

Flexibility of structure as a criterion of glass formation and stability

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Flexibility of structure and internal factors which prevent the ordering of structure randomness, as the indispensable condition of existence of the kinetically stable glasses, have been indicated. Based on the analysis of atomic interactions in solid structures, criteria of the formation of glass of different chemistry, including metallic and molecular glasses, are formulated.

1. Introduction

The structure, the obtaining and properties of glass continue to be the subject of interest of researchers, with the description and interpretation of the various aspects of vitreous state being specific to the particular discipline. Recent decades have been marked by rapid development of the knowledge of inorganic glasses, their properties and structure. New glass forming systems continue to be elaborated. The list of modern technical glasses includes, besides traditional oxide glasses (silica glass, silicate, borosilicate, borate, and phosphate glasses) aluminate glasses, heavy metal glasses, *etc.* A variety of halide and chalcogenide glasses are produced, and several elements (Si, Se, S, Ge, C and others) and metallic alloys in vitreous state (metallic glasses) have technical application. In the structure of glass chemically different species (oxides, nitride, carbides, halides, chalcogenides) can bind join together in the common network (mixed network glasses). Mixtures of ionic salts (sulfides, chlorides, nitrides, chromides, *etc.*) can be vitrified. Lately, organic compounds, built of molecules bond by Van der Waals interactions, have been vitrified by the mechanical alloying procedure [1]. One can see that a kinetic stable vitreous state can be obtained by substances chemically different, with different chemical bonds in their structure.

Problems concerning the formation and stability of inorganic glasses, considered from the point of view of the structural chemistry of solids, are subject of the present study.

The modern concept of the structure of glass is based on the theory of Zachariasen and Warren, which was formulated at the beginning of the 20th century, mainly using data on silicate glasses. According to this model, known as a random network model, glass structure has the character of a continuous network exhibiting only short range ordering, limited to the individual structural elements (coordination polyhedra). It is formed through polymerisation of tetrahedra (silicate, borate,

phosphate glasses) and less frequently triangles (certain borate glasses) or other polyhedra. These polyhedra are formed by cations (Si^{4+} , B^{3+} , P^{5+}) or other elements, known as network formers, which are surrounded by anions (O^{2-} , F^- or others). The polyhedra are joined vertices by common anion (bridging anion). In polycomponent glasses some bonds between the network polyhedra are broken by univalent or bivalent cations—modifiers.

This model is now not adequate enough to explain the structure many modern glasses. Lately, random array picture of glass structure, as a generalized form of the random network model has been formulated. According to this formula, glass is an X-ray amorphous solid, the structure of which consists of randomly arranged elements, and no unit of structure is repeated at regular intervals in three dimensions. However, the formula is too general to have practical application in the glass formation study.

Flexibility of structure and existence of some factors stabilising structure randomness as indispensable criteria of glass formation and stability are postulated in this paper.

In inorganic chemistry Pauling's electronegativity and ionicity values are universally accepted as standardised characteristics of chemical bonds and interactions between atoms of elements. The ionicity of bonds in the glass structure has been used here as a semi-quantitative indicator of the flexibility of the structure. An increase in the proportion of the non-directional ionic bond means an increase of its flexibility. Increasing covalence makes the chemical bond more rigid, but simultaneously increases its strength.

At present, the computer molecular dynamic simulation (MDS) of glass structure finds increasing application. The interatomic potentials used in the calculation are generally based on the Born model of solid, which includes a long-range Coulombic interaction, and short-range repulsion between electron charge clouds and the Van der Waals dispersive interaction [2]. It enables us to determine the distribution of the glass components in space. So far, structures that have been most thoroughly studied are those of relatively simple composition. Prediction of the kinetic stability of glass structure or its devitrification process is still out of the MDS procedure capability.

For better recognition of the regularities governing the processes of glass formation and crystallisation, especially of complex network glasses, analysis of the local atomic interactions is proposed in this study. The analysis of local atomic interactions of glass structure components is based on the simplified parameters, characterising their bonds and chemical affinity. It helps to predict the stability of glass and glass devitrification mechanism.

2. Glass as a solid of flexible structure

Solid bodies, both crystalline and amorphous, possess a property which can be described as the flexibility of internal structure. The physicochemical manifestation of the flexibility of the internal structure of solid may be, as assumed in the present

paper, the freedom of the displacement of the structure forming elements (atoms, ions, coordination polyhedra) without disturbing the continuity of the structure as a whole [3].

The structure is made flexible by the non-directional chemical bonds (ionic, metallic, van der Waals), and by the elastic anion bridges between the coordination polyhedra in polymeric structures and the like. Strong, covalent, directional bonds make the structure rigid.

