Se it is possible to have up to 22 at.% Pb. The ternary alloys have been obtained by vacuum melting from elementary components along 8 h at 1070 ÷ 1120 K. The total mass of the melt quenched in water (8 K/s) was 10 g on the domain of glass formation. The compositions in the middle of this domain can be obtained in the amount of 50 ÷ 100 g for quenching in air.

The high glass forming ability of the considered ternary alloys is indicated in particular by the fact that the material of the composition $(PbSe)_{0.4}(GeSe)_{0.3}(GeSe_2)_{0.3}$ can be obtained in the amount of 1 kg by usual cooling of the melt in air [594]. In the domain of compositions rich in selenium, one observes the stratification of the glass. The authors of the papers [158-160] evidence the weak influence of the composition of considered glasses on the glass temperature, which is situated in the in the range 509 ÷ 517 K.

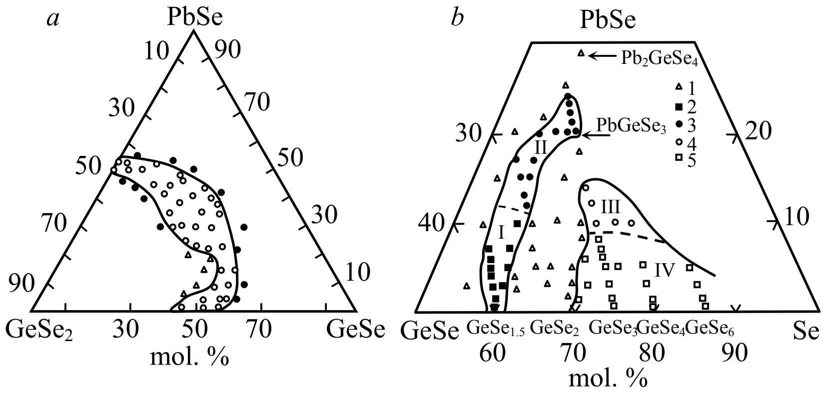

Fig. 6.15. The glass formation in the system Ge-Pb-Se after [158, 159] (a) and after [164] (b) 1 – crystalline alloys, 2 – homogeneous fragile glasses, 3 – stable for mechanical stress, homogeneous glasses, 4 – inhomogeneous stratified alloys, 5 – non - homogeneous alloys, enriched in selenium and germanium selenide.

Obviously, the phase diagram, drawn in the Fig. 6.15, shows that in the system PbSe-$GeSe_2$ exists one stable ternary compound $PbGeSe_4$, which can be obtained in the glassy state. The existence of the other chemical compound ($PbGeSe_3$) in the system Ge-Pb-Se has been not established, but, this composition, too, can be easily obtained in the glassy state [163].

The important peculiarities of the ternary glasses Ge-Sb-Se is the possibility to get the inversion of the type of conductivity from *p* to *n* by changing the chemical composition [162].

A more detailed study of the glass formation criteria and properties of the glasses in the system Ge-Pb-Se has been carried out by Albegova et al. [164] for the sections $GeSe_{1.5}$-Pb, $GeSe_2$ – Pb, $GeSe_3$ – Pb, $GeSe_4$ – Pb, $GeSe_6$-Pb and $GeSe_{1.5}$ – PbSe. The alloys have been synthesized from elementary compounds by vacuum deposition. The maximum synthesis temperature was 1073÷1123 K. At this temperature the samples were maintained for 6 h. The cooling of the melt was made by quenching in air with the average rate of 2 K/s.

