

Glass Chemistry: Problems, Perspectives, and Application (A Review)

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Abstract—The correlations have been revealed and the regularities of glass formation have been determined for systems and materials of different compositions from generalized notions on the basis of a minimal number of fundamental (atomic–structural) substance characteristics. The problem of describing the relationship between the values characterizing the degree of delocalization of valence electrons, the electron network of chemical bonds, nucleus charge, and glass-forming ability has been formulated and solved in general terms for the first time. A qualitative criterion of the substances’ glass-forming ability, which enables one to predict and estimate the possibilities of fabricating materials of different compositions in the glasslike state, has been grounded and developed. A self-contained field of chemical sciences, glass chemistry, has been created and suggested for consideration. Based on the above approach, glass of numerous new compositions has been identified and synthesized, its physical–chemical characteristics have been investigated using structure-sensitive methods, and the potential fields of their practical application have been determined.

Keywords: glass chemistry, fundamental characteristics, new glass, practical application

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INTRODUCTION

Accumulation and generalization of new knowledge observed in chemistry, physics, and other fields of science are the result of the development of basic science and the practical needs of progress in science and technology for creating novel materials. One of the R&D fields promoting this progress is concerned with the chemistry and physics of disordered materials, in particular, glasslike and amorphous ones. The discovery of chalcogenide glasslike materials characterized with electronic conductivity (chalcogenide glasslike semiconductors (CGSs)) by N.A. Goryunova and V.T. Kolomiets served as a start of extensive works devoted to the synthesis and study of their physical–chemical properties [1–7]. Thus, the oxide glasslike materials known since the era of M.V. Lomonosov were supplemented by a new class of disordered materials of inorganic origin, which has been recently appended by amorphous materials characterized with electronic (Si, Ge) or metallic (metallic glass) conductivity.

The focused interest in amorphous and glasslike materials has been recently related to a number of unusual interesting phenomena found in them and inherent exclusively in this class of substances, for example, reversible photostimulated changes in the CGS properties, and the prospects of application in

optoelectronics in the spectrum long-wavelength range. The latter can be used in creating efficient registering media and high-resolution photoresists for microelectronics and the printing industry. The needs of various industries, in particular, those that emerged on the creation of electronic, radio engineering, optical, and other devices of versatile purposes call for the necessity of research and development of novel materials meeting the ever-complicating requirements demanded from their properties. Here, the full potential of glass can be realized only when one manages to exhaustively describe its structure, as well as properties and processes occurring in it [8].

To sum up, the availability of a generalized scientific approach, general theory, and general criteria of creation of such materials is of crucial importance. This will not only enable one to consider isotypical and similar classes of known materials that are different in composition from generalized points but also make it possible to determine the strategy for the search for novel materials and predicting their properties [8, 9]. Here, the point is in the development of generalized principles of the approach to the whole range of known and new glasslike materials with the main focus on chalcogenide materials. It is very likely that the fundamentals and principles of such an approach can be useful for other classes of compounds.

The above approach can be based on a field in chemistry devoted to studying the properties of glass depending on its composition, electronic structure, mutual local coordination of the atomic (molecular) particles, and ways of combining their structural units (s.us.) (or clusters) into a glasslike (disordered) network providing the intermediate- and long-range chemical order. It is suggested to separate this field (or chapter) into a self-contained one and name it "glass chemistry." Glass chemistry must not be identified with the "chemistry of glass": the latter must be concerned with studies of the interaction of glass of specific compositions with different chemical media in different aggregate states [7].

One of the main directions of glass chemistry consists in studies of the glass-forming ability of substances, revealing the origin of glass formation from melts of different compositions, and determination of criteria, which could serve as a basis for creating new glasslike (in general—noncrystalline) materials with valuable practical properties. Thus, one can formulate that glass chemistry is a field of science devoted to substances capable to transform from the melt to a glasslike (disordered) state and studying the reasons of such a transformation and chemical bond, structure, and properties of such substances, as well as their dependence on the composition and external conditions.

The analysis of a large number of works demonstrates that the majority of studies of the disordered state have been devoted to the examination and generalization of results on some specific groups or properties of amorphous and glasslike materials, but rarely considered them from generalized notions with an emphasis on disordered materials [7, 10, 11]. Indeed, in spite of numerous theoretical and experimental studies, the problems of the nature of glasslike and amorphous states and the glass-forming ability of substances have not yet found proper solutions.

The objective of the present work was to develop the fundamentals of glass chemistry including the regularities of the formation and prediction of various types of glass (in particular, chalcogenide ones) and to work out new and develop the known methods of investigation and analysis of the structure and chemical bonds in these objects. Here, the following tasks were to be solved: development and grounding of a simple, reliable, and universal criterion of the glass-forming ability of substances of different compositions; prediction of new glasslike systems and development of methods of their synthesis and study; and examination of perspectives of practical application of glasslike materials, first of all, chalcogenide ones.