The existence of kinetically stable amorphous structure, topologically disordered and especially the ability of many substances to assume the glassy form, may be treated as a consequence of sufficient flexibility of their structure. Similarly, a relatively easy amorphisation of certain crystalline bodies by grinding or heat treatment is possible when their structure is flexible enough.

It has been assumed that glasses are solid bodies possessing considerable flexibility of structure as a factor indispensable for the glass structure to maintain its topological disorder.

In the structure of an ideal crystal, atoms occupy the positions in the nodes of the crystal lattice which are the points of the equilibrium of forces operating between the atoms forming the given structure. Owing to this, an ideal crystalline structure is free from internal strains. In an amorphous structure, devoid of the crystallographic ordering, this equilibrium is disturbed. This fact must induce the occurrence of strains inside the structure. If they are strong enough, they will break the bonds in the structure, which will enable the ordering of its elements and the crystallisation of amorphous substance. If the amorphous structure possesses sufficient flexibility, relaxation of these strains or their reduction below the critical value may occur through rotation of the coordination polyhedra around the bridging oxygen bonds linking them, or through displacements of the structure elements without disturbing its continuity. The relaxation of the flexible amorphous structure manifests itself as the glass transformation effect, which is a characteristic feature of glassy state of solids [3]. Such an amorphous structure has considerable kinetic stability and its crystallisation ability is minimal.

The flexibility of the glass of polymeric structure is due to the freedom of changing the angle of bonds between the network former tetrahedra. In silicates the angle of Si—O—Si bonds may change in the range 125–165°, in phosphate the P—O—P bond varies in the range 123–180°; a considerable freedom of change of the angle of B—O—B bond is observed in boron-oxygen rings in the structure of borates. The above substances possess particularly strong glass forming properties.

The tetrahedral configuration of oxygen atoms in oxide glasses seems to be the preferred one, as the oxygen bridges between the tetrahedra guarantee the necessary flexibility of the glass network. Transition of components from crystalline to glassy state is often accompanied by change of the coordination number (CN) from 6 to 4. Compounds containing $[\text{SiO}_6]$ groups (SiP_2O_7 or $\text{K}_2\text{Si}_4\text{O}_9$) are the example.

The flexibility of structure of the oxide glasses also results from the possibility of obtaining various CNs in relation to oxygen by some of the glass components, in particular Si (CN 4, 6), B (CN 3, 4), Al (CN 4, 5, 6). Lead, besides varying CN (4, 6), is also characterized by the ability of deforming the coordination polyhedra.

However, a number of glasses have nonpolymeric structure. Some of them are made of halides or oxides with small dispersed islands of coordination polyhedra of other components. There belong the superionic, conducting glasses, based on silver halides and P_2O_5 , B_2O_3 , SiO_2 clusters as admixtures stabilising random glass structure. Vanadium borophosphate glasses (70–90 wt% V_2O_5) have probably a similar structure. Structure of these glasses is described by “a cluster and tissue pseudophase model” [4].

The model of a continuous homogeneous, polymeric structure of glass and the cluster and tissue pseudophase model represent extreme cases. The structure of the real glass has an intermediate character, depending on the chemical composition of glass and the mode of its formation.

Taking into account the statements considered above, the chemical-structural criteria of glass existence and glass formation ability are:

1. Flexibility of structure to a degree allowing the component elements (atoms, cations, coordination polyhedra) to take various positions with respect to each other, free from long-range ordering, without simultaneously inducing strains able to break it. The relaxation transformation of the glassy state (glass transition) is the consequence of structure flexibility, and it is its indicator.

2. The operation of agents stabilising the state of topological disorder of the structure and preventing its ordering under the influence of external factors (crystallisation) such as polymeric network with elastic but sufficiently strong bonds, admixtures or structural inhomogeneities in non-polymeric glasses.

The surface of solid can also be a vitreous state stabiliser for thin layers (Pb–Bi surface layers, obtained by hydrogen reducing Pb, Bi silicate glass [5]) or glassy coatings.

Chemical interactions between glass components are known to be of acid-base character [6]. The oxygen atoms in glasses behave as Lewis' bases and transfer part of their negative charge to the cations. The ability of oxygen to transfer the negative charges is the greatest when it is situated in the surroundings of weak cations such as the alkalis. When oxygen is fixed with strong bonds, as in the $[SiO_4]$ or other network-former tetrahedra, its basicity is lower and the possibility of transferring part of the charge to the metal cation is also smaller. Acid-base interactions and chemical affinity should determine the distribution of components in the structure of glass and at the same time the formation of chemical inhomogeneities (clusters). Their existence is possible if the amorphous structure is flexible enough.

