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THERMOCHEMISTRY OF SOLIDS WITH FLEXIBLE STRUCTURES

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Abstract

The flexibility of the internal structures of solids, both crystalline and amorphous, is a result of the freedom of the displacement of their elements, without disturbance of the continuity of the structure as a whole. This article discusses peculiarities of solids with flexible structures. The effects of flexibility in the thermal reactions of the creation of new compounds in the internal structure of solids, and the phase transitions, are considered. Flexibility is indispensable for random amorphous structure formation. The glass transition effect is a consequence of the high flexibility of the structure of glasses.

Keywords: amorphous solids, chemical affinity, crystallization, glasses, glass transition, structure flexibility, thermochemistry

Introduction

The surroundings of a material exert significant effects on the structural mechanism and on the kinetics of chemical processes which occur in it, particularly those which are thermally activated. These effects have been discussed earlier on the example of processes taking place in the structures of various solid bodies as the reaction medium [11].

A chemical reaction medium is a definite material medium, gaseous, liquid or solid, where the atoms creating this medium, which do not participate directly in the reaction or affect the rate of displacement of the reagent atoms, influence of the frequency of active collisions, and thereby the progress and the micromechanism of the reaction (the diluent effect), although they themselves take no part in the act of reaction.

The influence of the medium on the course of the reaction, among other things, is responsible for the fact that the operation of the generally known laws and functional relationships established for reactions in vacuum or in gases requires occasional correction, or their application with reference to the reactions in liquids or solids is limited. An example here is the Arrhenius equation. This influence is included in the values of the thermodynamic activity coefficients.

A solid medium can differentiate, to extents depending on the temperature and pressure, the mobilities of the chemical components, thereby limiting and

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modifying the decisive function of the chemical affinity as a force which drives and selects the possible chemical processes. These new phases can be formed only in a solid-state reaction, whose components are mobile enough to be accessible in the given region of the structure of the solid.

Accordingly, in the solid-state processes, the formation of crystallites of a new compound is possible when the concentrations of the chemical components constituting this new phase attain locally appropriate values in a volume exceeding the critical size of its nucleus, in spite of the low average content of any one of these components in the whole volume of the solid.

A specific feature of the structures of some solid bodies is the considerable flexibility. Besides the natures and the strengths of the chemical bonds between the components, resulting in their mobility and chemical activity, the flexibility of the structure of a solid body may exercise a substantial effect on the character and the course of the reaction of synthesis of a new compound and the phase transitions taking place in it.

Flexibility of the internal structure of a solid

The flexibility of the internal structure of a solid body, either crystalline or amorphous, is demonstrated as the freedom of its elements to undergo displacement without disturbing the continuity of the structure as a whole. A flexible structure subjected to the action of external factors undergoes ready transformation, usually of a reversible character. Flexibility can make the structure capable of incorporating atoms, molecules or even particles of new components.

The structure is made flexible by the possibility of changes in the angles between the neighbouring coordination polyhedra, the freedom to change the coordination number or the shapes of the coordination polyhedra of certain components, facile translation of the structure elements over small distances, e.g. of the shear type, etc.

Flexibility is acquired by the structure thanks to non-directional (ionic, metallic, Van der Walls) bonds, elastic anion bridges between the coordination polyhedra, etc. Examples are given in Table 1.

Substances with a flexible crystalline structure may demonstrate quick, reversible polymorphic transformations of the rearrangement type (low-temperature polymorphic SiO_2 transformations), phase transitions of order II and relaxation processes such as the glass transition effect.

The flexibility of a structure may be limited to only one particular crystallographic direction or plane. Polytypy of layer structures (C, SiC, MoS and others) should be treated as the result of structure flexibility in some definite crystallographic plane parallel to the layer.

Table 1 Factors determining glass structure flexibility (examples)

Freedom of the bridging anion-cation angle change:		
Si–O–Si		125–165°
P–O–P		123–180°
Deformable coordination polyhedra:		
	Pb–O polyhedra	
Change in coordination ability:		
Al and Ti		4, 5, 6
Si		4, 6
B		3, 4
Direction-free chemical bonds:		
ionic	metallic	Van der Waals

Flexible structure peculiarities

Structure flexibility and the amorphous state of solids

Some inorganic substances may occur not only in a crystalline form, but also in an amorphous form, when their structure lacks long-range crystallographic order.

The typical example is SiO_2 which, under both natural and artificial conditions, forms amorphous bodies such as gels and glasses with completely disordered structures, or displays a differentiated but rather low degree of crystallinity (opals). The amorphous state, although thermodynamically unstable, may be characterized by exceptionally high kinetic stability. The amorphous silica minerals and the preserved antique glasses can serve as examples here.

