

Crystallochemical aspects of structure controlled processes in oxide glasses

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Nano size crystals formation in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2(\text{ZrO}_2)$ glasses as a structure controlled process is described. The applicability of the structure – chemical parameters for prediction and modelling of the middle range ordering in glass as a nanocrystals precursor are presented.

Keywords: oxide glasses, middle range structure ordering, nano-crystallization, glass-ceramics.

1. Introduction

Oxide glasses, mainly those of the polymeric structure, like silicate, borate and phosphate glasses, and mixed network glasses, like alumino-silicate, boro-silicate, phospho-silicate glasses or other three and more network-formers containing glasses have a unique ability to include into their structure a wide range of chemical components. The components which do not form stable chemical compounds can coexist together in oxide glass structure. Oxy-nitride, oxy-halide, oxy-chalkogenide glasses are the examples. Chemical components of the glasses are joined together by the oxygen atoms forming oxygen bridges, and the glass structure can be regarded as a net of the oxygen bridges. Thanks to the ionic-covalent character of oxygen-cation chemical bonds, the oxygen bridges are strong and flexible, and oxide glasses have high stability and are able to incorporate into their structure a considerable quantity of different components. This property makes them a host for radio-nuclides; that is why borosilicate glasses are used as immobilizers of waste from atomic power stations.

According to the standard Zachariasen–Warren concept, glass structure is a uniform, homogeneous construction build of network formers and modifiers. The differences in the mutual chemical affinity of components cause that the distribution of multicomponent glasses in the structure is not uniform. Due to this fact, the chemical components group together according to their affinity.

According to GALLENER *et al.* [1], a short range and a middle range ordering can be distinguished. The short range ordering is represented by coordination polyhedra formed by the cation and the surrounding anions. Their composition and shape are determined by the chemical affinity between the chemical elements and the directions of bonds in the polyhedron in the case of covalent and covalent-ionic bonds, and the charge in the case of glasses with ionic bonds. They are formed in accordance with the crystalchemical rules of PAULING [2] and GOLDSCHMIDT [3] for solid crystal bodies and transferred to glass by DIETZEL [4, 5]. The middle range ordering is characterized by the presence of a complex of polyhedra in the form of clusters, occasionally in the form of chains or rings. In glasses with mixed network, their chemical composition may vary. It is determined by the chemical affinity of the components the measure of which, according to PRIGOGINE and DEFAY [6], is the value of free enthalpy of interaction between them.

The loose, flexible, amorphous structure of glasses gives to chemically different species the freedom of grouping into combinations, even such that are rarely found in crystalline structures. This causes that the middle range ordering assemblages of atoms need not be analogs of the elements of the structure of the crystalline equivalent to a given glass. In literature there can be found many descriptions of middle range groupings in glasses. The structure of phospho-silicate glasses is here the example [7].

Middle range order groups have an influence on the properties of glass and create some specific phenomena. Rare earth elements incorporated in the middle range groups in oxy-fluorine glasses give a fluorescence effect making them optically active materials which have many applications in optoelectronics [8, 9].

An important group of nanosize crystalline glasses are optically transparent materials with a zero value of the thermal expansion coefficient [10], which are used among other things in large telescope mirrors, plates of kitchen ceramic electrical heaters [11]. In these materials, the nanocrystalline phase is SiO_2 solid solution of a high temperature quartz structure, stuffed with Li, Mg and Al atoms (high-quartz s.s.). Transparent glass-ceramics is perceived as comprising a perspective group of materials possessing specific optical, magnetic and electrical properties [12]. At present, glasses containing dispersed dots of sub-wavelength dimensions, down to a few nanometers, in the form of noble metals nanoparticles or nanometric size crystals, are an object of special interest in modern optical technology [12, 13]. The crystallization of these dots and their spatial distribution, necessary for their application in integrated optics, is induced through laser irradiation of the glass and successive annealing [14, 15].

Laser induced crystallization techniques may be used for the patterning of nanocrystal lines consisting of nonlinear optical ferroelectric and ion or electron conducting crystals. Crystal lines fabricated by laser irradiation consist of an assembly of crystals oriented along the lines of crystal growth directions. It is possible to write in glass two-dimensional crystal bending or curved line lines by changing the laser scanning direction [15].