These studies have shown that in the system Ge-Pb-Se exist in fact two glass formation domains (Fig. 6.15 b). Both domains are ascribed to the binary glass system GeSe, and, one of them is extended along the section $GeSe_{1.5}$-PbSe, while the other, along the section $GeSe_3$ – Pb. Between the two glass formation domains in the concentration triangle is situated a great part of the crystallizated alloys, mainly along the sections: $GeSe_2$-Pb and $GeSe_2$-PbSe. On the indicated sections, only the alloys with high content of Pb (12 ÷17 at.%) on the section $GeSe_2$-Pb (~22 at.%), along the section $GeSe_2$-PbSe have been obtained in the glassy state. Along the section $GeSe_3$ – Pb in the compositions of the glassy alloys enters in two glass formation domains from 0 to 10-12 at.% Pb, and from 20 to 23 at.% Pb. Thus, in air cooling regime of the samples in the composition of the glassy germanium selenides it is possible to introduce up to 23 at.% Pb. The glass formation in the system Ge-Pb-Se allows for the interaction of all elements with the formation in the melt of complex three-component structural units that contain Pb [597]. Along the all above indicated sections the density of the glasses increases linearly with the increase of Pb concentration. The glass temperature of these glasses changes in the range 503 ÷ 523 K. For the sections GeSe1.5-Pb, $GeSe_{1.5}$ - PbSe and $GeSe_2$ – Pb the increase of the Pb content the glass temperature decreases, approaching to some constant value ~523 K, characteristic for the glass $PbGeSe_3$ (density: 5.60 g/cm^3).

The ternary glasses Ge-Pb-Se are stable against acids and not against oxidants [158]. The NaOH concentrated solution slowly dissolves the glasses.

2.3 Glass formation in the systems A^{IV}-B^{V}-C^{VI}

2.3.1. System Ge-Sb-S

The study of the glass formation in this system has been approached in many papers [165-171], because, as normally, the results of different authors do not agree (Fig. 6.16). This, obviously, firstly is related to the existence of different conditions for the preparation of these glasses that are used for every concrete research. A not negligible role is played by the purity of the initial elementary components, which are used for synthesis.

Firstly, the glass formation in the system Ge-Sb-S has been studied along the partial quasi-binary section GeS_2 – Sb_2S_3 in [165]. The alloys have been obtaind by melting together the chemical compounds GeS_2 and Sb_2S_3 in nitrogen atmosphere. According to [165] the glass formation domain along the given section extends from 45 to 68 mol.% GeS_2. By using more pure components and water quenching, the authors of [171, 172] obtained glasses along all the section GeS_2 – Sb_2S_3, including glassy Sb_2S_3. During preparation of glassy Sb_2S_3 the total mass didn’t overcame 5 g, and cooling rate of the melt reached more than 100 K/s.

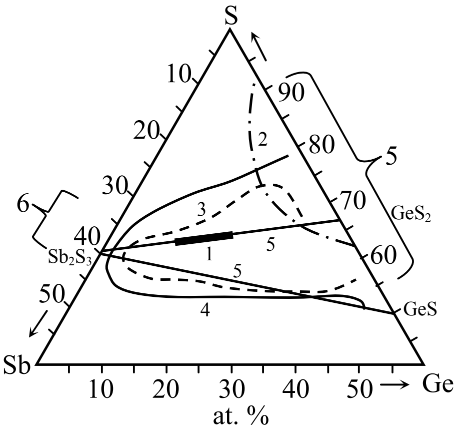

Fig. 6.16. Glass formation in the system Ge-Sb-S: 1 – after [165], 2 – after [166], 3 – after [170], 4 – after [167, 168], 5 – after [170, 171], 6 – after [172].

During the investigation of the glass formation domain in the quaternary system, the authors of the paper [166] have determined the shape of this domain and for the partial triple system (Fig. 6.16). After the data of [166] the glass formation domain in the ternary system Ge-Sb-S is situated on Ge-Se side of the concentration triangle. The same authors (Turjanitsa et al. [166]) show that ternary glasses with high sulphur content are, in this system, inhomogeneous.

Significantly larger glass formation domain in the system Ge-Sb-S has been established in [167-170]. The alloys have been obtained and reported in all these papers by vacuum synthesis from elementary components, with the total mass of 5 g. The maximum temperature of the melt, from where the quenching was performed, has been determined by the liquidus line in the double systems Ge-S and Sb-S and changed from 973 to 1273 K. After long time maintaining of the melt at this temperature, it was used the method of quenching in air or in water, that corresponds to a cooling rate of 100 K/min. The largest part of the glass formation domain is situated in the partial system, formed by three binary sulphides (GeS – GeS_2 – Sb_2S_3), and the domain is strongly extended in the direction of the Sb_2S_3 compound (Fig. 6.16). According to [167], the domain of glass formation in the system Ge-Sb-S is situated in the intervals 55 ÷80 at.% S, 10 ÷40 at.% Ge, 5 ÷40 at.% Sb.