On the other hand, the majority of elements and inorganic compounds can be transformed into a stable glass only by means of special technical procedures, such as ultra-quick undercooling of the melt to the solid state. Such vitrification, however, is very unstable.

Present-day glasses, whose chemical composition is varied, and for the production of which almost all the chemical elements are used, possess kinetic stability high enough for their practical application.

Although the art of producing glass has a long history and investigations on the production of new types of glasses are carried out by many scientific centres, the rules by which the components should be chosen so as to obtain glass of a new chemical composition, and desired properties have not been established as yet. The criteria of the existence of the glassy state that have been worked out so far refer to oxides, especially the silicate glasses, and their validity has been found to be limited.

In the structure of an ideal crystal, the atoms occupy positions at the nodes of the crystal lattice, which are the points of equilibrium of the forces operating between the atoms forming the given structure. Thanks to this, an ideal crystalline structure is free from internal stresses. In an amorphous structure, devoid of crystallographic ordering, this equilibrium is disturbed. This must induce the occurrence of stresses inside the structure. If they are strong enough, they will break the bonds in the structure, which will allow the ordering of its elements and crystallization of the amorphous substance. If, on the other hand, the amorphous structure demonstrates sufficient flexibility, relaxation of these stresses or their reduction below the critical value may occur through rotation of the coordination polyhedra around the oxygen bonds limiting them, as is the case in the oxide glasses, or through other displacements of the structure elements without disturbance of its continuity. Such an amorphous structure is characterized by considerable thermal stability and its crystallization ability is minimal.

The majority of known glasses, but especially the oxide (silicate, borate and phosphate) glasses, have polymeric structures. The model is a three-dimensional continuous, but geometrically disordered network, composed of network-former coordination tetrahedra, in which some of the oxygen bridges combining these tetrahedra are broken by cations of uni- or bivalent metals (modifiers): the Zachariasen model.

Besides glasses with a polymeric homogeneous continuous network, one can distinguish glasses with a continuous, but inhomogeneous network. Among these are glasses with a mixed network, built up of coordination polyhedra of various network formers. Aluminosilicate, borosilicate and aluminosilicate-phosphate glasses are examples.

Several glasses have a discontinuous polymeric network made up of chains or rings of tetrahedra linked by the surrounding cations (some phosphate and borate glasses).

A number of glasses have a non-polymeric structure. Some of them are made up of oxides or halides with small dispersed islands of coordination polyhedra of other components. The superionic conducting glasses based on silver halides belong among them. Their structure is made up of a matrix formed by Ag^+, (I^-, Cl^-, and Br^-). Sets of tetrahedra of P, B, As, Cr, Mo and Si oxides (clusters) are firmly fixed in this. Vanadium borophosphate glasses, which contain 70–90 mol% of V_2O_5, probably possess a similar structure. The structure of these conducting glasses is interpreted as 'a cluster and tissue pseudophase model' [2].

This can also be applied to Se–P glasses, such as $P_4Se_3I_2$, in the structure of which there appear clusters of Se atoms [3].

The model of a continuous, homogeneous, polymeric structure of glass and the cluster and tissue pseudophase model represent extreme cases. The structures of real glasses have an intermediate character and, depending on the chemical composition of the glass and the mode of its formation, are closer to the structures represented by the first or the last model.

The particular features which are in general characteristic of the glassy state are: an internal structure free from long-range crystallographic ordering, the structure flexibility necessary for the existence of this disorder, and the presence of agents which stabilize this disordered state of the structure. A general model of glass, proposed by the author [4], demonstrates the above features.

According to this model, glass is a solid body with a flexible random structure. The construction and uniformity of the structure depend on the chemical composition, the origin and the history of the glass.

Agents stabilizing the random arrangement of elements of the structure of glass are: a polymeric network with strong chemical bonds of glass (silicate, phosphate and borate glasses), inhomogeneities as clusters in nonpolymeric glasses (silver halide glasses) or admixtures in silver glassy metals and admixture-stabilized glasses [5].

The criterion of structure flexibility and the factors preventing ordering of the structure as indispensable to the existence of glasses comprise all well-known particular criteria which have so far been considered necessary conditions for the existence of this form of solid.

This refers, among other things, to the Goldschmidt and Zachariasen crystallochemical criterion of the existence of a three-dimensional glass network, built up of tetrahedra or triangles joined with each other in the corners by oxygen bridges, which in fact are indispensable if the network is to be flexible. Of similar significance is Smekal's criterion of the necessary existence of mixed chemical bonds, i.e. the directed ones (covalent bonds), but also the non-oriented ones (ionic or Van der Waals bonds), that is those which permit freedom of the displacement of the structural elements making the glass structure flexible. Sun's criterion requiring that the glass-forming substance possess high bond energy (about 90 kcal mol^{-1}) corresponds to the strength of the spatial network in polymeric glasses necessarily being strong enough to prevent the breaking of chemical bonds by internal strains during the vitrification process and to inhibit the ordering of the random structure of glass.

