Structure and Crystallization of Multicomponent Glasses

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Abstract

Specificity of structure of inorganic glasses of complex chemical composition is discussed and structural mechanism of their crystallization considered. Recent data indicate that for a glassy state to exist the glass network must possess enough elasticity to enable the network-forming elements to occupy varying positions and adjust each other to a degree sufficient to give their arrangement the character of a random array. Agents must also operate to stabilize these random arrangements.

Conditions for the formation of glasses of a mixed polymeric network, which are composed of chemical components differing in their properties and in the nature of their chemical bonds to the degree of excluding the creation of direct bonds between them, are presented. They exist when a buffer component able to join together the unbound components is introduced.

Glasses of a non-polymeric structure (halide-oxide glasses) consist of a random matrix stuffed with small groups of polyhedra which prevent the ordering of the matrix and crystallization. Some admixtures may play a similar role (ionic salt glasses).

Heterogeneous transformations in solids may proceed in a diffusionless way by correlated displacements of whole blocks of atoms (polymorphic transformations of martensitic type) or diffusional translations of individual atoms at longer distances (processes with considerable changes in the chemical composition). These mechanisms as well as mixed, i.e., diffusionless (anion sublattice rebuilding) and diffusion (change in cation positions) mechanisms are applied in order to explain the successive stages of the crystallization of glasses of the composed chemical composition at temperatures not far from the glass transformation (Tg) point.

1. Introduction

Inorganic glasses belong to materials of particularly wide application and are being indispensable in many fields of modern technology. The advantage of these materials is that their properties may be changed and controlled by suitable modification in their chemical composition. Research on glasses of new chemical compositions and functional properties have been done for a long time. Nevertheless, glasses made up of new sets of chemical elements and possessing new properties are still being discovered.

The amount of information on glasses and their properties is growing rapidly but knowledge on their structures and the conditions necessary for formation of a glassy state is still inadequate. Current views on the structure of glass do not account for many properties of glass, especially those of the new generation. They are also of little use in designing new glasses. This refers in particular to glasses of composed, unconventional chemical composition.

It is possible to induce rebuilding of glass structure and initiate bulk crystallization through suitable heat treatment at a temperature close to the glass' transformation point where glass still retains the features of a solid body. Glass-ceramic materials of a micro-crystalline character are obtained in this way. These materials have much more advantageous properties than the parent glasses and find numerous applications, particularly as special structural materials and in electronics. Bioactive glass-ceramic materials are used as implants in surgery and dental prosthetic. Ceramic high-temperature superconductors can be produced with the glass-ceramic technique.

The processes of crystallization of glasses often proceed in several stages and crystal phases formed as well as the sequence of their formation depend on the structure of the precursor glass. These phenomena can hardly be explained by means of the traditional theory of nucleation and growth. This theory actually refers to the crystallization of liquids and explains well crystallization of molten glasses or, in this case, high values for the diffusion coefficients of components of the compound crystallizing in a solid state.

In the present study, the specificity of the structure of complex chemical composition glasses is discussed and the structural mechanism of their crystallization considered in light of the author's own investigations and recent data available in current literature. The interpreta-
tion of certain phenomena given here occasionally differs from the currently accepted views but it seems to be more adequate to explain the stability and mode of crystallization of some glasses, especially unconventional ones.

In view of various applications of glasses and glass-ceramic materials, their crystallization is now important to technological processes of wide application.

2. Glassy State of Matter

Solid bodies exist in a crystal or in an amorphous form. The ability to easily take and retain the amorphous form is only possessed by some solids. Their number, however, is rapidly growing with advances in the chemistry and physics of solids. The structure of many amorphous substances, on the other hand, can be seen as a combination of coordination polyhedra similar to those occurring in crystalline bodies of related chemical composition. The distribution of these polyhedra and their mutual orientation, however, does not have the geometric repeatability in three directions characteristic of a crystal lattice.

Several substances, namely, glass, gels and solids, which were rendered amorphous by solid state transformation of crystal forms through subjection to the action of some external energy (temperature, pressure shock, radiation, mechanical energy) belong to the group of amorphous solids.

Gels are formed as a result of chemical polymerization processes in solutions. They usually have a microporous structure. Thermal decomposition of certain substances, especially silicates, borates and phosphates, is followed by the destruction of their primary structure. The decomposition products of many of them are amorphous /1/. Metamictic mineral (zircon) are substances rendered amorphous by natural high energy radiation whereas so-called diaplectic minerals are the effect of amorphisation under the action of a pressure shock induced, for example, by the impact of a meteorite. Similar amorphisation methods are applied at present under laboratory and industrial conditions. The degree of degradation of the crystal structure to an amorphous one may vary. An amorphous substance formed by the destruction of the crystalline structure of the precursor may have retained the elements of the original structure which show ordering in one or two crystallographic directions. The amorphous products of the thermal dehydroxylation of layer silicates are an example /2/.

Inorganic glasses are amorphous substances which until recently were obtained through appropriate cooling of the liquid. The destruction of the primary crystal structure of the raw materials from which they are produced is then attained by melting them. Cooling freezes the disorder structure of the liquid.

At present, glasses are also produced by gelling metal oxaloholates solutions and heat treatment of the obtained gels. The glassy layers are obtained by condensation of vapours on various substrates, sputtering, ion implantation, surface oxidation of mono-crystals, etc.

To date no precise definition of glass exists which describes its specificity. In earlier definitions, the fundamental criterion for glass is its origin as an amorphous solid formed through supercooling of liquid. In view of other glass formation procedures known at present, these definitions are no longer valid.

The characteristic feature which distinguishes glass from other amorphous substances is their uniformity and isotropy of macroscopic features. The uniformity differs in glass and amorphous microporous products of thermal amorphisation of solids (dehydroxylated layer silicates and borates) and so-called dry gel and glass obtained from it in the sol-gel glass manufacturing procedure. The effect of the high uniformity of glasses is transmittance of visible or IR and UV light.

Hence glass is a uniform solid body of isotropic macroscopic features, the structure of which is made up of coordinated polyhedra and occasionally of their complexes arranged in a disordered mode so that the given element of the glass structure does not occur again at the same intervals in three directions in space.

Glass perceived in this way will be the subject of further consideration.
A. Structure of Inorganic Glasses

The modern concept of the structure of glass is based on the theory of Zachariasen and Warren, which was based on the crystallo-chemical criteria of a glassy state formulated by Goldschmidt. The theory was created at the beginning of the twentieth century mainly using data on silicate glasses.