To solve the above tasks, various theoretical and experimental methods, techniques, and approaches applicable in chemistry, physics, solid state physics, etc., were used. The position of the elements in the Periodic Table and determination, on its basis, of a number of fundamental properties of the substance

atoms characterizing the degree of delocalization of valence electrons (metallization of a chemical bond), the electron network of chemical bonds (structural rigidity) with ligands, and atoms' nuclear charges serve as a basis for the criterion of glass-forming ability (GFA) of substances of different compositions. Algorithms and programs for finding the type of the dependence of the substance glass-forming ability on the number of electrons in systems have been created. Their computer-assisted implementation allowed identification, calculation, and, thereafter, synthesis of new chalcogenide and other glasslike materials in different systems.

APPROACH AND SCIENTIFIC NOVELTY

As was mentioned in [12], the notions of order—disorder and/or ordering—disordering were most often used without strict quantitative characterization. In studies of amorphous and crystalline substances, the properties of materials of identical composition are often compared: glass—polycrystal, glass—monocrystal, and glasslike sample—amorphous sample. However, not every comparison is consistent in this case. A basis for a correct comparison can be provided, for example, by the most probable (hierarchical) scheme of the genesis of amorphous and crystalline bodies [13]. As follows from this scheme, in the course of transformation from a melt (or from the gas phase) into the solid state, all these substances form two groups: those in disordered (amorphous) and ordered (crystalline) states. Here, in both bases a substance can be present whether in a monolith (glass, monocrystal) or in a finely dispersed (amorphous powders, polycrystal) state.

Leaving aside the nature of liquid crystals as a product of the transformation of the disordered state into the ordered liquid state at a decrease in temperature, let us note that in the group of disordered solids polycrystals have analogs as finely dispersed amorphous substances (amorphous powders, amorphous films), while the analogs of monocrystals include monolith amorphous substances (glass, resins, solid glues, etc.). Thus, one can see that in studies of glass—crystal transitions the most reliable data can be obtained by comparing the properties of glass and a monocrystal of identical compositions or of a pair of amorphous film—polycrystals. Using such an approach, one can, for example, unambiguously explain the low concentration of their own paramagnetic centers in glass and monocrystals of identical compositions.

One of the most probable ways of substance transformation from the gas to the liquid phase, along with a temperature decrease and without changes in the chemical composition, is the transition gas \rightarrow liquid \rightarrow solid with the formation, in some cases, of intermediate associates and aggregates. Here, the substance in a solid state obtained through liquid cooling

at a fixed rate could have a long-range order in the locations of atomic, molecular, and other particles (i.e., it could be crystalline) or just a short-range order; i.e., it could be a disordered and noncrystalline solid (amorphous or glasslike).

The prospects of the application of noncrystalline materials to a significant extent depend on the peculiarities of the substance's glasslike state, degree of disordering, and forms of the disordering manifestation, as well as on the reliability of the prediction of the properties and stability (with boundary conditions) for disordered materials. The solution of these problems requires the definition of the general criteria and approaches to glass formation in substances of any composition.

With regard to the melt's ability to form glass at a fixed cooling rate, for instance, under conditions of spontaneous cooling to room temperature, all the substances (both simple and complex) can be divided into two groups: glass-forming and crystallizing ones. What is the reason for the different behavior of a melt's substances in the course of transition into a solid state? Starting from the 1920s, numerous works by various authors have been devoted to finding an answer to this question in qualitative (seldom in semiquantitative) terms or for individual classes (groups) of substances using structural chemistry, thermodynamic, or other parameters: G. Tamman, R.L. Muller, Sun Kyan-Han, V.V. Tarasov, J.D. Mackenzie, A. Winter-Klein, H. Rawson, A.A. Appen, V.F. Kokorina, J.S. Philips, S.V. Nemilov, H. Fritzche, G. Careri, E.V. Shkol'nikov, M.D. Bal'makov, and others (reviewed in [7]). Leaving aside a detailed description of the above authors' works, let us mention some statements made by some of them.

Based on the analysis of the structure of a number of tetrahedral crystalline oxides, Zachariasen established that simple compounds could form glass under specific conditions: the coordination numbers (CNs) of the central atom are small (from 2 to 6); oxygen tetrahedra are linked to each other through vertices (to form a continuous three-dimensional network); and oxygen tetrahedra must not have common edges and faces. Such an approach is of the crystallographic character and does not take into account the role of chemical bonds [14].

Stanworth used the difference in electronegativity (ΔEN) of the atoms of atoms according to Pauling as a criterion of the substances' glass-forming ability [15]. However, this criterion was found to be of poor usability. In particular, it contradicts the possibility of producing the glasslike state for simple substances and compounds with a significant fraction of the ionic character of the chemical bond. The Stanworth criterion appeared to be contradictory even in the case of one group of oxide glass: ΔEN for SiO_2 and SnO_2 is about the same, but it is impossible to obtain SnO_2 in the glasslike state using conventional methods.

Sun used the chemical bond strength as a criterion of glass-forming ability: the easiness of glass formation is proportional to the strength of the chemical bond [15].

Rawson suggested the ratio of the element–oxygen bond energy to the melting point as a criterion of glass-forming ability. In other words, he modified Sun's criterion [15]. Nevertheless, the mentioned criteria of Sun and Rawson are not suitable, for example, in the cases of V_2O_5 and CO_2 .