The flexible structure as a characteristic feature and the criterion of its existence are also valid with reference to other amorphous solids.

It should be assumed that the differences between the particular amorphous substances are due to the different degrees of flexibility of their structure and their micro- or macrohomogeneity. The effect of the transformation of the glassy state (vitrification) which distinguishes glasses from other amorphous solids is possible due to the greater flexibility of the internal structure and hence the lower ability for crystallization in comparison with other amorphous bodies.

Vitreous state transition phenomenon

During cooling and heating, glasses exhibit the structural strain relaxation phenomenon termed the glass transition effect. These strains result from the disordered structure of the glass and the random arrangements of the glass structure elements. Relaxation of strains accompanies the weakening of a proportion of the chemical bonds in the glass structure with temperature increase. Up to the transition temperature (T_g), glass behaves as a brittle body with a rigid structure. At the transition temperature, the viscosity decreases rapidly to $10^{13.3}$ dPas, and above this temperature glass has viscoelastic properties.

The glass transition is defined as the phenomenon whereby a substance exhibits a sudden and reversible change in its properties, such as heat capacity, thermal expansion coefficient and viscosity, from crystal-like to liquid-like values.

The shapes of the curves illustrating the changes in the given property with temperature are similar to those which are characteristic for the order II phase transformation according to the thermodynamic classification.

The glass transition temperature (T_g) and the changes in the glass properties with temperature that accompany this transition depend on the chemical composition of the glass and also, to a considerable degree, on its history and especially the rate of cooling of the melt.

A particular characteristic of the transformation effect of the glassy state is the jump-like change in the molar heat capacity ΔC_p, well visible in the DSC curves of glass. It is used to determine T_g. According to the author's observations, ΔC_p is an important parameter connected with the chemical composition of the glass and its structure. The value of ΔC_p is particularly greatly influenced by the nature and the number of cation modifiers with respect to the network formers, as well as the character and the strength of the chemical bonds between the modifiers and network components.

The greater the number of modifiers in the glass and the more ionic their bonds with the network, the more elastic is the structure and the correspondingly less energy-consuming is the transition from the state of a rigid body to the viscoelastic state. The above statement is supported by the fact that the transition of a pure silicate glass, i.e. one without modifiers, is difficult to record by the methods of thermal analyses on account of the very small change in C_p accompanying this transition.

Accurate measurements of ΔC_p of borate glasses have been carried out by Wacławska [6]. The glasses she examined, with the compositions defined by the respective chemical formulae, gave the following ΔC_p values (kJ mol^{-1} $°C^{-1}$): $2CaO{\cdot}3B_2O_3$ – 0.51; $4CaO{\cdot}5B_2O_3$ – 0.92; $K_2O{\cdot}2MgO{\cdot}6B_2O_3$ – 0.34; $Na_2O{\cdot}2B_2O_3$ – 0.16. These data are in agreement with the above-formulated statement.

Occasionally, the existence of a relation between ΔC_p and the ability of a glass to crystallize can be observed. Glasses crystallizing easily, even at a temperature close to T_g, are distinguished by a greater change in C_p within the range of transformation as compared with glasses that crystallize with difficulty. This means that the relaxation of the glass structure is accompanied by its deeper rearrangement preceding the formation of crystalline regions.

The cited investigation of the effect of borate transformation [6] revealed that thermally amorphized crystalline borates exhibit the typical effect of glass transition, but ΔC_p is considerably smaller than in the case of the glass of the same composition obtained by cooling the melt. This means that part of the structure of this material has not yet reached the state of disorder comparable with that of a typical glass.

It is seen from the above observations that ΔC_p is a sensitive indicator providing information as to the degree to which the structure has attained the randomness and the ability for relaxation specific for the glassy state.

The transition of the glassy state is thought to be an important criterion distinguishing glasses from other solid bodies. According to the definition of the U.S. National Research Council [7], glass is an X-ray amorphous material exhibiting the glass transition effect.

It has been demonstrated by Suga *et al.* [8, 9] that the phenomena of structure relaxation corresponding to the glass transition effect occur in certain crystalline substances. They are also manifested by the anomaly in the curve of heat capacity as a function of temperature, which is reversible and depends on the thermal history of the substance in the same way as the transition of glass. Suga has termed the substances exhibiting this phenomenon 'glassy crystals'.