According to this theory, glass structure has the character of a continuous network exhibiting only short-range ordering ("random network" model). It is formed through polymerization of tetrahedra (silicate, borate and phosphate glasses) and less frequently triangles (certain borate glasses) or other polyhedra. These polyhedra are formed by cations of Si, B, P or other elements, which are known as the network formers, and are surrounded by anions (O\textsuperscript{2-}, F\textsuperscript{−} or others). The polyhedra are joined vertices by means of common anions (bridging anions). Linking of network polyhedra by common edges or faces is less frequent.

A more modern and generalized form of this model, which takes into account elements greater than a single polyhedron, is known as the "random array" model.

According to this theory and current prevailing opinions, the existence and stability of glass is governed by the components forming its network - network formers. The cation-anion bonds within the network are usually stronger than the bonds between the anions and cations located outside the network-forming polyhedra. In oxide glasses, the network-forming components are, for example, B\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, P\textsubscript{2}O\textsubscript{5}, As\textsubscript{2}O\textsubscript{3}. They may form glass by themselves or with the participation of other components /3/.

A large group of substances exists which, in a pure state, do not form glass; however, the substances attain glass-forming ability together with other chemical components. They are referred to as transition or intermediate glass components. Some substances which belong to this group are Al, Ti, Zn, Cd, Pb, Be, Zr oxides. Molten Al\textsubscript{2}O\textsubscript{3} crystallizes very easily whereas it participates in the formation of the network substituting silica in silicate glasses. Al\textsubscript{2}O\textsubscript{3} forms glass in the presence of alkaline earths elements. The range of chemical composition of such aluminate glasses is narrow.

In the CaO-Al\textsubscript{2}O\textsubscript{3} system, it is restricted to the region adjoining the eutectics between 5CaO 3Al\textsubscript{2}O\textsubscript{3} and CaO Al\textsubscript{2}O\textsubscript{3}. Pure PbO does not form glass either; it occurs, however, as the main component in many glasses. In the SiO\textsubscript{2}-PbO system, the range of glasses reaches 90 mol.% of PbO. When the PbO content is greater than 40 mol.%, it becomes a network-forming component.

Components defined as modifiers occur in glasses made up of more than one component. They occupy positions outside the coordination polyhedra of the network. Their presence modifies the network structure and properties of the glass. In oxide glasses, the modifiers are most often alkalies and alkaline earths oxides. This role may also be performed by intermediate components depending on their content and on the chemical composition of the glass (PbO below 40 mol.%).

Introduction of modifiers usually leads to depolymerization of the network and its weakening. The degree of depolymerization depends on the chemical properties of the modifier and on its function in the structure. Weakening of the bonds leads to a decrease in the softening temperature of the glass and a diminishing in its viscosity. The physical and chemical properties of glass undergo changes depending on the kind, valency and concentration of the modifier as well as on the network formers. The Ca\textsuperscript{2+} included traditionally in the modifiers radically increases the melting temperature, chemical durability and other properties of P\textsubscript{2}O\textsubscript{5} glass.

The modifiers usually reduce the ability of glass to crystallize. However, when the degree of network depolymerization exceeds the admissible value, the tendency for crystallization increases rapidly. Melted silicates with a composition close to Na\textsubscript{4}SiO\textsubscript{4} easily crystallize. In this compound's structure, only isolated tetrahedra SiO\textsubscript{4} occur, and the concentration of Na\textsubscript{2}O is already too high to permit polymerization.

The search for a universal criterion in glass-forming ability in order to predict which substances will form glasses under standard vitrification conditions has been carried out for a long time. Attention has been given mainly to the chemical bonds in the structure or properties connected with them (acid-base theory of oxide
glasses /4/) as the factors determining the glass-forming possibilities of the substances. Smekal /5/, for example, supposed that mixed bonds are a necessary condition for the existence of glass. Glass-forming oxides have ionic-covalent bonds; in chalcogenide glasses covalent bonds occur inside the chains and Van der Waals bonds between them. However, at present, glasses are known to exist with purely ionic bonds (halide glasses) and with virtually all other types of bonds and their various combinations. This as well as many other criteria of glassy state formation appear to be relatively useful. So far it has not been possible to find such a universal criterion.

With the accumulation of data regarding the properties of glass, it was noticed that the curves of the dependence of some properties of glass on their chemical composition change their character at certain points. These often correspond to the boundaries of the fields of existence of some definite phases on the responsible diagram of the phase equilibria or to the points of composition of compounds /6,7/. Attention has been directed to the fact that a change in the refraction index or other structurally sensitive properties of two-component glasses rich in SiO₂ show inflection within the temperature range of the polymorphic transformation of cristobalite /6,8/.

The above phenomena can be explained assuming that in the glass structure there exist regions with chemical compositions and structures close to those of appropriate crystal substances. Accordingly, the glass micro-structure would not be uniform to a greater or smaller degree. Modern research methods (IR and Raman spectroscopy, XANS, EXAFS, etc.) have confirmed the non-uniform character of the glass structure. It is conceived to be made up of clusters of the structure similar but not very close to the proper crystal phase /9/. They are thought to be separated by interfacial surfaces saturated with non-bridging oxygens. Hence, they represent real surfaces similar to the boundaries of crystal grains. While stabilizing the amorphous state, the existence of these surfaces makes crystallization difficult. Stresses exist along the clusters' boundaries which are responsible for the fact that the network bridges break easier than those inside the domains. That is why glass has a wide softening range.

It has been found that chemical components are not distributed uniformly in glass. Sodium and lithium cations occur in pairs beside non-bridging oxides. They accumulate around the clusters' boundaries /10/. The nonuniform distribution of alkalis leads to phase separation in sodium silicate glass (spinoidal decomposition).

In aluminosilicate glasses, a step-like change in the index of refraction when the Al/Na ratio is greater than 1 takes place, which means that the amount of sodium is insufficient to compensate for the deficiency of the positive charge induced by the substituting Al³⁺ for Si⁴⁺. Lucy /11/ attributes this to the existence of triclusters formed as a result of binding three tetrahedra SiO₄ and AlO₄ instead of two by one oxygen atom. Similar triple groups, (Al, Si)₃O₁₀, are found in the structure of mullite.

The concepts of a continuous uniform glass network, of clusters' structures and also of a chemically nonuniform structure in complex glasses do not represent any dichotomy. They express the different aspects of the glassy state of substances, not excluding each other. Glass with continuous and uniform network and glass made up of clusters with distinct internal interfacial surfaces should be regarded as extreme, theoretical cases, in between which exists a number of real glass structures of intermediate character.

Data on the structure of other amorphous substances are less accurate. Models of the internal structure of glass developed so far may be extended to include these substances.