A significant effect of the short-range order in the atoms' location on the physical–chemical properties of solid bodies of different compositions was mentioned in the works by A.F. Ioffe and A.R. Regel' [16].

A crucial role of covalent bonds in glass formation was for the first time indicated by R.L. Muller and, thereafter, Ditzel, Stevels, Weil, Stanworth, and others [7, 14, 15, 17]. However, most of these authors put the main focus on the chemical bond energy, thus explaining the special place of glass-forming oxides; however, they left the place of other substances having strong covalent bonds, but not forming glass (carbon, silicon, etc.), undefined.

Kauzmann formulated an empirical rule of “two-thirds” relating the temperatures of glass transition (T_g) and melting (T_m), according to which in glass-forming systems, the T_g/T_m value called the reduced glass transition temperature is approximately constant and equal to $2/3$. As was shown within the scopes of the free volume theory, the T_g/T_m ratio could be described by the approximate equation $T_g/T_m = 0.5 + F$, where F is the function of frozen viscosity. For glasslike substances, at the cooling rates of $V \leq 10^{-2}$ K/s, this function's value is in the range of 0.10–0.15, while if $T_g/T_m > 0.5$, the bulk crystallization is suppressed, which promotes glass formation. However, this rule has many exceptions [7].

The authors of [18] attempted to find a relation between the formation heat and the affinity to glass formation. However, despite finding a certain correlation, there are many deviations.

To estimate the trend towards glass formation, Cosey and Turnbull [6] suggested using the reduced melting temperature (point) T_r :

$$T_r = PT_m/\Delta H_{ev},$$

where T_m is the melting point (temperature) and ΔH_{ev} is the evaporation enthalpy. The higher ΔH_{ev} and the lower T_m the stronger the trend towards glass formation for the melt. One should mention that this relationship is of a limited character and should be applied with the highest relevance to groups of glasslike compounds of similar compositions [6].

The authors of [19, 20] suggested a semiquantitative theory of glass formation based on an empirical

equation estimating the substances' ability towards glass formation (G):

$$C = 0.5(A + E)(\text{VEK} - C) = f(b_1, b_2, \dots, b_i),$$

where A is the number of elements in the composition of the substance, E is the number of types of structural units in the melt, VEK is the average number of valence electrons per substance atom, C is the coordination number of atoms in the melt, and b_1, b_2, \dots, b_i are the element's atom fractions. The $(\text{VEK} - C)$ difference is defined as the average number of electrons of lone pairs per atom of the substance. Application of this model is limited and not always feasible [21].

M.V. Vol'kenshtein and O.B. Ptitsyn [22–24] attempted to explain glass formation on the basis of general molecular-kinetic model points. However, glass formation is often far from being bound to the process of molecular regrouping. Moreover, this model leaves unsolved the problem of the physical nature of kinetic units.

K. Tanaka stated that the stability of some structures of chalcogenide glass depended on the average coordination number and is maximal at its value equal to 2.67 [25].

Ubbelohde related the substances' ability to form glass with the possibility of formation of specific anticyrystalline clusters and their concentrations [26].

One should mention that the latter works on the outlined problem are, as a rule, concerned with individual classes of substances and/or require the definition of many specific parameters for the compositions under study in case of their application. For example, in many cases of using thermodynamic approaches for the problem of glass formation, one must have a substantial and rather detailed bulk of data on the atomic–molecular level about the processes occurring in specific systems. For instance, a promising and reliable thermodynamic criterion of glass formation related to the decrease of the Gibbs energy (ΔG_{cr}) at crystallization of the overcooled melt (or glass) suggested in [27]

$$\Delta G_{\text{cr}} = \sum_{i=1}^k \Delta G_{\text{cr},i} x_i - RT \sum_{i=1}^k x_i l_n a_i^{\text{gl}},$$

requires the knowledge of the following values:

$\Delta G_{\text{cr},i} = (\mu_i^{0,\text{cr}} - \mu_i^{0,\text{gl}})$ is the change in the Gibbs energy at crystallization of the pure component i : ($\mu_i^{0,\text{cr}}, \mu_i^{0,\text{gl}}$ is the chemical potential of the pure component i in the crystalline and amorphous states); and a_i^{gl} is the activity of the pure component in the glass-like state (x_i is the molar fraction of the component i).

The authors of [28] suggested a thermodynamic approach to estimating the glass-forming ability of the

melt. As a rule, the melt glass-forming ability increases, along with a decrease of the criterion K :

$$K = \lim_{m \rightarrow \infty} \frac{l_n N_m \varepsilon(m \varepsilon(T_n + Q))}{l_{n\text{max}} N_m(m \varepsilon \varepsilon)},$$

where N_m is the distribution density on the energies of the potential minima:

$$N_m = \delta(E) + \frac{\sigma(E - E_1) e^{\alpha m} - \frac{1}{2} \left(\frac{E - hm}{\gamma \sqrt{m}} \right)^2}{\gamma \sqrt{2\pi m} \Phi \left(\frac{E_0 - E_1}{\gamma \sqrt{m}} \right)}.$$

Here $\delta(E)$ is the Dirac delta function corresponding to the crystal minimum, E_1 is the minimal energy necessary for local changes in the structure of an ideal crystal, $\Phi(x)$ is the normal distribution function, γ, h are the parameters setting the Gauss distribution in the standardized form, m is the number of atoms, $\sigma(E)$ is the unit function, and T_n is the melting point (T_m)

defined at $m \rightarrow \infty$ as $T_n = h + \sqrt{h^2 - 2\alpha_j^2 / 2\alpha} (T_m)$. As a result, it was suggested to estimate the value of the thermodynamic criterion on the basis of the experimental data—of the temperature and heat of melting and the heat capacity jump upon melting. The necessity of using specific glass parameters is also present for other criteria, rules, and models [6, 18, 29], which prevents their application in predicting the possibility of producing new glass.