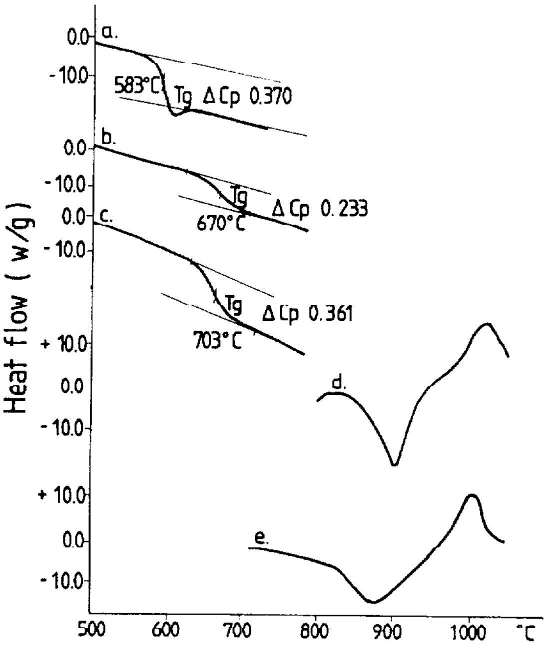

Fig. 1 DSC curves of the transformation of structures of amorphous solids;
– Glass transition (ΔC_p/J (g °C)$^{-1}$):
a – silicate glass SiO_2 73; CaO 12; Na_2O 15 (wt.%),
b – mixed network glass Na_2O 8; MgO 20; Al_2O_3 21; P_2O_5 18; SiO_2 33 (mol%),
c – mixed network glass SiO_2 35; P_2O_5 12; Al_2O_3 25; MgO 20; Na_2O 8 (mol%);
– Amorphous structure reconstitution irreversible endothermal peak preceding crystallization process (exothermal): d – montmorillonite, e – synthetic zeolite ZSM-5

These are crystalline substances in which at elevated temperatures some of the molecules forming them display orientational disorder. The disorder generally disappears discontinuously through a solid–solid phase transition to achieve a fully-ordered state (disorder–order transformation). The transformation has been observed in $B(OH)_3$ (290 K), $SnCl_2{\cdot}2H_2O$ (150 K), hexagonal ice (105 K), some hydrates and a number of organic compounds, etc., and it may be attributed to the randomness of the proton arrangement.

The described phenomenon is accompanied by an anomalous change in the heat capacity associated with the freezing of the orientational freedom or other small displacements of the several elements of the crystalline structure, which as a whole exhibits a high degree of ordering.

Suga's findings essentially modify the traditional view of the glass transition phenomenon. It has been visualized that a glass transition effect can occur in solid bodies, either amorphous or crystalline ones, when a certain disorder of the structure can be frozen and reversibly cancelled with temperature change.

It is obvious that such a structure must be flexible and at the same time strong enough for a change in the degree of disordering to occur in it, in accordance with temperature change, without disturbing the structure as a whole and inducing its substantial rearrangement, for example by way of recrystallization.

Amorphous bodies, which are not glasses, do not exhibit the phenomenon of transformation connected with reversible structural rearrangement resulting from the relaxation of structural stresses. During heating, silica gel displays only the exothermic effect of the crystallization of cristobalite. Amorphous aluminium oxide, obtained through the rapid thermal decomposition of aluminium hydroxides, is recrystallized into γ-Al_2O_3. During heating at about 600°C, the layer silicates such as kaolinite, montmorillonite and illite undergo dehydroxylation and new anhydrous substances are formed, which are X-ray amorphous. They remain amorphous up to about 900°C and then undergo recrystallization. The exothermic effect of the crystallization of montmorillonite and illite is usually preceded by the endothermic effect of rearrangement of the amorphous structure. This effect is irreversible. Synthetic zeolites with high silica content exhibit an irreversible endothermic effect at about 800°C, associated with the reconstruction of the structure, which becomes transformed from a loose, microporous one into a dense, but amorphous structure. It subsequently undergoes recrystallization with the formation of cristobalite [10].

The internal structures of the above-described amorphous substances are apparently too rigid for the stresses occurring in them to relax without disturbing the continuity of the structure. The stresses of the structure become released by its disruption and rearrangement into the structure of the new crystalline phases which will be formed from it.

The effect of the glass transition, on the other hand, is demonstrated by hydrated borates amorphized by dehydroxylation [6].

It may be concluded from the above discussion that the glass transition effect is an indicator of the high flexibility and uniformity of the internal structure of an amorphous solid.