B. Mixed Network Glasses

The majority of data collected so far on glass structure and its effect on glass properties refers to glasses of relatively simple composition. These usually contain one or two components forming the network, while the proportion of eventual other network formers is rather small. The effect of network components on glass properties is little known, where many of them are present. Introducing appropriately chosen components into the network extends the possibilities of modifying glass properties and crystallization ability through their chem-
The effect of the structure and composition of the network on glass properties becomes distinctly visible when one of the glass components, which does not participate in the network formation due to a change in the chemical composition of the glass, becomes a network former or vice versa. Then, a jump-like change in the composition-property appears on the curves, usually referred to as an anomaly. The aluminum anomaly is particularly well known.

Oxynitride glasses with a network formed of \( \text{SiO}_4 \) tetrahedra, of which some contain N instead of oxygen in one of the vertices \( /12/ \), have distinctly different properties compared to similar silicate glasses.

It is proposed that the term glasses of mixed network be used when referring to glasses whose network is made of two or more different chemical components (in the sense used for the component in the phase rule) or when the same component is incorporated into the network in the form of various coordination polyhedra (triangles, tetrahedra, etc.) or as differently built molecules.

Information on the conditions which must be satis-
fied to obtain glasses of mixed network has been supplied by recent investigations on some glass-forming systems, especially the Na O-CaO-Al2O3-P2O5-SiO2 glasses /13,14/. Their networks are made up of the tetrahedra SiO4, AlO4 and PO4. Stable glasses, whose networks are built of these three tetrahedra, can be formed only when suitable proportions are maintained between the content of the network formers as well as those which are referred to as modifiers. The existence of mixed network glasses like these is evidence that the formation of stable glass may be the effect of joint interaction of all its chemical components.

Silica glass (V-SiO2) obtained by cooling of the melt accepts limited amounts of P2O5 in its structure (only SiO2-P2O5 glass films deposited by CVD across the whole composition range of this system may be obtained). In the PO4 tetrahedra, one oxygen forms a double P = O bond, and it is not able to bind with Si. Hence, introducing P2O5 to V-SiO2 leads to an increase in the non-bridging oxygen content which, on the one hand, rapidly reduces the softening temperature but, on the other hand, reduces the range of homogeneous glasses in the SiO2-P2O5 system.

The alkalies and alkaline earth metals form bonds with oxygen leading to the disappearance of a double P = O bond /16/. Usually it is accompanied by an increase in the softening temperature of the P2O5 glass.

In crystalline silicates, substitution of Si4+ by P5+ is rare and only seen in structures with silicate anions of a low polymerization degree in the SiO4 tetrahedra (garnets, olivines, pyroxenes) and those containing Al /16,17/. These are the substances in which complex silicate anions possess a possibly great number of non-bridging oxygens.

In glasses of the SiO2-P2O5 system, SiP2O7 polymorphs crystallize. Structural data show /18/ that in this compound structure all Si atoms are octahedrally coordinated and all P atoms are tetrahedrally coordinated by oxygen atoms. The phosphate tetrahedron shares one of the vertices with a second tetrahedron, thus forming diphosphate groups, P2O7, surrounded by SiO6 octahedra. All the oxygen atoms are twofold coordinated, bridging either two P atoms or one P and one Si atom. SiP2O7 glass has a structure significantly different from its crystalline polymorphs, possessing PO4 units with P = O bonds along with SiO4 units. The silicon coordination changes from 4 to 6 upon devitrification of this glass and devitrified sample contains cubic SiP2O7 crystals. The change in coordination of the Si atoms occurs due to the formation of more P-O-Si linkages at the expense of P = O bonds in the glass structure /19/.

It is supposed that binary phosphosilicate glasses of high P2O5 content have a random network consisting of i) Si atoms in fourfold coordination with oxygens, all of which are bridged; ii) only three of the four oxygens coordinating each P atom are bridged, the fourth remains as P = O; and iii) the bridging oxygens bridge a pair of silicon and/or P atoms, which are randomly distributed in the quasi-lattice /19/.

Raman spectra of glasses in the system Na2O-SiO2-P2O5 indicate that Si4+ ions do not substitute into P5+ sites even in low SiO2 concentration. No evidence was found of silicate structures having non-bridging oxygen ions, which implies segregation of non-bridging oxygen ions and Na+ ions into phosphate structures.

Silica forms a three-dimensional structure. The type of phosphate structure present in glass depends on the Na2O to P2O5 mol.% ratio. As the P2O5 content increases, the dimer phosphate (pyrophosphate) structure polymerizes into chains, followed by a cross-linked structure. Na2O associates mainly with P2O5 to form a sodium metaphosphate network while the silicate network retains its bridging structure. The non-bridging oxygen atoms are associated specifically with phosphate units /20,21/. All of these indicate that phosphosilicate glass have a mixed network composed of different structural elements joined by bridging oxygens.

Our investigation of the glass-forming ability in the Na2O-Al2O3-P2O5-SiO2 system /13,14/ has shown that at a normal cooling rate glass is formed when the Na2O content equals at least 15 mol.%. The glass region, however, is then very small. It increases quickly with the growing content of Na2O. When the Na2O content attains 30 mol.%, the glass region extends along the line connecting the points of the SiO2 and AlPO4, which are the main network components (Fig. 1, field D). It is assumed that glasses of this type have net-
works formed of the tetrahedra SiO$_4$ in between which pairs of AlO$_4$ and PO$_4$ tetrahedra become incorporated, replacing two SiO$_4$ tetrahedra. The isostructural nature of AlPO$_4$ and SiSiO$_4$ is responsible for the fact that such substitutions are possible.

It also follows from this investigation that glasses from the upper part of the glassy state field have aluminosilicate networks formed by SiO$_4$ tetrahedra, some of which is replaced by AlO$_4$ tetrahedra. The number of the latter is greater the higher the ratio of Al/P. Pairs of AlO$_4$ and PO$_4$ are incorporated into this network. The glass network in the lower part of the glassy state area is formed by pairs of AlO$_4$ and PO$_4$ tetrahedra in between which there are situated SiO$_4$ tetrahedra.

Segregation of chemical components occurs during cooling in melts. Where the composition of melt lies outside the glassy state area; it results in crystallization or liquation.

When Na$_2$O becomes entirely replaced by CaO in the glasses under consideration, the glass region undergoes considerable reduction (Fig. 1, fields A, B, C). The glass which is formed shows almost stoichiometric proportions of all the components corresponding to the formula CaO Al$_2$O$_3$ SiO$_2$ 2P$_2$O$_5$ or SiO$_2$ 2AlPO$_4$ Ca(PO$_3$)$_2$.