Accordingly, glass can be considered as an amorphous solid body of flexible internal structure with stabilised disorder. The construction and the degree of inhomogeneity of the internal structure depend on the chemical composition and the history of glass – model of flexible disordered structure.

This definition includes criteria indispensable for kinetically stable glass formation, comprising all well known particular criteria which have so far been considered as a necessary condition for the existence of this form of solid. Moreover, it explains the ability of metal alloys to form metallic glasses as well as halide-oxide and other nonpolymeric glasses formation.

3. Local atoms interaction and glass structure stability

Temperature and extent of devitrification process are the indicators of the glass structure stability. In the crystallisation process, especially at a temperature close to T_g , i.e., in the state of a rigid body, and in the visco-elastic state of glass, the role of atomic interactions in the glass structure is very distinct [7]. For better understanding of these glasses of polymeric network, built of the tetrahedra $[\text{SiO}_4]$, $[\text{AlO}_4]$, $[\text{PO}_4]$ and $[\text{BO}_4]$ in various quantitative proportions (mixed network glasses) have been studied. These tetrahedra are of similar dimensions, but differ in strength and ionicity of the central cation-oxygen bonds and, as a consequence, the ionicity, the strength and flexibility of oxygen bridges in the glass network. The cations-modifiers are Na^+ , Ca^{2+} and Mg^{2+} , whose oxygen bonds also differ in ionicity. The glasses under examination belong to the system $\text{Na}_2\text{O}-\text{CaO}(\text{MgO})-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ and $\text{AlPO}_4-\text{BPO}_4-\text{SiO}_2$.

Crystallisation of glasses under study has a multi-stage course and proceeds through formation of the intermediate metastable phases, while the phase composition corresponding to the equilibrium state is not attained until the liquidus temperature is reached.

Bulk crystallisation of glasses in the Na_2O (10 mol%)- MgO (20 mol%)- $\text{AlPO}_4-\text{SiO}_2$ system starts near the glass transformation temperature (650 °C) and aggregates of small rounded grains of AlPO_4 -cristobalite modification are formed. At a slightly higher temperature needles of $\text{Mg}_3(\text{PO}_4)_2$ crystallise. Above the glass softening temperature (about 900 °C), $\text{Mg}_3(\text{PO}_4)_2$ crystals dissolve in the glassy matrix and AlPO_4 recrystallises into well-shaped dendritic crystals. Glass containing more Al_2O_3 than the corresponding AlPO_4 formula, crystallises with the formation of corundum (Al_2O_3) and $\text{Mg}_3(\text{PO}_4)_2$ crystals in a glassy matrix.

Partial substitution of MgO by CaO changes the crystallisation order. For example, glass containing $8\text{Na}_2\text{O} \cdot 8\text{MgO} \cdot 9\text{CaO} \cdot 20\text{Al}_2\text{O}_3 \cdot 17\text{P}_2\text{O}_5 \cdot 38\text{SiO}_2$ (mol%) crystallises above 650 °C (T_g) AlPO_4 , and $\text{Ca}_3(\text{PO}_4)_2$ and next $\text{Ca}_7\text{Mg}_2\text{P}_6\text{O}_{24}$ are formed. Above the glass softening point (900 °C) Ca , Mg -phosphate disappears, AlPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ recrystallise.

Glasses from the K_2O (10 wt%)- CaO (20 wt%)- $\text{MgO}_x-\text{SiO}_{2y}-\text{P}_2\text{O}_5$ (15–20 wt%) system start to crystallise at the glass transition temperature and Ca phosphate (whitlockite or apatite) is formed first. Forsterite (Mg_2SiO_4) crystallises next. Afterwards, above the softening temperature, kaliophillite (KAlSiO_4) crystallises in the glassy matrix.

In inorganic chemistry Pauling's electronegativity and ionicity values are universally accepted as standardised characteristics of bonds and chemical interactions of atoms. A similar factor characterising crystallochemical properties of cations and atoms has been introduced by Görlich. This is the effective nuclear charge of atomic core, defined as $Z_{\text{eff}} = \sqrt{I'_v}$, where I'_v is the ionisation energy in the Rydberg units, needed to remove the v valence electrons from an atom. Its values are closely related to Pauling's electronegativity. The effective nuclear charges of atomic cores order chemical elements according to the specific character of their homeo-

polar bonds [8], [9]. The relative difference of the nuclear charge of the two bonding atoms constitutes the factor determining the ionicity of the heteropolar bond. The ionicity i_G or asymmetry of the chemical bonds between different atomic cores or cations is measured by the relation $i = 1 - Z_{\text{eff}1}/Z_{\text{eff}2}$, where $Z_{\text{eff}1} < Z_{\text{eff}2}$. Intrinsic affinity between two different atoms forming a heteronuclear compound is directly connected with the value of ionicity of a chemical bond [9].