These processes are termed a control structure technology, which is based on the control of short distance interactions of components in glass and on the supramolecular groups self-organization to trigger off nanosize hetero-phase separation. Periodic and aperiodic two- or three-dimensional structures formation, three-dimensional optical and electric circuits of high accuracy drawing.

The application of crystallochemical parameters as an indirect criterion and a measure of short range interactions is proposed. Crystallochemical modelling of the middle range ordering in glass, clusters composition, and the prediction of nanocrystals formation is the subject of this study.

2. Middle range order clusters as nanocrystals precursors

The presence in the glass structure of middle range ordering and chemically different local structures should influence the glass crystallization process and kinetics of a newly formed crystal phases, especially near transformation temperature T_g .

A relation between middle range ordering and nanocrystals formation was studied on the example of the glass elaborated by PINCKNEY and BEAL [16] with a well described crystallization process. The glass has the following composition: 47.1SiO₂, 22.0Al₂O₃, 16.9MgO, 1.7ZnO and 12.3TiO₂ wt%. In experiments, TiO₂ was substituted by ZrO₂ and ZrO₂ + TiO₂ mixture. The glasses were obtained by melting the mixtures of chemical grade purity oxides in Pt20Rh crucibles at 1520 °C. The melt was cast on a steel plate of 6 mm thickness to vitrify. Crystallization was studied using pieces of these glasses heat treated at different temperatures for 4 hours.

Crystal phase formation in glass at increasing temperature was investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The early stages of crystallization were studied using high resolution transmission electron microscopy (HRTEM) and EDAX, in order to determine the character and size of nanocrystallites; the investigations were carried out at the Silesian University in Katowice (Poland). The results are presented in Tab. 1. A detailed description of the crystallization mechanism can be found in [17].

These investigations were complemented later by EDAX determination of the chemical composition of phases formed at an early stage of crystallization. The relative accuracy of the determination of components content by EDAX is $\pm 0.5\%$. The results are presented below.

The model glass structure rebuilding has several stages (Tab. 1) and starts at 650 °C as a change of colour from yellow-brown to dark blue. Raman spectroscopy has revealed a supramolecular groups formation in the glass. Some of them have an anatase (TiO₂) structure; moreover, two types of groups of weakly ordered structure, probably anasovite (Ti₂O₃, TiO₂), have been found [18].

Glass nanocrystallization begins near the T_g temperature. There appear crystal phases of 3–10 nm diameter, of structure detectable by XRD and electron diffraction methods, namely (Mg,Al)-titanate and a high-temperature form of quartz stabilized with admixtures of various elements, called high quartz solid solution (high quartz

Table 1. Glass 47SiO₂22Al₂O₃17MgO2ZnO12TiO₂ (wt%) crystallization.

650 °C	TiO ₂ /Ti ₃ O ₅ (anatase/anosovite)	Pre-crystallization stage
750 °C	T_g	
	MgTi ₂ O ₅ -Al ₂ TiO ₅ (s.s.) - I	
750-825 °C	SiO ₂ -(Al,Mg,Ti) (s.s.) (high quartz) Glass	T_g -(visco-elastic state) nanocrystallization stage
825-950 °C	SiO ₂ -(Al,Mg,Ti) (s.s.) (high quartz) MgAl ₂ Ti ₃ O ₁₀ - II	
950-1100 °C	MgAl ₂ Ti ₃ O ₁₀ , MgSiO ₃ (clinoenstatite), Mg ₂ SiO ₄ (forsterite) Glass	Recrystallization stage
1100-1200 °C	Mg ₂ Al ₃ [AlSi ₅ O ₁₈] (indialite/cordierite), MgAl ₂ Ti ₃ O ₁₀ MgSiO ₃ (clinoenstatite), Mg ₂ SiO ₄ (forsterite)	T_L - liquidus crystallization stage

Table 2. Chemical composition of crystallite, examples (at%).