Replacing part of CaO by Na$_2$O extends the glass area in the direction of the SiO$_2$-P$_2$O$_5$ side, which implies increased participation of both these components in the glass network. Further reduction of the CaO proportion causes the expansion of this field in the direction of the Al$_2$O$_3$-SiO$_2$ and Al$_2$O$_3$-P$_2$O$_5$ sides, which means that the network may accept an appropriately greater number of the respective tetrahedra (Fig. 1).

The above relations can be accounted for as follows: sodium weakens the silica network, leading to its partial depolymerization. As has been found, this is the necessary condition for pairs of AlO$_4$ and PO$_4$ to become incorporated into the network. The presence of sodium is also a necessary condition for the incorporation of Al$^{3+}$ into the silica network and of its rebuilding into the aluminosilicate network according to the relation Na$^+$Al$^{3+}$[O$_{1/2}$]$_4$$^4$$^-$ = Si$^{4+}$[O$_{1/2}$]$_4$$^4$$^-$.

The PO$_4$ tetrahedra form bonds with the silicato- and oxygen tetrahedra on a limited scale. However, they may become bound with them easily through the AlO$_4$ tetrahedra, which were taken over by the network formed of SiO$_4$ tetrahedra (Fig. 2).

The bivalent Ca$^{2+}$ cation is able to form bonds through the bridging oxygens with all three types of tetrahedra occurring in the network. Thanks to this, it may join various elements in the network. On the other hand, its bonds with oxygen are stronger than those of sodium and the bivalent calcium seems to make the glass network more rigid and strained at the same time. This is probably why the presence of CaO restricts the region of the glass existence and makes the quantitative proportions of chemical components of glass very narrow.

Moreover, it follows from the above data that elements differing in their chemical properties and in the nature of their bonds with the network anions (with O$^2$- in the case under consideration) to an extent excluding the existence of common bonds between their polyhedra may together create a common glass network when there occurs beside them a component able to join simultaneously with all of these elements through the anion bridges. This component is thus a "buffer" glass network-forming component.

Metaphosphate glass has a structure built of long

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Fig. 2: Function of Al$^{3+}$ in the network of Na$_2$O-Al$_2$O$_3$-SiO$_2$-P$_2$O$_5$ glasses (non-uniform, continuous network).
chains constructed by PO₄ tetrahedra; network-modifiers are located between those chains. When some fluoride (for example NaF) is introduced into the glass, the P-O-P bonds are disrupted to form PO₃F tetrahedra and become the terminals of the metaphosphate chains. When the fluorine content increases (fluorophosphate glasses), PO₃F groups are gradually formed and the metaphosphate network is continuously disrupted. The glass structure is changed from metaphosphate to pyrophosphate /22/. Studies on glass formation in the Al(PO₃)₃-AlF₃-RF₂-R system (where R Ca, Sr, Ba, Mg, Li, Na, K) revealed that AlF₃ enlarges the glass formation range and increases stability and chemical durability of fluorophosphate glasses with low (15 - 10 mol.%) Al(PO₃)₃ content. It is supposed that AlF₄ tetrahedra reconnect the disrupted chains (Fig. 3), improving glass formation ability. MgF₂ and LiF play a similar role /22/.

For pure metaphosphate glass or fluorophosphate glass with high content of Al(PO₃)₃, the main crystallization products are metaphosphates, while for glass with low Al(PO₃)₃ content, the main crystallization products are pyrophosphates or AlF₃ and AlPO₄. The basic structural groups of metaphosphate glass are the same as those for the corresponding crystals, that is to say during crystallization the basic structural groups remain unchanged.

At present, glasses are known, the structure of which does not correspond to the traditional models. It is not possible to distinguish in their structure a network as one composed of polymerized polyhedra with strong bonds and weaker bound modifiers. Silicate glasses containing less than 50 mol.% of SiO₂ belong among others to this group. Only isolated silicon-oxygen tetrahedra or their groups each comprising several such tetrahedra (Fig. 4) may occur in these glasses. They are mutually bound through the alkalies and Ca, Ba or Sr into a three-dimensional structure since the content of SiO₂ is too small for a three-dimensional silicon-oxygen network to be formed. These glasses have been called "invert glasses" /23/.

Only isolated SiO₄ tetrahedra or Si₄O₁₂⁸⁻ rings and short chains of tetrahedra occur in the PbO - SiO₂ glass structure above 70 mol.% of PbO. They are incorporated in a lead-oxygen matrix formed by double chains made up of pyramids of PbO₃ joined with common edges. The remaining pyramids are joined with them in their vertices, and simultaneously their other vertices become linked with the SiO₄ tetrahedra /24,25/.

Fig. 3: Function of Al³⁺ in fluorophosphate glasses (non-uniform, discontinuous network).

Fig. 4: Scheme of the structure of "invert" glass /23/.
The elasticity of structural elements necessary for the formation of a random amorphous lead-oxygen matrix is due to the easy deformation of the lead-oxygen polyhedra and the change in the length of the Pb-O bonds.

A special type of structure is found in the superionic conducting glasses based on silver halides /26,27/. A large group of these glasses belongs to the AX-Ag2O-M$_x$O$_y$ system, where X = I, Br, J, and M$_x$O$_y$ represents P$_2$O$_5$, V$_2$O$_5$, As$_2$O$_5$, CrO$_3$, MoO$_3$, B$_2$O$_3$, SiO$_2$, and GeO$_2$. The structure of these glasses is made up of silver halides, among which are incorporated non-polymerized metal-oxygen tetrahedra of a proper oxide or complexes of several such tetrahedra (Fig. 5). In the case of glasses containing B$_2$O$_3$, these are complexes of triangles and tetrahedra, while germanium occurs in the form of GeO$_6$ octahedra. The Ag$^+$ ions surrounded by the halide ions contribute to the electrical charge conduction. Other Ag$^+$ ions form strong, partly covalent bonds with oxygens at the vertices of the polyhedra. Researchers examining these glasses suppose that the so-called glass-forming components are not contained in such glasses /26/.

Some ionic salts may form stable glasses (nitrite, sulfate, carbonate glasses). The regions of the glassy state are usually close to the nearest eutectic in the proper phase equilibria system. The tendency for vitrification is shown in systems of salts of these cations, where the field of strength does not differ more than 0.7 /28/. The salt systems are regarded as non-network glass-forming systems.

C. Elastic Network Model of Glass Structure

A strong polymeric network composed of so-called network-forming components, polyhedra and network modifiers, which usually have weaker cation-anion bonds and act as the depolymerizers of the network, was supposed for a long time to be indispensably necessary for the existence of multicomponent glass. However, as is now known, many modern glasses lack larger polymerized elements in their structure. Nevertheless, when describing their structures, researchers following tradition attempt to distinguish network-forming components and modifiers, regarding them as the indispensable attributes of a glassy state. If this does not prove feasible, they introduce the term non-network glasses. This inconsistency provides sufficient reason to revise the concept of the glass network and to search for an universal model of inorganic glass which would be more adequate to the structures of all the inorganic glasses examined so far. Therefore, it seems justified to extend the concept of a network to include also the structure of glasses which lack distinguishable large elements formed by polymerized polyhedra.