The Z_{eff} and i_G values are a direct measure of the Lewis acidity of atoms and cations [8], [9], the higher the Z_{eff} , the higher the Lewis acidity. These values can serve for comparison at they are changing proportionally in different chemical structures (see Table).

Table. Ionicity of chemical bonds and oxygen bridges.

Cation-oxygen bonds			
	L	i_G	i_p
Na-O	1.400	0.807	0.832
Ca-O	1.725	0.707	0.794
Mg-O	1.830	0.670	0.712
Al-O	2.147	0.546	0.603
B-O	2.307	0.476	0.535
Si-O	2.410	0.428	0.488
P-O	2.640	0.314	0.350
Oxygen bridges			
	ΔL	i_G	Δi_G
Na-O-P	1.240	0.560	0.493
Ca-O-P	0.925	0.510	0.393
Mg-O-P	0.810	0.492	0.293
Al-O-P	0.493	0.430	0.232
B-O-P	0.303	0.395	0.162
Si-O-P	0.230	0.377	0.114
P-O-P	0.000	0.314	0.000
Na-O-Si	1.010	0.617	0.379
Ca-O-Si	0.685	0.567	0.279
Mg-O-Si	0.580	0.549	0.179
Al-O-Si	0.263	0.487	0.121
B-O-Si	0.103	0.452	0.048
Si-O-Si	0.000	0.428	0.000
P-O-Si	-0.230	0.377	0.114

In the present study, the ionicity value of bonds of the component atoms with oxygen i_G has been applied as a parameter characterising the strength of the bonds. It increases with decreasing ionicity. Another parameter is the "localisation of the bonding electron" $L = \bar{Z}_{\text{eff}} = \sqrt{Z_{\text{eff}1} \cdot Z_{\text{eff}2}}$ [9]. Its value increases with the covalence of bonds with oxygen. This parameter has been accepted as a measure of the rigidity of bonds.

In the present paper, on the other hand, the values i_G and L proposed by Görlich, have been used as a measure of both strength, flexibility and acid-base interaction on a local scale, with reference to individual bonds in the structure of glass. An increase

in the proportion of non-directional ionic bonds means an increase of the structure flexibility. Increasing covalence of chemical bonds makes the structure more rigid, but simultaneously increase its strength. Ionicity of modifiers of the silicate glasses decreases in the following order: $K > Na > Ca > Mg$. Network formers have ionicity below 0.500, which decreases in the direction $Al > B > Si > P$ (see Tab.).

The stability of polymeric structure of oxide glasses is determined by the oxygen bridges. As a measure of strength of oxygen it is proposed to accept the difference in the value of i_G of the bonds of cations with the oxygen linking them. The difference in the value L between these bonds (ΔL) is a measure of the rigidity of oxygen bridge. The difference in the i_G values (Δi_G) also supplies information in this case.

Pauling's ionicity of bonds with oxygen of the glass components has been used by BALTA [10] to calculate the value of basicity of the glass as a whole, depending on its composition.

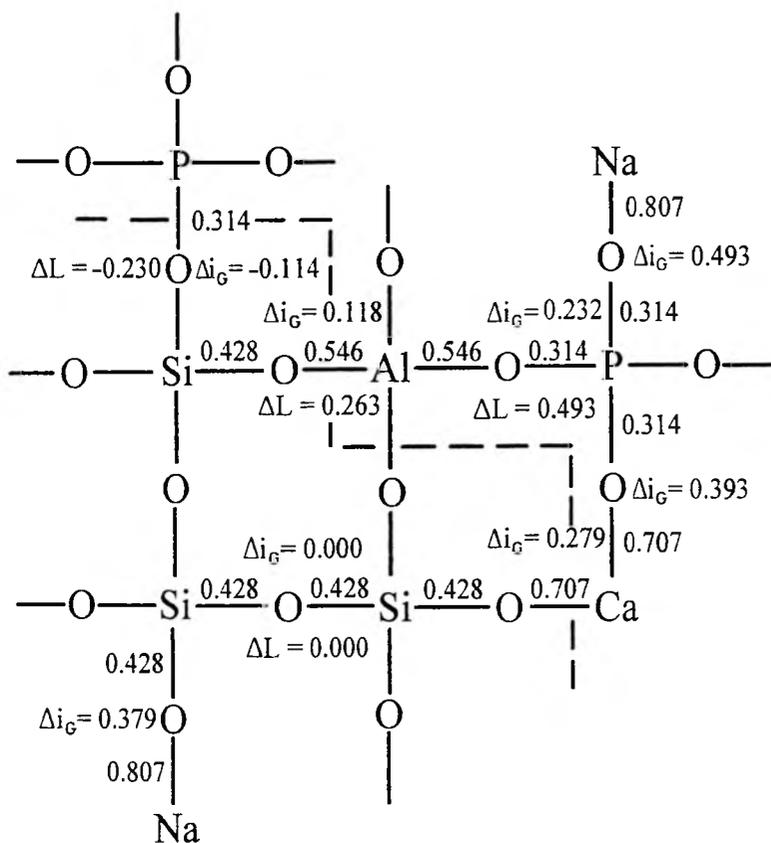
According to [8], [9], in this study difference in ionicity of bonds Δi_G in the oxygen bridge determines the degree of local chemical affinity to the oxygen of the joined cations and acid-base interactions in the bridge.