Adoption of alien phases

Due to the flexibility of their structures, crystalline and amorphous solids are able to accept foreign phases such as crystals, liquid or gaseous inclusions without disturbing the continuity of the structure as a whole.

Silicate glasses accept colloidal particles of Au, Cu or Ag, as well as particles of sulfides, fluorides and phosphates. They precipitate on appropriate heat treatment of the glass and act as colorants and opacifiers. In many glass-ceramic materials, the crystalline grains of various dimensions are surrounded by a glassy matrix. These phenomena are not accompanied by any strong stresses at the interphase, as is the case with alien inclusions in crystalline substances with rigid structures.

One result of the thermal decomposition of certain substances is the formation inside them of inclusions in which the gaseous products of the decomposition are collected and retained. The dehydration and dehydroxylation of borates (colemanite, pandermite and ulexite) and layer silicates (dickite, pyrophyllite and muscovite) afford appropriate examples of this phenomenon [11].

The newly formed molecules of water vapour are located in the empty spaces of the framework. They accumulate along the macro- and micro-defects of the crystal grains, trying to escape outwards. In substances with a high degree of crystallinity and a uniform structure, with a small number of defects, such escape routes are not available and the pressure of the confined gases increases with temperature. When the pressure exceeds the critical value, the weakest bonds in the structure burst and the enclosed gases are liberated suddenly [12].

Recrystallization and multistage crystallization in solids with flexible structures

Crystallization mechanism and order

A specific feature of flexible structures is that they are able to rearrange. They also represent a specific medium in which there may occur processes of reassembly of the components and the synthesis of new compounds, which are often subjected to further rearrangement with temperature increase: multistage crystallization. The compactness of grains of a multiphase substance formed in this way is permanently retained.

An example of such a rearrangement is the reversible, rapid polymorphic transition of low-temperature quartz into high-temperature quartz, consisting in a change in the Si–O–Si bond angle between the tetrahedra from 142 to 156°.

This involves a change in the symmetry of the tetrahedron rings from trigonal to hexagonal. The structural rearrangement accompanying the reversible transitions of tridymite and cristobalite is of a similar character. Another example is a change in the CsCl structure (with ionic bonds) that accompanies the polymorphic transition; this consists in the change of the coordination number Cs from 6 to 8.

An example of a multistage rearrangement process connected with a change in the chemical composition is the dehydration of $Pb_2P_4O_{12}{\cdot}4H_2O$ to $Pb_2P_4O_{12}$ through several progressively less hydrated phases. It is accompanied by a corresponding rearrangement of the internal structure by way of the displacement of the pieces of the primary structure elements (chains and layers) [13].

Examples of multistage crystallization are provided by hydrated borates of the alkali metals and alkaline earths or layer silicates. In the course of heating, they undergo dehydration and dehydroxylation, forming anhydrous solids with amorphous structures. With increasing temperature, they are subject to recrystallization, which consists in the formation of new crystalline phases inside the amorphous structure through reassembly of the components forming this structure [6].

In the case of borates such as pandermite ($Ca_2[B_5O_8(OH)_3]{\cdot}2H_2O$) or kaliborite ($HKMg_2[B_6O_8(OH)_5]{\cdot}4H_2O$) the first to crystallize in the amorphous, anhydrous structure are the borates of bivalent cations with low ratios of the number of boron atoms to the number of cations in the chemical formula. This means that their structure contains complex anions involving a low degree of polymerization of the BO_4 tetrahedra.

They are formed in the amorphous fabric enriched with B_2O_3. In the case of pandermite, CaB_2O_4 crystals are formed in the amorphous CaB_4O_7 fabric. If the compound contains alkali metal ions, they are retained in the amorphous fabric and the next crystallization step at a higher temperature is the crystallization of the alkali metal borates.

In kaliborite, the Mg-borates are the first to crystallize in the amorphous matrix of composition KB_7O_{11}, in which the crystallization of KB_5O_8 occurs next. The newly formed crystalline borates are surrounded by B_2O_3, which preserves the amorphous state up to the melting temperature. If the borate contains Ca and Na, the calcium borates formed in the first stage of crystallization are dissolved, and double CaNa borates next crystallize, surrounded by amorphous B_2O_3.

The high-temperature phase transformation of layer silicates also comprises a multistage crystallization process.

Kaolinite, $Al_4Si_4O_{10}(OH)_8$, in its dehydroxylated form has an X-ray amorphous structure. It consists of a distorted tetrahedral silicon–oxygen sheet. During dehydroxylation, an octahedral sheet of the kaolinite structure is transformed into regions of distorted Al–O tetrahedra. At 970°C, the amorphous structure is transformed into γ-Al_2O_3 or Al-rich (Al,Si)-spinel and defective mullite in an amorphous SiO_2 fabric. At higher temperature, it recrystallizes mullite and cristobalite with ordered structures are formed.