The glass network should be understood here as a spatial skeleton, made up of randomly distributed elements (atoms, ions, polyhedra, molecules or their complexes), which impart to the glass the features of a rigid solid body with isotropic macroscopic properties.

In this approach, the glass network becomes equivalent to the crystal lattice in crystalline solid bodies.

The uniformity of the glass network may be diverse, from almost completely uniform to a network of strongly pronounced cluster structures with distinct boundaries between the clusters and marked by deficiency of bridging bonds and increased concentration of voids. It
depends on the chemical composition of the glass and to a high degree on its origin and history. The glass-formation process (cooling of melt, gelification of solution, vapour deposition, etc.) determines the degree of dispersion of glass-forming components and then the homogeneity of their distribution in the structure of the glass. The non-uniformity of the glass network corresponds to the non-homogeneity and defectiveness of the structure of the real crystals.

Among glasses, the network of which contains polymerized elements, we can distinguish glasses with a uniform continuous network, besides glasses of a non-uniform network.

Glasses with a uniform continuous network are those which contain only one network-forming component, able to polymerize or in which the proportion of other components having such ability is rather small. Silicate glasses, some fluoride glasses, vitrified oxides, chalcogenides and some vitrified chemical elements are examples.

Borosilicate, aluminosilicate, aluminosilicate-phosphate and oxynitride glasses, etc. belong to the glasses with non-uniform continuous network. Their network is formed by polymerized polyhedra of different chemical compositions and different dimensions or shapes.

Glasses with non-uniform and non-continuous networks are those built of short polymerized elements in the form of chains, rings, etc. joined with each other by cations, usually bi- or trivalent (i.e., phosphate and fluorophosphate glasses and ZnCl₂-based halide glasses).

In glasses with non-uniform, discontinuous networks, the polymerized elements (chains, rings) are bound into a spatial structure by means of cations regarded as modifiers. The higher the valency of cations, the more durable are these glasses (vitreous P₂O₅ and CaO-P₂O₅ glasses). The smaller the difference between the strength of the bonds within the polymerized polyhedra and the bonds of the non-bridging anions of chains or rings with the modifiers, the less distinguishable are the structural functions of the components termed as network-formers and modifiers.

A separate class comprises glasses which have retained their amorphous state in spite of the absence of large, polymerized elements in their structure: non-polymeric network glasses. With reference to these glasses, the division into network-forming components and modifiers may be meaningless. One group in this class are the oxide "invert glasses" and the halide-oxide glasses, containing Ag and described earlier in this paper. Their structure consists of a matrix composed of appropriate simple oxides or halides, stuffed with tetrahedra or with small associations of silicate, phosphate or oxide (in halide-oxide glasses) tetrahedra (Figs. 4 and 5). The cation-anion bonds in these tetrahedra are stronger than in the matrix. They prevent the ordering of the matrix and its recrystallization and reinforce as well as stabilize the glass structure. These glasses may be termed as glasses with non-uniform, stuffed or reinforced network.

Glasses of a strongly pronounced cluster nature, with clusters having the structure of different polymorphic varieties of the glass-forming substance may by their coexistence mutually stabilize the glassy state. Glassy carbon may be an example of such glass. Clusters of graphite and diamond structure have been observed in its structure /29/. According to Goodman's model of stressed clusters /30/, the structure of silicate glasses is made up of clusters of different polymorphic varieties.

Glassy, anhydrous and hydrated salts and metallic glasses can be regarded as glasses with a non-polymeric uniform network. Their structure is built of simple units which usually easily undergo reorientation, and the salts crystallize rapidly. Their ability to retain the glassy state is attributed to the admixtures (hydrogen ions, HSO₄⁻) or presence of molecules and complex ions of asymmetric shape (sulfates) /28/. They hinder re-orientation and ordering of salt ions or molecules in the course of cooling the melted eutectic mixtures. The admixtures allow the transfer of the metal alloys into metal glasses /31/. For this reason, it is proposed to call the network of such glasses a uniform network stabilized by admixtures or a self-stabilizing one (asymmetric ions or molecules).

The division of glasses based on the above proposed criteria is shown in Table 1.

The phenomena considered above indicate that for glassy state to exist at least two conditions must be satisfied:
1. The glass network must possess enough elasticity to enable its elements to occupy varying positions with respect to each other and to adjust each other to a degree sufficient to give their arrangement the character of a random array.

2. Agents must operate to stabilize the random arrangement of the network elements and counteract their displacement to orderly arranged positions of equilibrium, i.e., the crystallization of glass. Elasticity of the network implies the ability to displace and rotate its elements without breaking the bonds between them. It must be high enough so that the internal strains which appear at the moment of vitrification of liquid and adoption of the features of rigid solid body cannot break the bonds of the network, permitting its reconstitution and the crystallization of glass.

Hence, according to the proposed glass structure model, glass is a solid body with an elastic random network. The construction and uniformity of the network depend on the chemical composition and the origin as well as the history of the glass.

Table 1
Structure of Inorganic Glasses

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>GLASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Polymeric network</td>
<td>silicate and fluoride glasses, glassy chemical elements, and simple compounds (oxides, fluorides, chalcogenide)</td>
</tr>
<tr>
<td>A. uniform, continuous</td>
<td></td>
</tr>
<tr>
<td>B. non-uniform, continuous</td>
<td>alumosilicate, borosilicate, alumosilicate-phosphate, and oxynitride glasses</td>
</tr>
<tr>
<td>discontinuous</td>
<td>phosphate and ZnCl₂ based glasses</td>
</tr>
<tr>
<td>2. Non-polymeric network</td>
<td></td>
</tr>
<tr>
<td>A. non-uniform</td>
<td>&quot;invert&quot; oxide glasses, halide-oxide glasses, glassy C</td>
</tr>
<tr>
<td>stuffed with small polymerized groups or clusters</td>
<td></td>
</tr>
<tr>
<td>B. uniform</td>
<td>ionic salts and solution glasses metallic glasses, etc.</td>
</tr>
<tr>
<td>self-stabilizing or admixtures stabilized network</td>
<td></td>
</tr>
</tbody>
</table>
In the case of a polymerized network in which the cation-anion bonds in the polyhedra and in between the polyhedra are mostly covalent, the elasticity of the network is the consequence of the variation of the angle of the bonds between the polyhedra or within them.