In the present work, an attempt has been made for the first time to lay the ground for a fundamental approach to the problem of the glass-forming ability of substances of any composition and its quantitative description. In view of this, it is required to answer a few questions sufficiently unambiguously, and in particular, the reason behind the different behavior of melts of different substances on cooling. Also, the question on why under identical conditions of the cooling of the liquid (or gas) phase some substances are capable of transforming into a solid disordered state, while others are not.

Muller [7] indicated for the first time the crucial role of the directed covalent bonds of the types $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ or $-\text{Be}\leftarrow\text{F}-\text{Be}-$ responsible for the formation of intertwinement in the molten state for the glass formation and amorphization of substances. For instance, as early as in 1940, he wrote “The knowledge of the main structural unit and the nature of its chemical bond is essential for the problem of the glasslike state. The affinity of some substances to glass formation is related to the predominance of directed covalent bonds with the reduced range of action in them.” [30]. The Winter–Klein notion on the optimal number of p electrons per atom [7] is, in fact, derived from the second condition of glass formation formulated by Muller.

As was stated in the works of Muller, Goryunova, and Kolomiets [1, 2], the ability of a substance toward

glass formation decreases significantly on the metallization of the chemical bond due to the delocalization of valence electrons. A decrease of the melt glass formation upon cooling is also promoted by its molecular structure observed, as a rule, in the case of substances consisting of light atoms [2]. This raises the question on whether it is possible (and if possible, then how) to take into consideration the glass-forming ability of substances of different compositions in totality and on the basis of general fundamental principles. It also raises the question on what the basis of such a consideration will be. Hereinafter, we will try to answer all these questions.

QUANTUM CHARACTERISTICS OF SUBSTANCE ATOMS

Rawson [15] wrote: “Probably, it is difficult to create a sufficiently general theory of glass formation covering all possible cases. The problem consists not only in the necessity to explain the glass-forming ability of a limited quantity of simple compounds but also in the need to consider double and more complex systems and explain the location of glass formation areas.”

At present, the majority of works of general character devoted to noncrystalline (amorphous and glass-like) materials can be divided into two groups. The first one includes the works on general theoretical notions on the nature of localized electronic or atomic states in these materials and studies of the respective energy excitations [31–34], the second one includes the analysis of the experimental results with the formulation, in some cases, of qualitative generalizations [4, 6, 35]. The authors of a much fewer number of works deal with revealing the nature of noncrystalline objects of study, in particular, the nature of glass formation and its interrelation with the substance’s fundamental characteristics.

The properties of substances of different compositions are known to be determined by the positions of component elements in the Periodic Table. In view of this, it appears reasonable and well-grounded that the strictest approach to the glass-forming ability of substances must be based on the Periodic Table of Elements. The fundamental character of the Periodic Table of Elements is manifested, in particular, in the fact that “its cells correspond not to numerical coefficients and individual functions characterizing elements of interest, but to the extensive arrays of functions and more complex mathematical dependences that are essentially different from each other and specific for each element” [36]. In such an approach, each element must be considered as a supermatrix. The element position in the Periodic Table determines not only the chemical individuality of its atoms but also their valence features (coordination) in different compounds, depending on the number and type of external electrons forming the electronic network of chemical bonds (ENCs). To sum up, in our case, one

can assume that an element’s position in the Periodic Table of Elements determining its fundamental characteristics allows the “first principles” characterization of the glass-forming ability both of the element itself in the form of a simple body and its compounds.

One of the main characteristics of the atoms of any chemical element is the principal quantum number n . As was indicated in a number of works, the substances’ glass-forming ability decreased during the metallization of chemical bonds [2, 6–8, 37] due to delocalization of valence electrons, whose principal quantum numbers were sufficiently high. As mentioned in [38, 39], n characterized the degree of orientation of the chemical bonds between the selected and other atoms. As was shown in [38], using the values of atoms’ quantum numbers in chemical compounds, one could separate the structures of normal valence compounds with octahedral and tetrahedral atom coordination and “compounds with covalent and ionic order” [40]. The diagram “Degree of metallization—Degree of ionic character of the chemical bonds for metals, dielectrics, and semiconductors” was built based on n [7, 40].

Thus, the usage of n can be rather useful and necessary in investigating different classes of chemical compounds. Here, one must remember that n takes into account the contribution of some specific type of atoms having their own types of delocalization of valence electrons.

However, there are many known cases when substances of the same composition with the same n are characterized with different properties; this fact is related to polymorphism and the presence of polymorphous modifications for many substances [7].