When pyrophylite ($Al_2[Si_{14}O_{10}](OH)_2$) is dehydroxylated above 900°C, the step-like crystallization of mullite begins in its structure; this occurs at about 1100°C and is followed by the recrystallization of the amorphous silica matrix into cristobalite.

When dehydroxylated, muscovite ($KAl_2[AlSi_3O_{10}](OH)_2$) recrystallizes with the formation first of (Al,Si)-spinel, which later recrystallizes into cristobalite.

After loss of the OH groups, magnesium-rich montmorillonite (Cheto-type) recrystallizes with the formation first of a solid solution with a quartz structure and enstatite ($MgSiO_3$). Aluminium is initially included in a high-cordierite ($Mg_2Al_3[AlSi_5O_{18}]$), which at higher temperature is replaced by sapphirine, $(Mg,Fe)_4Al_8Si_2O_8$. At 1200°C the quartz-like component and amorphous matrix are completely transformed into cristobalite.

The phenomenon of multistage crystallization is a consequence of the limited mobility of the reagents participating in this process as components of the structure of a solid body [14]. Only those chemical components which at the given temperature have the possibility to undergo rearrangement or displacement, measured for example by their diffusion coefficients, may participate in the formation of new phases. The diffusion coefficients of the components of the solid structure increase with increasing temperature, but the increases are different for the different chemical components. If it happens that at various temperatures different chemical components become capable of forming new compounds, then, during the heating of the mineral, substances differing in chemical composition successively crystallize.

Significance of crystallochemical and thermodynamic factors

The relations between the chemical compositions and the structures of amorphous substances and the natures of the crystallizing compounds and the sequence of their occurrence have not been fully explained as yet. For their determination, investigations have been carried out on the crystallization of glasses in several selected systems. Bulk crystallization was studied as a function of temperature under conditions of static and dynamic temperature increase.

Attempts have been made to establish to what extent the formation of compounds during the multistage crystallization of the examined glasses is determined by the chemical affinity of the reacting substances, expressed by the Gibbs free energy of their formation. Since the formation of these compounds takes place in a homogeneous medium, such as the glass structure, characterized by the absence of crystallographic ordering, it has been assumed that the substances crystallizing in it are formed by free oxides. This assumption corresponds to the crystallization at the liquidus temperature. At lower temperatures, especially near T_g, there may be limitations resulting from the insufficient mobility of some of the components forming the glass network.

Glasses with the aluminophosphate-silicate network, i.e. containing network-formers with various chemical properties, capable of combining with the modifiers to form various compounds, have been chosen as models in investigations of multistage crystallization.

Glasses containing SiO_2 and $AlPO_4$ as the network-forming components, and Na, Ca and Mg as modifiers, were studied. Stable glasses of such composition are formed when the proportions between the network components and cation modifiers fall within appropriate and narrow ranges of values. A Na_2O content of more than 15 mol.% is necessary to obtain the mixed network SiO_2–$AlPO_4$ glass in the Na_2O–Al_2O_3–P_2O_5 system. During the crystallization of $AlPO_4$-rich glass the tridimite or cristobalite modification of $AlPO_4$ is formed, while later $NaPO_3$ crystals appear in a glassy matrix. Increase of the SiO_2 and decrease of the P_2O_5 content causes the $NaPO_3$ to disappear, and $AlPO_4$ becomes the only product of crystallization. Replacement of Na_2O by CaO increases the ability of glass to crystallize. Glasses containing 10 mol% of Na_2O and 20 mol% or more of CaO start to crystallize with formation of the $AlPO_4$ cristobalite modification; later, $Ca_3(PO_4)_2$ and apatite crystals grow around aluminium phosphate crystals. When Na_2O is replaced by MgO, the cristobalite modification of $AlPO_4$ and next $Mg_3(PO_4)_2$ crystallize in these glasses.

As an example, the bulk crystallization of glasses in the Na_2O (8 mol%)–MgO (20 mol%)–$AlPO_4$–SiO_2 system starts near the glass transformation temperature (650°C) and aggregates of small, rounded grains of the $AlPO_4$ cristobalite modification are formed. At a slightly higher temperature, needles of $Mg_3(PO_4)_2$ crystallize. Above the glass-softening temperature (about 900°C), $Mg_3(PO_4)_2$ crystals dissolve in the glassy matrix and $AlPO_4$ recrystallizes into well-shaped dendritic crystals. Glass containing more Al_2O_3 than the corresponding formula $AlPO_4$ crystallizes with the formation of corundum (Al_2O_3) and $Mg_3(PO_4)_2$ crystals in a glassy matrix [15].