The angle of the bonds Si-O-Si between the SiO₄ polyhedra may vary, as is known, within the range 125-165°. The angle of the Pb-O bonds in the pyramid PbO₃ in lead glasses changes within the range 106-130° and in crystalline lead silicates within the limits 60-155°, their length changing as well. Both these substances have a relatively great ability for glass formation.

In a polymeric glass network, the tetrahedra are most often joined by their vertices, which gives the network a considerable elasticity. In the early theory of glass structure formulated by Goldschmidt, the occurrence of tetrahedra sharing the vertices was regarded as a necessary condition for the existence of a glassy state. The elasticity of a non-polymeric network is due to the existence of direction-free ionic bonds or Van der Waals' attraction forces.

Thanks to the elasticity of the network, there may exist within it colour complexes like NaFeS₂ /32/ in silicate amber glass or colloidal particles of Au, Cu or other metals and sulfides particles giving colour effects, and the glass reveals actual solution or colloid solution features.

In the structure of crystalline oxides, some halides and many other solids, diffusional mobility of the anions is much smaller than the cations and the anions sub-lattice is less deformable and more stable as compared to the sub-lattice of the cations. The same relation exists in the amorphous solids. The electrical conductivity mechanism as well as the crystallization mechanism of many glasses confirm the much higher mobility of cations.

Anions dimension and interaction influence strongly the shape and size of network-formers polyhedra. Then, the anions' skeleton of glass network determines in fact the stability of glass, and anion-cation chemical bonds determine its properties. Fast ion conducting glasses are an instructive illustration of this. Uniformity of strength of the network anion-cation bonds (basicity) corresponds to the chemical and geometric uniformity of the network (indicated in Table 1) and may be applied as its measure.

In light of the data presented above, the concept of glass network-formers and modifiers should be verified. The components of the glass structure known at present may be defined according to their function in the following way:


2. Modifiers: components which break the bridging bonds in the network and cause their depolymerization and weaken or strengthen the bonds within the polyhedra forming the network.


In conclusion, the following conditions for the formation of glasses with a mixed network may be specified.

Components differing in their chemical properties and in the nature of their bonds to a degree excluding the creation of bonds between them may form a common network when besides them there is present a buffer component able to form bonds simultaneously with both these components. Such a buffer compensates for the crystalo-chemical and geometrical differences between the network-forming components. Modifiers breaking the bonds of a polymeric network increase its elasticity and facilitate the incorporation of other components into it.

Examples of this are the Ag-halide and oxide glasses in which the Ag⁺ ions linked with the oxide tetrahedron bind them with the surrounding matrix made up of Ag halides. The AgI-Ag₂SO₄-Ag₂WO₄ glasses synthesized by Senapati and Angel /35/ seem to exist thanks to such a phenomenon.

Aluminium linking chains in the structure of fluorophosphate glasses is another example. Aluminium promotes the incorporation of the PO₄ tetrahedra into the silicon-oxygen network if it becomes partly depolymerized under the influence of Na⁺.
3. Crystallization of Glasses

A. Multistage Crystallization of Glass

Intrinsic processes of internal structure reconstitution occur in the solid bodies among which are: 1. thermal decomposition; 2. structure rearrangement and new compounds formation; 3. oxidation-reduction processes; and 4. ion exchange reactions. They proceed within the bulk of the solid grain. The solid product of these processes are formed inside the structural framework of the parent substance (precursor), often remaining in a topotactic relation to the primary structure (topotactic reactions). The nature of these processes is so specific that a general term, "intraframework" or "internal" processes, is proposed for them /34,35/.

Internal reactions are realized by the displacement of the structural elements inside the rigid structure of the precursor. Transport in solids is slow as compared with liquids. Rates of the displacement of particular atoms and ions as expressed by their diffusion coefficient are different and change with temperature. In oxides, for example, the diffusion coefficient of the oxygen anions is much smaller than cations. The consequence of this is a multistage course of the reactions and step-by-step mode of establishing the equilibrium state.

During the heat treatment of glasses, reactions take place, the nature of which corresponds to the internal processes mentioned above. The present paper is an attempt to indicate the specific features of certain internal processes occurring in glasses.

This is done by taking as an example the rearrangement of the structure accompanying crystallization of oxide glasses in the range of temperatures close enough to the transformation point, where the structure of glass does not differ significantly from that of the rigid solid body.

The path along which these processes proceed leads through metastable intermediate stages as a result of the step-by-step reconstitution of the structure of glassy precursor and later on, neoformed crystalline products.

The crystallization of inorganic glasses has been the subject of intensive research in connection with the production of new glass-ceramic materials /36/. In light of data known now the following general regularities referring to the process of glass crystallization may be formed.

Depending on the composition of silicate glass, the first to crystallize are usually compounds of simple composition, made up of components occupying the structural positions outside the SiO4 network or, if they enter into the composition of the network, their oxygen bonds are the weakest. Magnetite in glasses rich in Fe oxides, spinel MgO,Al2O3 or Al2Ti2O7 in glasses rich in aluminium and magnesium and containing an admixture of TiO2, etc., crystallize first. Completion of the crystallization of these compounds usually initiates spontaneous bulk crystallization in the course of which substances of complex composition are formed with the character of a solid solution but rather far from their proper chemical composition and close to the composition of glass.

To such substances belong solid solutions with the structure of quartz and the formula Li2·2(x+y) Mg2Zn2O3.2SiO2. At higher temperatures, the ordering of the structure of these solutions follows, connected to the segregation and redistribution of the chemical compounds and their compositions are gradually transformed into the composition of a crystal phase proper for a glass of a given chemical composition.

In glasses of the Li2O·Al2O3·SiO2 system, the first to form is a quartz solid solution (s.s.) which, with the passage of time and/or temperature, increases, is transformed into spodumene s.s., and next into the true spodumene Li2O·Al2O3·5SiO2. In glasses with the composition of cordierite, the first to form is quartz s.s., and subsequently, by way of a successive rearrangement of structure, sapphirine and finally true cordierite, 2MgO·2Al2O3·5SiO2.

In glasses of the Na2O·CaO·Al2O3·SiO2 system, crystallization of wollastonite with the composition NaAl(SiO1.5)2 takes place.

Pyroxene solid solution crystallization from CaOMgO(Li2O,Fe2O3)-SiO2 glasses (37) is an instructive example of a multistage process running by the redistribution of chemical components of the neoformed phases. In this system, glasses of low iron content crystallize at 860 °C and diopside solid solutions with LiFeSi2O6.
groups in the structure form. At 900 °C, redistribution of chemical elements takes place. Due to this, part of LiFeSi$_2$O$_6$ included in the diopside structure dissociates. At 900 °C, redistribution of chemical elements takes place. Due to this, part of LiFeSi$_2$O$_6$ included in the diopside structure dissociates. Another example of multistage crystallization is

LiFeSi$_2$O$_6$ included in the diopside structure dissociates. At 900 °C, redistribution of chemical elements takes place. Due to this, part of LiFeSi$_2$O$_6$ included in the diopside structure dissociates.