The reasons for the correlation between glass formation and the number of polymorphous modifications must be sought in the energy and structure—chemistry features of simple solid bodies, taking into consideration the chemical compounds formed based on them. A certain basis for such a consideration can be provided by the theory of the v , the well potential ($v \geq 2$) [41], and the multimimum adiabatic electron term [42]. Atoms of substances with a large number of polymorphous modifications can have different energy states, which promotes glass formation. A useful contribution to the solution of this problem can be provided by the method of molecular orbitals, and in particular, the analysis of variants of the occupancy of different molecular orbitals and the number of polymorphous forms. For example, Fig. 1 shows the scheme of the variants of the valence electrons’ distribution for the selenium atom [7] showing that the number of polymorphous forms is equal to the number of variants of selenium electrons’ distribution over bonding and antibonding states.

A possible scheme of the distribution of the stationary states corresponding to different polymorphous modifications is shown in Fig. 2, where the mentioned

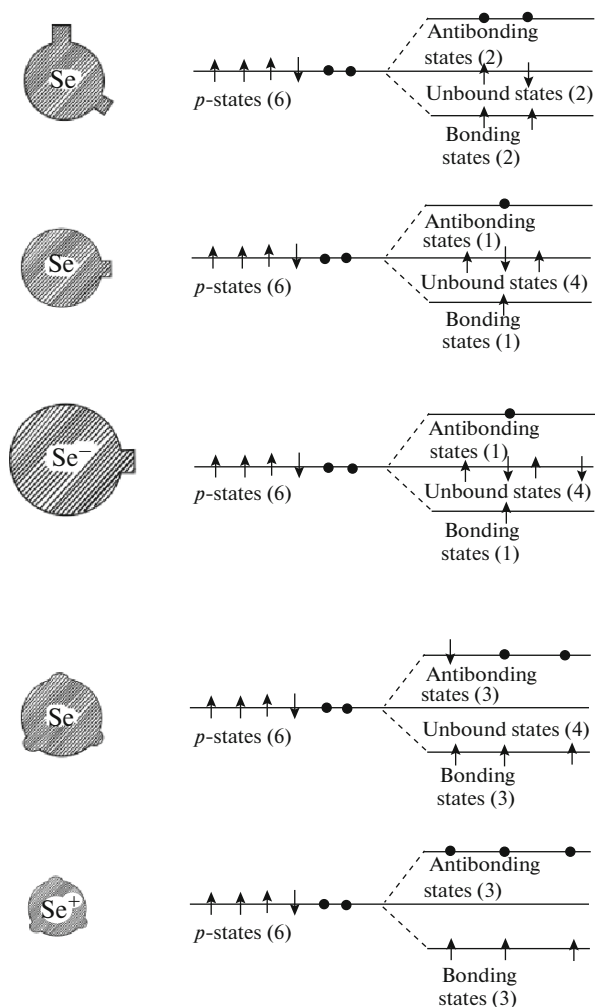


Fig. 1. Possible variants of the distribution of the external electrons of selenium atoms.

stationary states are grouped into zones (1–2, 3–4, 5–6). Here, zone 7–8 corresponds to the glasslike, amorphous, and liquid media [42]. In this case, both zones overlapping and the location of one zone inside another one are possible. The heterogeneous states emerging here and realized, for example, at phase equilibria will be located in the forbidden zones (2–3, 4–5, 6–7).

As is clear from the above discussion, to determine the substance glass-forming ability, it is insufficient to use only the principal quantum number n . It is also necessary to take into consideration both the chemical bond type and the structural rigidity determined by the electronic network of chemical bonds.

GLASS-FORMING ABILITY AND CHEMICAL BONDS

As was mentioned above, attempts at the quantitative characterization of the correlation between the

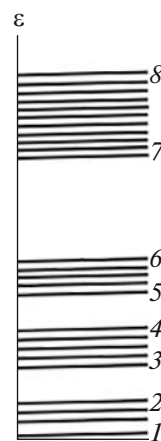


Fig. 2. Scheme of the energy spectrum corresponding to the homogeneous condensed states: $\varepsilon = \frac{E}{m}$, where E is the energy of the system's stationary states and m is the number of atoms.

glass-forming ability (GFA) and the type of chemical bonds have been made repeatedly.

It is well known (see, for example, [2, 43, 44]) that the following factors must be taken into account in the search for such a correlation. First, the presence of metallic bonds in the melt structure dramatically decreases its GFA, since these bonds are characterized with small values of the switching activation energy. Second, a significant role in the process of glass formation belongs to bonds of the link type.

According to [38], the arithmetic average of the principal quantum numbers of the valence electrons of the atoms of a binary compound (\bar{n}) can be used as the degree of the metallization of the covalent bond. The larger \bar{n} values correspond to easily crystallizing substances (a long-range geometric order was established at the minimal overcooling of the melt), and the melt's polymeric structure transformed into the coordination lattice. On the other hand, the small \bar{n} values correspond to substances with a tendency to form molecular (closed) structures linked to each other by weak van der Waals forces. The role of link-type bonds can to a degree be characterized by the value of the average number of chemical bonds per substance atom (\bar{K}). The value $K = 2$ is known to be the most favorable one for glass transition; a significant increase in K corresponds to the increase of the rigidity of the short-range order structure and, therefore, to the decrease of the GFA substance [44].