Partial substitution of MgO by CaO changes the crystallization sequence. Glass containing $8Na_2O$, 8MgO, 9CaO, $20Al_2O_3$ and $38SiO_2$ (mol%) crystallizes above 650°C (T_g) and $AlPO_4$ and $Ca_3(PO_4)_2$ and next $Ca_7Mg_2P_6O_{24}$ are formed. Above the glass-softening point (900°C), Ca, Mg-phosphate disappears, and $AlPO_4$ and $Ca_3(PO_4)_2$ recrystallize.

Glasses from the K_2O (10 wt.%)–CaO (20 wt.%)–MgO (x)–SiO_2 (y)–P_2O_5 (15–20 wt.%) system start to crystallize at the glass transition temperature and Ca-phosphate (whitlockite or apatite) is formed first. Forterite (Mg_2SiO_4) crystallizes next. Afterwards, above the softening temperature, kaliophyllite ($KAlSiO_4$) crystallizes in the remaining glassy matrix.

Attempts have been made to establish to what extent the formation of compounds occurring during the multistage crystallization of the examined glasses is determined by the chemical affinity of the reactants, expressed by the Gibbs free energy of their formation. Since the formation of these compounds takes place in a homogeneous medium, such as the glass structure, due to the absence of crystallographic ordering, it has been assumed that the substances crystallizing in the glass are formed in a reaction between the appropriate oxides. This assumption represents a good model of crystallization near the liquidus temperature. At lower temperatures, especially near T_g, there may be considerable deviations from such a simplified mechanism, resulting from the insufficient mobility of certain components, particularly those present in the glass network.

The values of the Gibbs free energy (ΔG) of the reactions of synthesis of the respective compounds are listed in Table 2. These data refer to standard conditions. Calculation of the changes in these values with temperature was not possible because of the lack of adequate thermodynamic data. From the available data, it follows that for the components under consideration the effect of temperature on the ΔG reaction values is so small that the proportions between them practically do not change.

Table 2 Free energy (ΔG) of synthesis of compounds crystallizing in glass from oxides

Compound	ΔG for standard conditions/	
	kJ mol^{-1}	kJ mol^{-1}per PO_4^{3-} group
$AlPO_4$	−152.30	
$Mg_3(PO_4)_2$	−491.20	−245.60
$Ca_3(PO_4)_2$	−709.60	−354.80
Na_3PO_4	−546.43	
$CaSiO_3$, parawollastonite	−100.00	
Mg_2SiO_4, forsterite	−60.25	
$KAlSiO_4$, kaliophyllite	−250.62	

The ΔG values of the reactions of synthesis of compounds forming in the glass in the process of its crystallization per anion (PO_4^{3-} or SiO_4^{4-}) according to the formula of the given compound may be used as a measure of the chemical affinity between the cation modifier and the components of the glass network.

From the experiments carried out so far, it follows that in the process of the multistage crystallization of glasses, the particular compounds are usually formed in a sequence, beginning with those which are characterized by the most negative value of ΔG for the reaction syntheses, i.e. the greatest chemical affinity, and ending with the compounds with the highest value of ΔG for the reaction syntheses.

A comparison of the sequence of crystallization of the particular compounds in the glasses of various compositions presented above, with the ΔG values of their synthesis (Table 2), shows that the first to crystallize are not always those whose formation is associated with the most negative ΔG value, as might be expected.

In aluminophosphate-silicate glasses, $AlPO_4$ is the first compound to crystallize. Ca, Mg or Na-phosphates crystallize next, at higher temperatures, although the lower ΔG values suggest that they should be formed first, before $AlPO_4$.

Similarly, among the silicates, the first to crystallize in these glasses is forsterite, while kaliophyllite with considerably more negative ΔG values is formed at higher temperature.

These deviations from the sequence dictated by the ΔG values for the syntheses of the compounds show that chemical affinity is not the only criterion determining the sequence of crystallization in glasses. Deviations occur particularly at temperatures close to T_g, i.e. when the degree of disintegration of the glass network by thermal vibrations, as indicated by the high viscosity of the glass, is not great, and thus not all the glass components have been given sufficient freedom of displacement to be able to participate in the reaction of synthesis of new compounds.

When the glass structure contains two modifiers, e.g. Ca and Mg, the first to crystallize is the compound with the greater affinity for the respective component of the framework. The crystallization of $Ca_3(PO_4)_2$ is an example. When the content of this component (P_2O_5) is high enough, the next to crystallize is the compound containing both these modifiers ($Ca_7Mg_2P_6O_{24}$). The behaviour of sodium is different. It remains permanently bonded with SiO_2, forming with it a glassy fabric, in which the above-mentioned phosphates crystallize, in spite of the most negative value of ΔG being that for the synthesis of sodium phosphate, much lower than those of Ca and Mg-phosphates (Table 2) which are formed in it.