IR spectra show that the silicate network of glass I contains pyroxene-like elements, whereas that of glass II contains elements of anorthite and pyroxenes. In both glasses, Al$^{3+}$ occurs in the silicate network, while almost all the iron is found outside the network performing the function of the cation-modifier. From the Mössbauer's spectrum, it follows that Fe$^{2+}$ occurs in the coordination 6 (70% of the total Fe content). Most Fe$^{3+}$ (20% of Fe) have the coordination 6, and only a small amount of Fe$^{3+}$ (10% of Fe) has the coordination number 4 and occupies the position of Si$^{4+}$.

The crystallization of titanomagnetite takes place as a result of the rearrangement of iron occupying positions outside the silicate network. Heating the sample under oxidizing conditions increases the proportion of Fe$^{3+}$ and causes intensive precipitation of hematite in its whole volume. Through X-ray micro probe analysis, it was found that pyroxene I, which crystallizes first, has a composition close to the chemical composition of glass. At a higher temperature, it recrystallizes with the separation of some components and its composition becomes Ca$_{0.9}$Mg$_{0.6}$Fe$_{2+0.3}$Ti$_{0.1}$[Al$_{0.3}$Si$_{1.7}$O$_6$]. Simultaneously olivine, Mg$_{1.7}$Fe$_{0.3}$[Si$_4$O$_4$], is formed from released components. The remaining Ca$^{2+}$ and the rest of the elements of the silicate network enriched with Al$^{3+}$ form anorthite.

The above processes begin to appear just above the Tg point as an endothermic reaction (distinct DTA peak at 700 °C). It can be explained as an energy consumption to break some of the chemical bonds in order to displace the cations and reorganize the elements of the glass structure towards the structure of the new phase to be formed. Long range ordering of the pyroxene-like clusters in the glass structure in order to form pyroxene crystals is accompanied by the exothermic effect (DTA peak at 840 °C). Further heating and temperature increase facilitates the displacement of cations and permits the rebuilding of a pyroxene structure with the simultaneous formation of olivine (exothermic deflection of the DTA peak at 860 °C). The formation of anorthite, whose structure has the highest SiO$_4$ tetrahedra polymerization degree (framework silicate), is possible near the liquidus temperature.

Another example of multistage crystallization is
supplied by glasses in the CaO-P₂O₅ and CaO-P₂O₅-SiO₂ systems, with a mixed network modified by additions of B₂O₃ and Al₂O₃ and containing small admixtures of Na₂O, MgO and CaF₂ /14/. 

Glasses whose composition is close to calcium pyrophosphate, Ca₃P₂O₇, and metaphosphate, Ca₃(PO₃)₂, become crystallized in the following sequence: glass - Ca-metaphosphate - Ca-pyrophosphate.

The course of the crystallization of glasses in which the proportion of the percent content of CaO/P₂O₅ exceeds 1.0 is as follows: glass - Ca₃(PO₄)₂ - apatite Ca₁₀[(PO₄)₆O]. When the SiO₂ content exceeds 30 wt%, crystallization sequence is: glass - wollastonite CaSiO₃ - Ca₃(PO₄)₂. When the SiO₂ content is smaller, part of it becomes incorporated into the structure of apatite, while the remaining content forms a glassy matrix which crystallizes with difficulty.

The course of crystallization of these glasses may be characterized as follows: Calcium phosphates crystallize in a rapid manner already at 800 °C from glasses poor in SiO₂. The temperature of crystallization increases with increasing the SiO₂ content, since destruction of the strong silica network requires a higher temperature. The destruction of this network seems to be a condition of the crystallization of the glass. That is why wollastonite does not crystallize until about 900 °C. Then, besides wollastonite, apatite is formed simultaneously. This process is facilitated by sodium as the depolimerizer of the network.

The presence of aluminium and/or boron in the silica network makes the crystallization of glass and wollastonite formation difficult, shifting it to higher temperature. In that case, redistribution of these components of the network is necessary, and they pass to the residual glassy phase. In the presence of alkalies, boron inhibits crystallization of calcium phosphate. It does not crystallize when the glass is free of boron. It seems that the mixed network undergoes reconstitution; boron together with alkalies and calcium phosphates form glass of high stability and silica have to crystallize as wollastonite.

In glasses from the (Na₂O,CaO)·SiO₂·Al₂O₃·P₂O₅ system, Al(PO₄), metaphosphates of sodium and aluminium or apatites are the first to crystallize, depending on the percent proportions of the particular components.

These phenomena may be explained as the consequence of the differing strengths of the links between the phosphate elements of the network and the silicate elements. Binding through aluminium or calcium cations is weaker than the bonds within the silica network elements. Their disruption releases some of the components of the mixed network of glass, which are able now to form separate crystal phases.

Some metaphosphate glasses may crystallize even below the transformation temperature, Tg. This is possible when the crystal structure and the glass network are built of phosphate chains. In glass with a chain network, crystals built of phosphate rings are formed only above the Tg temperature /38/.

B. Structural Mechanism of Crystallization of Multicomponent Glass

The data referring to the multistage crystallization of glass gathered so far and considered in the previous chapter allow us to state that multistage crystallization proceeds according to some general rules.

Crystallization usually starts with the diffusional rearrangement of the most weakly bound and most mobile elements in the glass structure. In glass with a polymeric network, they are the glass modifiers and other non-network components. As a consequence, simple compounds like spinels, oxides, fluorides, etc. tend to be the first to crystallize. The nucleating agents of glass-ceramic materials (TiO₂, ZrO₂, CaF₂, Cr₂O₃, etc.) belong to them.

Bulk crystallization of glass starts with the formation of a substance whose composition and structure are as close as possible to the structure of glass. Crystallization of quartz-like solid solutions, pyroxenes, solid solutions and wollastonite of anomalous chemical composition are examples. They are usually transitional, metastable phases. At higher temperatures, when the diffusion processes are intensive enough, decomposition of transitional phases, redistribution of chemical compo-
ments and formation of crystal phases proper for the thermodynamic equilibrium state take place.

Crystallization of amorphous products of the thermal decomposition of solids also follows these general rules /1,34,35/.

These rules may be formulated as follows:

1. Crystallization of multicomponent glass begins with the formation of simple compounds made up of chemical elements which are weakly bound in the structure and are most mobile at the given temperature.