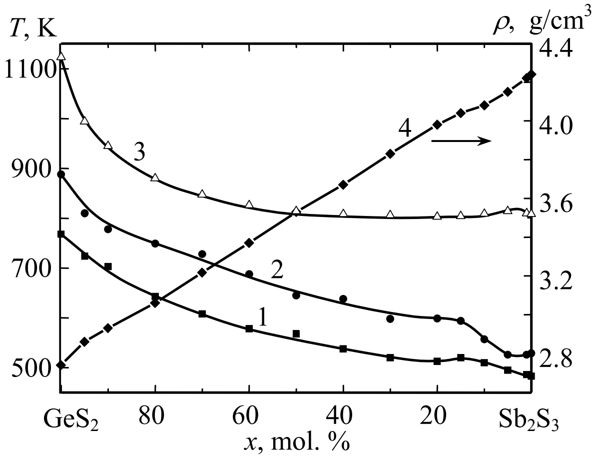

Fig. 6.17. The glass temperature versus concentration (1), crystallization (2), melting (3) and density (4) of the glasses $(GeS_2)_x(Sb_2S_3)_{100-x}$.

In the system Ge-Sb-S have been evidenced two stratification domains, which correspond to two stratification domains in the partial system Sb – S. For higher sulphur content in the partial system GeS_2-Sb_2S_3 the glassy phases coexist with the upper layer, rich in sulphur, and in the partial system GeS_2 – Sb_2S_3 – Sb with the bottom crystalline layer, strongly enriched in Sb.

The dependence on concentration of the thermal characteristics and density of the glasses $(GeS_2)_x(Sb_2S_3)_{100-x}$ are presented in Fig. 6.17. Among the known chalcogenides, the germanium disulphide exhibits the highest glass temperature T_g=768 K. Adding Sb_2S_3 in the glassy germanium di-sulphide leads to the decrease of T_g. The non-monotonous character of glass temperature modification, glass crystallization temperature and of the melting temperature of the crystallized alloys (T_{melt}) in the composition domain $0<x<30$ and $80<x<100$ for the system $(GeS_2)_x(Sb_2S_3)_{100-x}$ (Fig. 6.17) allows to suppose that is produced a non-additive phenomenon of spatially different tetrahedra [GeS_4] and associated trigonal [SbS_3] structural units in partial topological disordering. The character of the change of the concentration dependence of the density indicates the formation of structural groupings [SbS_3], which, if compared with the tetrahedral structural units [GeS_4], occupy less volume and has a more dense packing. The positive deviation from the additivity rule for the density value (curve 4, Fig. 6.17) indicates the statistical character of the distribution of the given structural groupings in the glass matrix of the given system.

The glass temperature of the non-stoichiometric glasses of the system Ge-Sb-S decreases by the decrease of the germanium content from 630 K for $Ge_{35}Sb_{16.25}S_{48.75}$ up to 495 K for the glass $Ge_{7.5}Sb_{23.12}S_{69.38}$ [169, 170]. In the neighborhood of the glass formation domain, crystallizes the phases GeS, GeS_2, Sb_2S_3. The separation of the ternary compound crystals as a result of glass crystallization has not been observed.

The kinetics of the glass crystallization of the glasses from the system $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ in the isothermal regime has been investigated in [173]. From the comparison of the experimental curves of the dependence of the crystallized part on the isothermal time with the theoretical curves it has been concluded on the validity of the Johnson-Avrami model.

2.3.2. System Ge-Sb-Se

The study of the glass formation in the system Ge-Sb-Se has been carried out in many papers [174-187]. This system has a large glass formation domain, close to the selenium corner, in the concentration triangle close to the glassy domain of the binary system Ge-Se (Fig. 6.18, a).

In the ternary system Ge-Sb-Se there exists a significant domain of glasses stable against crystallization, obtained by quenching the melt in air, which comprises the compositions with germanium content 10 ÷20 at.% and antimony content up to 20 at.% [182]. The glasses stable against crystallization can be obtained also by slow cooling of the melt.