An attempt was made to empirically estimate the total influence of the two mentioned effects by the multiplication of the ($\bar{K}\bar{n}$) values and use of the result in the systematization of data in the literature on the correlation between the GFA of the binary compounds and the type of chemical bond through build-

ing the $\bar{K}\bar{n}-i_p$ diagram (i_p is the bond's ionic character degree according to Pauling) [40]. Here, the data are concerned with the glass formation examined, as a rule, at the regular cooling and melt tempering rates [7].

It is important to mention that examination of the correlation between the glass-forming ability and the position of the substance on the $\bar{K}\bar{n}-i_p$ diagram appeared to be useful and necessary [35]. A combination of the optimal average bond number and the optimal principal quantum number taken into consideration as a product of two glass formation characteristics (the probability of a complex event) was the first attempt to approach the qualitative estimation of the glass-forming ability of the substance. However, this approach did not allow us to find a strict dependence between the mentioned characteristics of the substance, but provided some relationship between them and the GFA. The above correlation is of a limited character, since it can be attributed only to simple substances and binary compounds containing just one type of chemical bonds [35].

GLASS-FORMING ABILITY AND POSSIBILITY OF ITS DETERMINATION FROM THE FUNDAMENTAL CHARACTERISTICS OF THE SUBSTANCE

As mentioned above, the properties and characteristics of the substances of different compositions depended on the positions of their component elements in the Periodic Table (PT) [36]. Therefore, the substance's glass-forming ability (GFA) must also depend on the component elements positions in the PT. Here, the atom of each element can be characterized by certain valence possibilities depending, finally, on the number and nature of the valence orbitals and their electron occupancies. In its turn, the atom type is determined by its chemical individuality: it depends on the nucleus charge (number of electrons), valence, and affinity distribution over the bonds [45]. To sum up, one can state that the element's position in the Periodic Table determines its capacity to form an electronic network of chemical bonds (ENCBS) with the ligands, which promotes whether glass transition or crystallization takes place at the cooling of the melt. The latter property can be characterized by the rigidity of the ENCBs determined by the ratio of the number of chemical bonds (m) in the structural unit (s.u.) to the number of atoms in it (g):

$$k = \frac{m}{g}. \quad (1)$$

The value of k depends on the number and nature of the valence orbitals of the central atoms in the respective s.u. reflecting the structural-chemical composition of the substance. Note that within the approach under development (unlike [35]), it is suggested to introduce, instead of the average number of

bonds per atom in the formula unit (f.u.) as one of the indexes of the glass-forming ability, a more correct value: the average number of chemical bonds per atom forming the s.u., taking into account the number of atoms in it. It is worth mentioning that k is related to the melt near (T_m) of the substance and characterizes the degree of the structure's rigidity during its transition to the solid state.

As seen from the above, k is the function of the orbital quantum number (l). For a complex substance, whose composition is expressed by several types of s.u., the rigidity of the ENCBs is calculated according to the formula

$$k = \sum k_i x_i, \quad (2)$$

where k_i is the rigidity of the ENCBs of element i forming its own s.u., x_i is the atomic fraction of element i , k is the average multiplicity of the bond per f.u. of a substance of the type $A_x B_y C_z \dots$, where $x + y + z + \dots = 1$.

For binary and more complex substances, one can use a more formalized method for calculating k :

$$k = bx. \quad (3)$$

Here b is the number of bonds formed by the central atom of the s.u. and x is the atomic fraction of the element forming the s.u. This method of calculation appeared to be the most useful in the case of multi-component glass. For example, a substance of the composition $0.5\text{GeSe}_2 \cdot 0.5\text{As}_2\text{Se}_3$ consists of the s.u. of $\text{GeSe}_{4/2}$ and $\text{AsSe}_{3/2}$. Through the calculations of k for germanium and arsenic selenides (Eqs. (1) and (2)), the total values can be found using the additive equation:

$$k = \sum k_i x_i, \quad (4)$$

where k_i is the rigidity of the ENCBs in the s.u. I and x_i is its molar fraction.

As mentioned above, the glass-forming ability of the substance decreases at sufficiently large and small n of the component atoms (for example, in the row $\text{S} \rightarrow \text{Se} \rightarrow \text{Te}$) [38]. Both of these effects influencing the ability of the substance toward glass transition can be taken into account quantitatively through the introduction of the principal quantum number of valence electrons (n) in f.u. The n value can be found from an equation similar to (2):

$$n = \sum_i n_i x_i, \quad (5)$$

where n_i is the principal quantum number of valence electrons of component i . Just as the ENCB rigidity (k), the value of the quantum number of valence electrons (n) calculated, taking into account the atomic fraction of the components in the f.u. for glass-forming melts, must fall into some specific range. The explanatory scheme for such a conclusion is shown in Fig. 3. The simultaneous realization of the optimal