2. The first product of the main bulk crystallization of glass is the crystal phase, the chemical composition and structure of which are close to those of the glass network or its microregions (domains or clusters).

3. The crystallizing glass has a tendency to reach an equilibrium phase composition corresponding to its chemical composition through gradual rearrangement of the structure of the earlier-formed phases and/or the segregation of their chemical components. As a result of this recrystallization, compounds of the next generation, usually of a simpler chemical composition, are formed.

According to the standard theory, crystallization of glass can be viewed as consisting of two distinct stages: nucleation and crystal growth. It is a process of drastic rearrangements within small, localized volumes connected with the formation of a well-defined interface between the parent glass and the crystal phase /39/.

The nucleation-growth theory has been developed for the crystallization of liquids and its validity has been extrapolated to heterogeneous transformations in solids, including the crystallization of glass. According to this theory, at the phase transformation temperature, when Gibbs free energy of the process \( \Delta G = 0 \), free energy of the nucleus with a critical or smaller radius is infinitely large, so its formation is not possible from a thermodynamic point of view /40/. This is a barrier limiting crystallization. The nucleating agents (nucleators) were introduced into the glass to overcome the barrier of nuclei formation and interface development (heterogeneous crystallization of glass).

The process of heterogeneous transformation in a solid state, however, may have a different mechanism. Some proceed in a diffusionless way, i.e., by correlated displacements of whole blocks of atoms or by way of diffusional displacements of individual atoms at distances longer than the interatomic distances in the crystal lattice. The first mechanism is typical of rapidly progressing polymorphic transformations. The second mechanism is characteristic of transformation processes connected with considerable changes in the chemical composition /41/.

Martensitic polymorphic transformations, typical for metals and their alloys, proceed according to the diffusionless mechanism /41/. They may occur also in oxide systems (transformation of \( \text{ZrO}_2 \) tetragonal-monoclinic) /42/. In these transformations, the displacements of the atomic groups occur in such a way that the coherence between the structure of the parent phase and that of the product at least in one crystallographic plane (habit plane) is retained. It constitutes at the same time the interface with the lowest possible thermodynamic potential. This is made possible because the displacements of the precursor structure during the transformation are similar to those which appear in the course of shearing (phase transformations of shearing with invariant habit plane).

This mechanism does not occur in its pure form. In oxide systems, the sublattice formed by the less mobile oxygen anions undergo little correlated redistribution, whereas the mobile cations become displaced at greater distances. An example of this is the structural changes corresponding to the formation of \( \text{MgO} \) from \( \text{Mg(OH)}_2 \) during its thermal decomposition. This mechanism may be called diffusionless-diffusional /43/.

The above transformation mechanisms are already known from the crystal solids; however, there is no reason why their operation during heterogeneous phase transformations in glasses should be excluded. The diffusionless mechanism with a coherent interface permits obviation of the thermodynamic barrier in the new phase nuclei formation.

The examples discussed above, in which the initial stage of the bulk crystallization consists of the formation of a crystal phase with chemical composition and
structure close to those of the precursor glass appear to favour the theory of the formation of nuclei little differing from the surrounding glass matrix. This ensures the coherence of the interface and makes nucleation easy. These nuclei may form through diffusionless displacements within the entire network of the glass or in selected clusters.

When the nuclei reach dimensions larger than the critical ones, the coherence of the interface no longer has any significance in the formation and growth of the crystals. Then modification of the chemical composition and ordering of the structure of the newly formed crystals of the first generation take place.

At higher temperatures, when the diffusional displacements are easy and fast enough, reconstitution of the earlier-formed crystals and of the glass matrix connected with the network decomposition becomes possible. Then the diffusional processes prevail and the system attains a state close to equilibrium.

Accordingly, the following stages of the crystallization of glasses of complex chemical composition and mixed network may be distinguished in the course of their heating:

1. Diffusional rearrangement of the weakly bound and most mobile components of the structure (simple compounds like oxides, titanates and fluorides crystallize);

2. Diffusionless translative rebuilding of the network (formation of a metastable crystal phase of the solid solution nature, whose composition and structure are close to the parent glass);

3. Diffusional-translative transformations (formation of new intermediate, metastable compounds of various composition and structure); and

4. Diffusive reconstitution (redistribution of chemical components, recrystallization of metastable phases and formation of stable phases proper for the equilibrium state of the system).

A similar sequence characterizes the crystallization of many other inorganic amorphous solids /1/. The division of the crystallization process of some glasses into the stages distinguished above is seen in Table 2.

The driving force of the diffusionless translations may be the strains of the network. The elasticity of the network makes this type of rearrangement in glass especially easy. Diffusive displacements are induced by local differences in chemical potentials.

4. Conclusions

Crystallization of glasses with complex chemical compositions, particularly those with a mixed network, belongs to the internal structure reconstitution reactions of the complicated multistage mechanism, which is not yet well understood. A strong relationship between precursors and product structures is a characteristic feature of these processes.

Crystallization of multicomponent glasses begins with the formation of simple compounds made up of chemical elements which are weakly bound in the structure and are most mobile at the given temperature (oxides, spinels, fluorides, etc. - nucleators in the glass-ceramic materials). The first product of the main bulk crystallization of glass is the crystal phase, the chemical composition and structure of which are close to those of the glass network or its micro-regions (clusters, domains). The crystallizing glass has a tendency to reach an equilibrium phase composition corresponding to its chemical composition through the gradual rearrangement of the structure of the earlier-formed phases and/or the segregation of their chemical components. As a result of this recrystallization, compounds of the next generation are formed.

The crystallochemical approach used here is a helpful procedure complementary to kinetic and thermodynamic studies of glass stability and crystallization. It makes possible modeling of the internal reconstitution processes in glass and predicting its real course via intermediate stages as well as metastable phase formation. It facilitates also the understanding of the position or function of different components of glass in its structure and the prediction of the course of technological processes.
### Table 2

**Stages of Crystallization of Multicomponents Glass**

*(Example)*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C</td>
<td>$\text{Li}_2\text{O}.\text{Al}_2\text{O}_3.7\text{SiO}_2$ glass $+ 10 \text{ wt}% \text{ TiO}_2$ nucleator</td>
<td>$\text{Al}_2\text{Ti}_2\text{O}_7 + \text{TiO}_2$</td>
</tr>
<tr>
<td>950 °C</td>
<td>$\text{Li}_2\text{O}.\text{Al}_2\text{O}_3.n\text{SiO}_2$ quartz solid solution</td>
<td>$\text{Li}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2$ spodumene solid sol.</td>
</tr>
</tbody>
</table>

### References