The cases presented here reveal the existence of deviations from the principle of the sequence of crystallization according to decreasing chemical affinity and increasing value of ΔG for the synthesis of compounds crystallizing from the components present in the glass.

The explanation of these irregularities should be sought in the characters and the strengths of the direct interactions between the components of the given glass, resulting from the nature of the bonds between them.

The concept of 'an intrinsic atomic affinity' between atoms as a result of the electrostatic attraction between their atomic cores or cations and the bonding electrons was introduced by Görlich [16]. Intrinsic affinity between two different atoms forming a heteromolecular compound is directly connected with the value of the ionicity i of the chemical bond. i is derived from the ionization energy of the chemical element [17]. It is closely related to the Pauling electronegativity, but is more precise in its physical meaning and describes the average interaction between electrons and the atomic cores of elements in compounds. The i value and the same intrinsic atomic affinity between cations and oxygen for the oxides decreases in the following sequence: K–O: 0.823; Na–O: 0.807; Ca–O: 0.707, Mg–O: 0.607, Al–O: 0.546; B–O: 0.476; Si–O: 0.428 and P–O: 0.314. The covalency of the bonds increases appropriately in the same direction.

Aluminophosphate-silicate glasses, used as model glasses in the investigations of multistage crystallization, have frameworks built up of $[SiO_4]$and $[PO_4]$

tetrahedra, joined by [$AlPO_4$] tetrahedra. Si and P oxides combine directly with difficulty on account of the significant differences in character of the chemical bonds. As a result, there occur pairs of [AlO_4] [PO_4] or $AlPO_4$ clusters. In such a framework, the P–O bonds have smaller ionicity and are thus more rigid than the Si–O bonds, so that they may reduce the flexibility of the framework, and in this way generate stresses which will cause its disruption. The [AlO_4] [PO_4] groups then released are ready to form $AlPO_4$ crystals, the structure of which is composed of such pairs of tetrahedra. Some of the liberated [PO_4] tetrahedra may combine with Ca and Mg to form phosphates of these elements.

Ca and Mg bonds with oxygen are characterized by high ionicity. Thus, being weaker and undirected they may give these elements the freedom of diplacement required to form compounds with the participation of [PO_4] tetrahedra even at a temperature only a little higher than T_g.

The alkali metals Na and K, which form bonds of highest ionicity with oxygen, do not form phosphates. They remain bound with silica, and together with it create a glassy matrix for the crystallizing phosphates. If aluminium is present in this matrix, aluminosilicates (kaliophyllite, leucite or nepheline) are formed at a temperature close to the liquidus. It can be assumed that, in the examined systems, silica together with alkali metals forms glasses with considerably flexible structures, which makes the amorphous state particularly stable; as a result, the alkali metals are retained in it and do not form crystalline compounds with phosphate. In this case, the factors of crystallochemical nature determine the preference of the alkali metals to form permanent bonds with silica.

It should be assumed that the particular flexibility of the silica framework with the participation of sodium is responsible for the fact that thermal vibrations cannot depolarize it to a degree allowing the crystallization of sodium silicate. Sodium silicate glasses crystallize when the ratio of Na_2O to SiO_2 is higher than in $Na_2Si_2O_5$. The high concentration of Na_2O then becomes the factor inducing depolymerization of the silica framework to a degree permitting the crystallization of silicates.

It should be noted that similar behaviour of sodium can be observed in borate-sodium-calcium glasses. In the course of the crystallization of these glasses, calcium borates are formed first, and Na_2O combines with B_2O_3 to give an amorphous glassy structure. Thus, B_2O_3 behaves similarly to SiO_2. The B–O bond has an ionicity of 0.476, which is very similar to that of the Si–O bond. This fact is probably responsible for these similarities.

Final remarks

Flexibility has been found to be a specific characteristic of many substances. It represents the cumulative effect of the interactions of the atoms participating in the formation of the given structure. The degree of structure flexibility exercises a significant effect on the progress of thermochemical processes occurring in it and on the mode in which the state of phase equilibrium is attained with temperature increase. In particular, flexibility is the essential factor determining the formation and stability of amorphous structures.

The study of the flexibility of the given structure and of its influence on the thermal processes is made possible through crystallochemical analysis of the natures of the bonds between the components of this structure. It represents an approach complementary to the thermodynamic and kinetic investigation of the thermal processes in solid bodies.

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