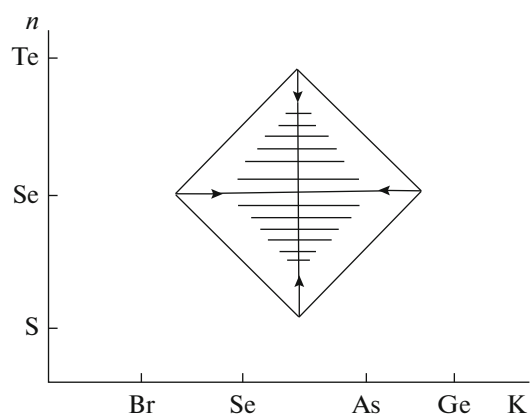


Fig. 3. Scheme explaining the existence of the optimal values of n and k (shaded area).

values of k and n comprises a necessary condition for the melt transition of the substance into a glasslike state and can be taken into account in the form of the product kn [35] or as a geometric average of the k and n values, i.e., \sqrt{kn} . The product or the geometric average of these characteristics still does not provide a sufficient criterion for the glass-forming ability of the substance [7, 40, 46]. To obtain such a criterion, the above product must be related to the unit value of one of the fundamental characteristics known for any substance and describing 1 mol of atoms. Taking into consideration all of the above and the results of [47], as well as the fact that the properties of elements and their compounds, just like their quantum characteristics, are determined by the charge of their atom nucleus (Z), the value of $1/Z$ was used as a multiplier (Z is the value of the nucleus charge in the f.u. of the substance). Z was calculated similarly to k and n :

$$Z = \sum_i z_i x_i, \quad (6)$$

where z_i is the charge of the nuclei of the atoms of component i .

To sum up, the ratio $\frac{kn}{Z}$ or $\frac{\sqrt{kn}}{Z}$ comprises the glass-forming ability of a substance per unit the averaged charge of its nucleus. Let us name this characteristic as the specific glass-forming ability (G) of the substance on transition from a melt into the solid state, so that one can see that G is determined only by the physical-chemical nature of the substance. The graph of the dependence of G on the ionic chemical bond used earlier is shown in Fig. 4. As seen from the figure, use of the ionic bond enables one to obtain only some specific diagram with areas for chalcogenide, oxide, and more ionic glass-forming substances, as was demonstrated in [7].

From the point of view of theory and practice, it was of interest to find the analytic dependence of the

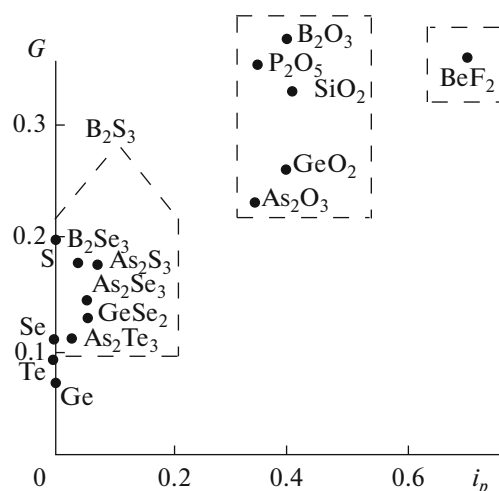


Fig. 4. $G = \frac{\bar{nk}}{\bar{z}}$ diagram is the ionic chemical bond for some simple substances and binary compounds.

G value on some other fundamental characteristic of the substance that can be determined easily and reliably (*a priori*). Analysis of the known characteristics showed that these requirements could be met using the total number of electrons per mol of the substance (N) or its average molar weight (A). Indeed, these values can be reliably determined for any hypothetical formula of a substance and do not even require the synthesis of such a substance. To establish the analytic form of the dependence of G on N , let us first perform the analysis for the known simple and binary glass-forming substances. An example is shown in Fig. 5 by presenting the positions of different simple and binary substances on the $G = f(N)$ graph. Figure 6 shows similar data for nonglass-forming substances of simple and binary compositions. The solid line on these graphs corresponds to the theoretical one calculated using a computer. As seen from Fig. 5, all the glass-forming compounds (simple and binary) of the substances fall on the theoretical curve or near it, whereas for nonglass-forming substances, the picture is different (Fig. 6). In other words, during the spontaneous cooling of a melt, all the glass-forming substances are subject to a certain regularity that can be approximated using the least-square method by a hyperbole of the type

$$G = \frac{1}{AN + B}, \quad (7)$$

where $A = 0.191 \pm 10$ and $B = 1.28 \pm 0.25$ [40].

Building the theoretical dependence allows, with the preliminary calculation of the G value for the hypothetical composition, its juxtaposition with the theoretical value determined using formula (7). In the cases of the equality these values or deviations of not higher than 5–6% (Fig. 5), one can assume that the

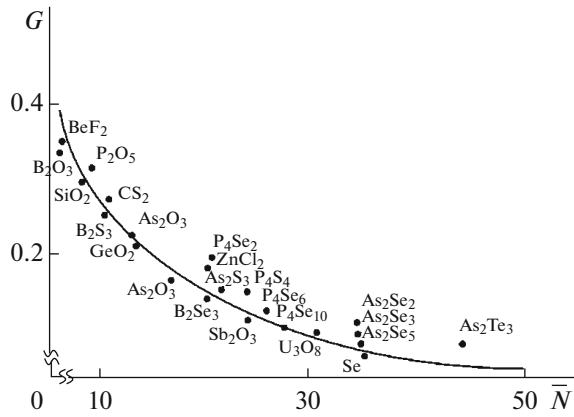


Fig. 5. The dependence of G on \bar{N} for some simple and binary systems of glass-forming substances during the spontaneous cooling of their melts.