The influence of the structuro-chemical composition of the glasses on their crystallization ability can be followed on the alloys of the section $GeSe_2$ – Sb_2Se_3. The introduction of antimony in the $GeSe_2$ favors the glass formation; as a measure of increasing of its concentration the stabilization of the glassy state increases and only for content higher than 20 at.% Sb increases its crystallization ability. Non-monotonous modification of the crystallization ability of the ternary glasses is related to the eutectic aspect of the melting diagram of the systems $GeSe_2$ – Sb_2Se_3 [183, 185, 186] and GeSe-Sb_2Se_3 (Fig. 6.18, b) [188]. The section $GeSe_2$ – Sb_2Se_3 is quasi-binary with the eutectic $GeSe_2$ – Sb_2Se_3, situated at 757 K and 15 at.% Ge. The eutectic composition ~60 mol.% $GeSe_2$, is situated in the limit of the glass domain [183, 184]. In the system GeSe-Sb_2Se_3 it was evidenced the ternary compound $Ge_4Sb_2Te_7$ that forms in a peritectic reaction at 781 K. The eutectic in this system is formed by a ternary compound and by solid solution based on sesquiselenide of antimony. The eutectic point corresponds to the temperature point 745 K and composition 59±2 mol.% GeSe. The presence of of the eutectic favors the glass formation along the section GeSe-Sb_2Se_3 in the composition domain 45 ÷ 46 mol.% GeSe [188].

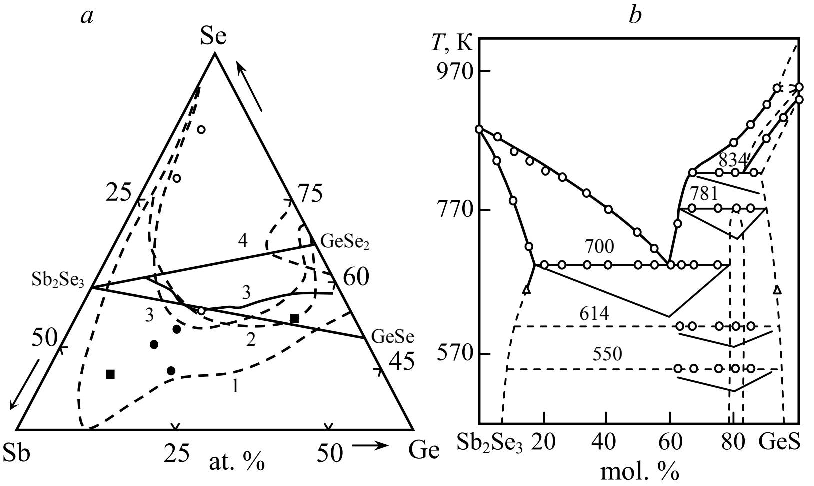

Fig. 6.18. a – Glass formation in the system Ge-Sb-Se: 1 – after [179, 180], 2 – after [176], 3 – after [177], 4 – after [181]; b – phase diagram of the system GeSe-Sb_2Se_3 [188].

The significant dimensions of the domain of the glasses Ge-Sb-Se, stable against crystallization, are the result of their complex, different structuro-chemical compositions that appear in relation with the formation of many spatially different structural units ($SeSe_{2/2}$, $GeSe_{4/2}$, $SbSe_{3/2}$, $GeSe_{2/2}$ and others) [184]. In the given system it is possible to separate in fact even two domains with different character of the structuro-chemical interactions. The glass formation of the alloys with relatively high germanium and antimony content favors the presence of the ternary eutectic, to which belong the crystallization branch of crystallization from the eutectic of partial systems GeSe-$GeSe_2$, GeSe – Sb_2Se_3 and $GeSe_2$ – Sb_2Se_3. The limitation of the glass formation domain in the ternary system Ge-Sb-Se by the limits of the partial system GeSe – Sb_2Se_3 - Se is conditioned by the non-ability towards glass formation of the binary compounds GeSe, Sb_2Se_3 and of the ternary compound $Ge_4Sb_2Se_7$, whose compositions are situated on the section GeSe-Sb_2Se_3 [183, 188].

In the domain of stable glass formation of the system Ge-Sb-Se it is possible to get glasses with a mass of several kilograms. The investigation of the results of glass crystallization in the system Ge-Sb-Se has shown that here is produced the vanishing of the Sb_2Se_3, GeSe, $GeSe_2$ and $Ge_4Sb_2Se_7$ crystals [182, 185].