In the glass network built of the tetrahedra $[SiO_4]$, $[AlO_4]$ and $[PO_4]$ there appear bonds differing considerably in their ionicity. This refers in particular to Si-O bonds ($i_G = 0.428$, $L = 2.410$) and P-O bonds ($i_G = 0.314$, $L = 2.640$). Such a great difference in the ionicity of bonds, which are rigid due to the high degree of covalence ($L > 2.100$), and acidic character of both components are responsible for the fact that in the oxygen bonds joining both tetrahedra there will appear considerable strains, which makes the bonds breakable. That is why glasses with a two-component network $SiO_2-P_2O_5$ are unstable and Si takes in these glasses the coordination VI with regard to oxygen, which imparts the basic character Si-O bonds in such an octahedron. So, it functions as a modifier with regard to the phosphate.

An earlier FTIR study [11] revealed that introduction of aluminium to phosphate glasses eliminates the P=O bonds and Si-O-P bridges are replaced by Al-O-P bridges. The more basic $[AlO_4]$ ($i_G = 0.546$) and the acidic $[SiO_4]$ ($i_G = 0.428$) and $[PO_4]$ ($i_G = 0.314$) form bonds in accordance with their chemical affinity ($\Delta i_G = 0.118$). There are formed then relatively stable links of $[PO_4]$ and $[SiO_4]$ tetrahedra by means of $[AlO_4]$. The oxygen bridges Al-O-Si and Al-O-P formed then have their bonds differing less than those in the Si-O-P bridge (see Figure). However, a certain asymmetry of the bond is still retained, which results from stronger acid-base interaction within the Al-O-P bridge ($\Delta i_G = 0.232$) in comparison with Al-O-P bridge ($\Delta i_G = 0.118$). The latter, on account of a weaker Al-O bond in comparison with that appearing in the Al-O-P bond is easier to break. Due to this, the groups $[AlO_4]$, $[PO_4]$ can be released from the silicate network and the crystallisation of $AlPO_4$ takes place already near T_g , when the glass is still in the visco-elastic state.

Moreover, it follows from the above data that elements differing in their chemical properties and in the nature of bonds, such as SiO_2 and P_2O_5 , to an

extent excluding the existence of common bonds between their polyhedra, may together create a common glass network when there occurs besides them a component able to join simultaneously with both of these elements. An example is Al_2O_3 .



Local atomic interactions in phosphate-aluminosilicate glasses.

The breaking of the more strained bonds, release of aluminium phosphate domains of the network enables a simultaneous formation of crystalline calcium or calcium-magnesium phosphates. The chemical affinity of CaO to P_2O_5 , expressed as the difference in ionicity of the bonds with oxygen ($\Delta i_G = 0.456$) is much greater than for SiO_2 ($\Delta i_G = 0.279$) and the bonds in oxygen bridges are correspondingly stronger.

The behaviour of sodium is characteristic; binding with silica it forms unusually stable glassy phase which crystallises with difficulty. Its stability can be attributed to great flexibility of structure, and the strong acid-base interactions most probably strengthen the Na-O-Si bond. That is why in the glasses examined there is always left a glassy alkalis containing silicate matrix, not recrystallised.

4. Summary

Choosing properly chemical components able to give the solid structure indispensable flexibility, as well as component the structural position of which prevents ordering of the topological randomness of component distribution and introducing component joining chemically antagonistic elements, it is possible to obtain a variety of glasses of the original compositions and properties.

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