The solid line corresponds to the theoretical dependence

$$G = \frac{1}{AN + B}$$

melt of the tested substance will form glass at regular cooling rates.

The approach under development is the most interesting for triple and more complex formations; however, in the cases of such systems, the energy of the mutual exchange is not always available, secondary interactions are present in addition to primary ones, etc. Therefore, such an approach could contain elements of some uncertainty, in particular, in the calculations of K . Nevertheless, based on the earlier available data and on the known, real, or similar structural formations, we attempted to expand this approach to more complex substances of both the stoichiometric and nonstoichiometric compositions forming glass during the inertial cooling of their melts. The obtained data are shown in Fig. 7. It is clearly seen that for all the substances under examination the character of the G – N dependence remains the same both for simple and binary substances: in the case of efficiently glass-forming substances, the G values are on the theoretical curve or in its vicinity.

The established regularity enables one to predict whether a melt of a specific composition will solidify in the form of glass during its inertial cooling or whether this will require a higher cooling rate. Here, the larger the deviation of the calculated G value from the theoretical curve determined by Eq. (7) the higher melt cooling rate necessary for its transition into the glasslike state (with the other conditions being identical).

The found interrelation between the glass-forming ability of the substance and the characteristics of the atoms of the chemical elements present in it allows determining the glass formation area in any M -component system ($M \geq 1$) using only computer equipment without performing an experiment. Comparison

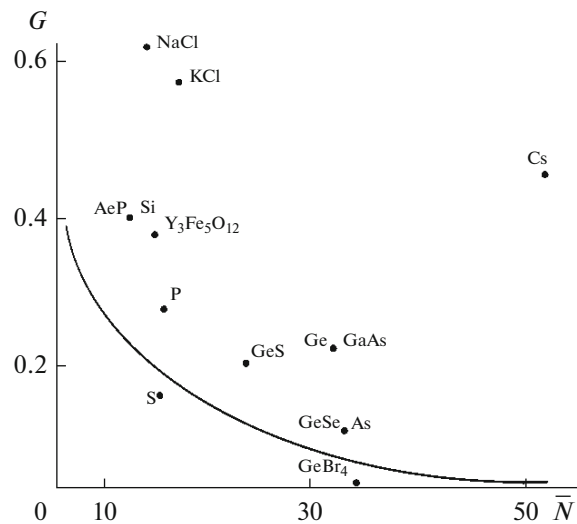


Fig. 6. The dependence of G on \bar{N} for a number of simple and more complex nonglass-forming substances during the spontaneous cooling of their melts.

of the calculation and experimental data over the known and new areas of glass formation in chalcogenide, oxide, sulfate–phosphate, borate, beryllate, oxyhalogenide, and other systems showed their close concurrence [7, 40, 47].

CONCLUSIONS

The examined extensive material reflecting the results of numerous studies either corroborate or do not contradict the developed approach to the glass-forming ability of the substances of various compositions. The ideas that are being developed the most thoroughly and strictly can be applied to substances that are relatively simple in composition, in which one

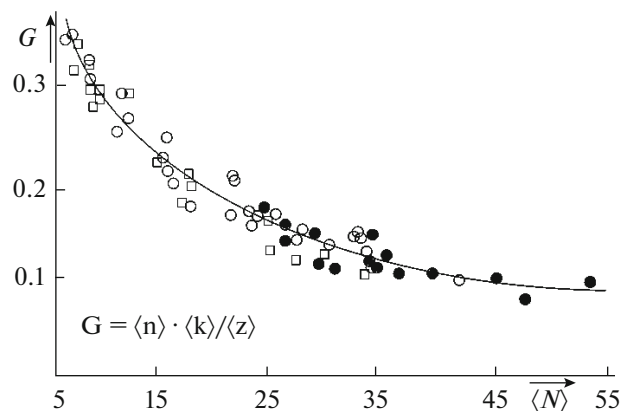


Fig. 7. Data on the dependence of G on \bar{N} : (1) simple and binary systems; (2) triple and more complex chalcogenides and halogen–chalcogenides; (3) silicates, borates, phosphates, fluoroberyllates, fluorophosphates, fluorosilicates, and others.

can reliably estimate the structural formations and energies of the chemical interactions between the components (the energy of interexchange). The kinetic aspect of this approach is taken into consideration in the boundary conditions, since the melts undergoing glass formation upon inertial cooling are examined. The detailed results of the application of the suggested approach have been reported in reviews by the author [7, 40, 46].

More than 40 original methods, devices, and installations have been developed, patented, and tested for the synthesis and study of new compositions for versatile glasslike materials simulated within the scopes of the presented approach. Using this universal basis, crystalline compounds of carbon nitride of variable compositions with properties similar or equal to those of diamonds have been produced in macroquantities [48].

The performed study significantly facilitates and simplifies the search of novel glasslike materials and extends the possibilities of their practical application in different fields of science and technology.

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