It was established [181] that the structure of the glasses Ge-Sb-Se has a stronger action on the density and glass temperature, than in the case of the glasses of the system Ge-Sb-S. The glass temperature T_g for the glasses Ge-Sb-Se is lower than for the glasses of the system Ge-Sb-S and for all the sections, and increases with the increase of the Ge and Sb content, reaching the maximum values on the pseudo-binary section $GeSe_2$ – Sb_2Se_3, after which they start to decrease. The cause is the accumulation in the composition of the shown glasses of the spatial structural units [$GeSe_4$] and [$SbSe_3$], which accompany the decrease of the number of selenium chains. The glasses from the section $GeSe_2$ – Sb_2Se_3 are formed, excepting the structural units shown above. Ternary units could be formed [109, 184].

The crystallization processes of the glasses in the system Ge-Sb-Se are studied by TDA and XRD in isothermal regime and for constant rate of heating [185, 186]. The experimental results agree well to the Johnson- Meiller-Avrami-Erofeeva and to the Arrhenius law: $K(T)=K_o.\exp(-E/RT)$, where K_o is the preexponential factor, E is the effective activation energy, R is the universal gas constant. The parameters K_o and E raise for the Sb increase, taking the values of $10^6 \div 10^{16}$ s^{-1} and 74 $\div$227 kJ/mol, respectively, while for the index *n* in the equation JMAE, situated in the limit 1.1 $\div$ 2.5, has been not observed a clear dependence on composition.

2.3.3. System Ge-Bi-S

The glass formation in the system Ge-Bi-S has been studied in the papers [189, 190]. The alloys have been obtained by direct vacuum synthesis from elementary components of high purity, the maximum synthesis temperature reached 973 ÷ 273 K, the keeping at this temperature was 4 ÷ 15 h. The quenching has been performed in air or in water. In separate cases the ampoules before quenching have been kept several hours at temperatures 773 ÷ 973 K. The boundaries of the glass formation domain are given in Fig. 6.19.

The glass formation domain in the system Ge-Bi-S is close to the glass formation domain in the double system Ge-S and is extended along the sections GeS_3 – Bi [191], $GeS_{3.5}$-Bi [192] and $Ge_{20}Bi_xS_{80-x}$ [193]. In the GeS_3 glass it is possible to introduce up to 16 at.% Bi [191].

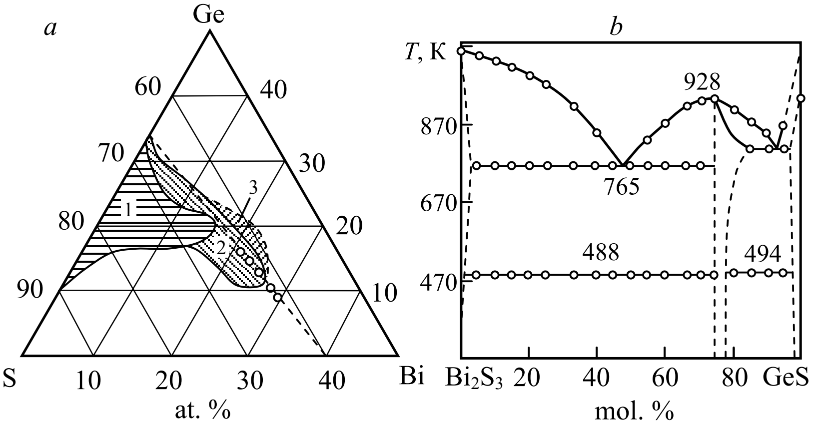

Fig. 6.19 a – The boundary of the glass formation domain in the ternary system Ge-Bi-S: 1- data from [197], 2 – [194], 3 – [195]; b – phase diagram of the system GeS-Bi_2S_3 [196].

In the first investigations [189, 197] (Fig. 6.19) have been found only several compositions of the quasi-binary section GeS_2 – Bi_2S_3 entered in the glass formation domain. They are situated close to germanium di-sulphide. Further studies [195] have shown that ternary glasses along the section GeS_2-Bi_2S_3 can be easily prepared from GeS_2 up to the composition with 50 mol.% Bi_2S_3. The maximum glass formation ability exhibits the alloy $(GeS_2)_{0.6}(Bi_2S_3)_{1-x}$, close to eutectic [195]. The most difficult is to prepare glasses $(GeS_2)_x(Bi_2S_3)_{1-x}$ in the composition domain of $0.9<x<1.0$. In this domain the total mass must not overcome 5 ÷ 7 g, and the cooling rate of the alloys must be ~200 K/s. By using high quenching rates, it is possible to get in the glassy state even the material of composition $(GeS_2)_{0.4}(Bi_2S_3)_{0.6}$ [199, 200].

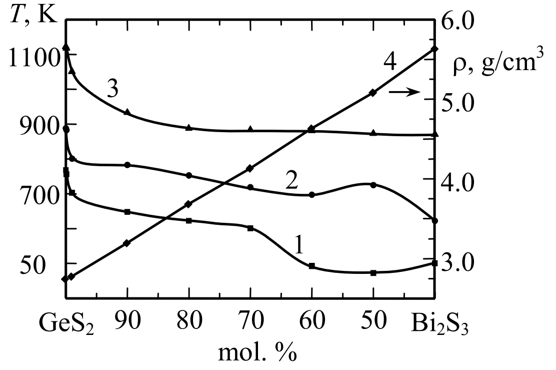

Fig. 6.20. The glass temperature (1), crystallization temperature (2), melting temperature (3) and density (4) of the glasses $(GeS_2)_x(Bi_2S_3)_{1-x}$, as a function of concentration of the components.

The dependence on concentration of the glass temperature T_g, crystallization temperature T_c and the melting temperature T_m, and the density of the glasses $(GeS_2)_x(Bi_2S_3)_{1-x}$ are represented in Fig. 6.20. One observes the non-monotonous character of the the changes of the thermal characteristics in the composition domains $0.9 \leq x \leq 1.0$ and $0.4 \leq x \leq 0.7$.

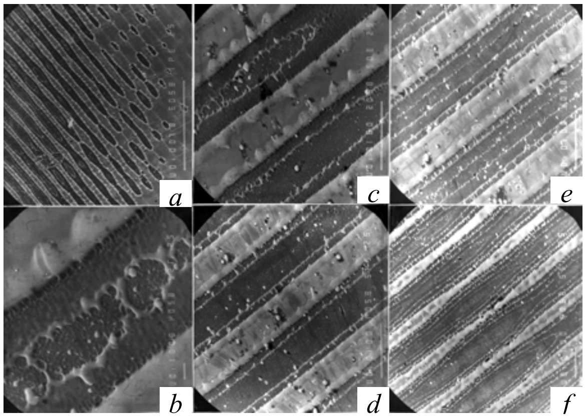

Fig. 6.21. The electron-microscope images of the holographic lattices, described on the surface of the films $(GeS_3)_{0.8}Bi_{0.2}$ in different stages of the process of relief formation [201].

The glasses in the system Ge-Bi-S show high crystallization ability, with the separation of the phases Bi_2S_3 and GeS_2. On all the thermograms are observed 1-2 exothermal effects of crystallization [194]. The maximum value of the glass temperature of these glasses is 636 K.

The crystallization kinetics of Bi_2S_3 for continuous heating of the glasses $(GeS_2)_{0.5}(Bi_2S_3)_{0.5}$ has been studied by DTA and reported in the paper [198]. The heating ratre of the samples was varied in the interval $0.083 \div 0.83$ K/s. By comparing the experimental results with different theories, which describe the crystallization mechanism, there was concluded that the best agreement with the experiment is got for the function $f(\alpha) = \alpha^m(1-\alpha)^n$, where α is the fraction of the crystallized material, $m=0.56$, $n=1.21$.

In the end of this chapter we point to the practical possibility to use the amorphous films $(GeS_3)_{1-x}Bi_x$ $(0 \leq x \leq 0.2)$ as medium for recording holographic lattices with unusual shape of the traces [201]. These authors were the first to evidence the layer structure in the ditches of the holographic lattice (Fig. 6. 21) that induces the crystallization of the amorphous films after heating by laser light and separation of the crystalline phases of the layered semiconductors GeS_2 and Bi_2S_3.

2.3.4. System Ge-Bi-Se

The boundaries of the glass formation domain and several properties of the glasses in the system Ge-Bi-Se, where it is possible the formation of the complex structural units with three components, has been studied in the papers [203, 204]. The alloys have been prepared by the method of vacuum synthesis from elements. The maximum synthesis temperature was 1223 K with keeping to this temperature for 2÷3 h. Then the temperature of the melt has been slowly lowered with 100 K and again keeping constant for 1 h, finally quenching the melt in air or water. The boundaries of the glass formation domain, so formed, are given in Fig. 6.22a (dotted line).

In this figure (thick line) it is shown, also, the boundaries of the glass formation domain, fixed by other group of authors [205, 206], which have prepared glasses by the same synthesis method. Nevertheless, the maximum synthesis temperature was higher, 1323 K, and the duration of the synthesis process reached 48 h. By using stronger quenching conditions in ice + water, the authors of the papers [205, 206] essentially enlarged the boundaries of the glass formation domain in the system Ge-Bi-Se (Fig. 6.22 a). The authors of [194, 202] succeeded to introduce in the ternary glass Ge-Bi-Se up to 15 at.% Bi. The largest formation domain for the glass with bismuth has been obtained for the alloys that contain from 20 to 30 at.% Ge and from 70 to 80 at.% Se. In this system the glass formation favors the presence of the eutectic along the section $GeSe_2 – Bi_2Se_3$ (Fig. 6.22 b). The eutectic point corresponds to the composition ~60 mol.% $GeSe_2$, and its melting temperature is 863 K [207].

The glass temperature of the ternary glasses Ge-Bi-Se increases from 351 to 569 K during the increase of Ge and Bi [203, 204]. Significant increase of the glass temperature is demonstrated by the glasses that contain more than 7 at.% Bi. In an analogous way behaves the value of the microhardness of the ternary glasses.

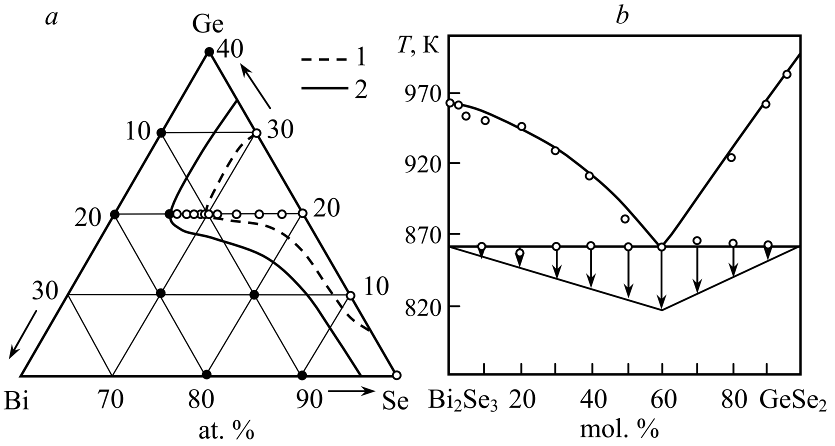

Fig. 6.22. a – Glass formation in the system Ge-Bi-Se: 1 after [203], 2 – after [206]; b – melting diagram of the system $GeSe_2 – Bi_2Se_3$ [207].

By comparing the glass formation domains (Fig. 6.18 and 6.22), obtained by cooling the melts by quenching in air, in the systems Ge-Sb-Se and Ge-Bi-Se one can see that for substitution antimony by bismuth it is produced the decrease of the ability of glass formation. The glass formation domain in the system Ge-Bi-Se is e.g. 7 times smaller than the glass formation domain in the system Ge-Sb-Se [203]. During substitution of arsenic by antimony, in agreement with the increase of the degree of metallization of the chemical bonds in the row As→ Sb → Bi, increases the coordination number of the atoms, and the glass forming ability decreases. The decreasing ability of glass formation is proved by the decrease of the glass formation domain.The size of the glass formation domain shortens with the increase of the atomic number of the element of the subgroup.

The glasses of the system Ge-Bi-Se shows high crystallization ability, and the maximum crystallization ability is exhibited by the glasses with maximum Bi content. According to the X-ray data, during the crystallization of such ternary glasses, the main crystalline phases are Bi_2Se_3 and $GeSe_2$ [204].

A remarkable particularity of the Ge-Bi-Se glasses, enriched in Bi, is the *n*-type electrical conductivity [205, 206, 208, 202, 209, 210].

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