	High quartz s.s.	Mg titanate	SiO ₂ -TiO ₂ s.s
Si	98	—	44
Ti	1	41	46
Mg	0.5	50	0.5
Al	—	—	10
Zn	0.5	8	—
O	omitted		

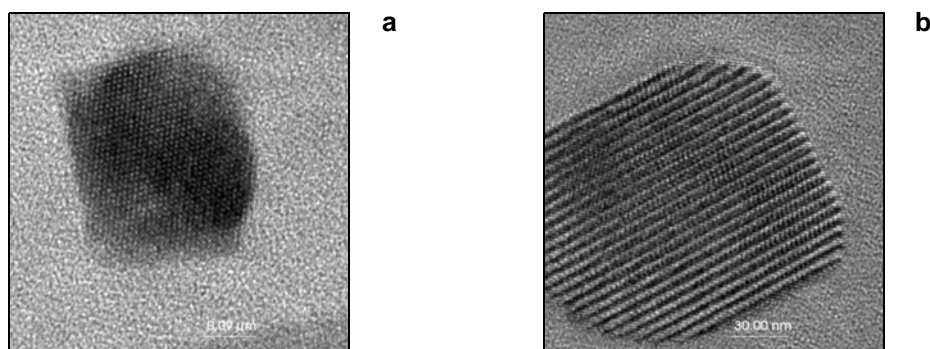


Fig. 1. HRTEM images of high quartz s.s. (a) and (Mg,Al)-titanate (b) crystals, formed after heat treating of glass at 800 °C for 4 hr.

s.s.). At above 825 °C bulk crystallization occurs. It consists in nanocrystals growth and recrystallization. The content of the quartz-like phase increases and it becomes the main crystal component, while the amount of titanate decreases. With further temperature increase, the liquid phase appears again and high quartz s.s. recrystallizes. Its structure is ordering, structural admixtures are removed and crystallizes as a well shaped crystals of Mg-titanate of II generation. Near 1000 °C high quartz s.s. disappears, the magnesium silicates (clinoenstatite and forsterite) crystallize, and successive crystallization in the melt takes place with formation of indialite or cordierite.

Nanocrystals formed near 825 °C are large enough to determine their chemical composition by EDAX (Fig. 1). About 100 of such crystallites were investigated. Their crystal structure has been confirmed by electron diffraction. The chemical composition of crystallites is listed in Tab. 2. EDAX shows that the chemical composition of nanocrystals, even the neighboring ones, is different. High-quartz s.s. crystallites represent about 45% of the examined crystallites. About 35% of them are the (Mg, Al)-titanate crystallites. The rest, about 24%, are the crystallites of solid solutions from the series $\text{SiO}_2\text{-TiO}_2$; the remaining 1% are the magnesium silicates and TiO_2 crystallites with admixtures of glass components in the structure.

The replacement of TiO_2 by ZrO_2 (5 wt%) changes the progress of crystallization and T_g temperature increases to 794 °C. Crystallization begins at 925 °C and baddeleyite (ZrO_2) appears. They react with the surrounding glass, forming ZrSiO_4 as an outer layer of the ZrO_2 grain. Around these grains, at about 1000 °C, spontaneous crystallization of large cordierite crystals takes place.

Glass activated by TiO_2 (7 wt%) and ZrO_2 (5 wt%) addition begins to crystallize stepwise, starting from the T_g temperature (749 °C). A net of large needles is then formed, which are crystals of the solid solutions ZrO_2 and TiO_2 of the composition changing within the range from $5\text{TiO}_2\cdot\text{ZrO}_2$ to $3\text{ZrO}_2\cdot\text{TiO}_2$.

At the beginning, crystallization of the examined glasses in the applied experimental conditions leads to the formation of crystallites of various composition, such as Mg-titanates, high quartz s.s. TiO_2 and SiO_2 or ZrO_2 solid solutions. They evidently correspond to middle range order clusters as precursors of nanocrystals. The nanocrystals are formed by small rearrangements of the clusters and/or diffusional income of the components from outside the network to a degree determined by great viscosity at the temperature of transformation (10^{15} Pa·s), limiting the mobility of the components. Accordingly, as the first there are formed the phases which are close to the primary structure and to the chemical composition of the parent glass structure, as it has been established. They are usually metastable phases. With increasing temperature and mobility of the chemical components, they become rearranged into phases closer to the equilibrium state, determined by the position of the glass composition on the respective phase equilibria diagram. High quartz s.s. formation is the example. To emphasize the specificity of this mechanism of nanocrystals formation, which is different from liquid melt crystallization, the term “crystal structure organization” is used here.

The results also indicate that the crystallization process can be modified by introducing to glass the components modifying the middle range ordering by partial substitution of crystallization activators as TiO_2 by ZrO_2 . It can be an example of the structural control of nanocrystallization process.

3. Crystallochemical factors and short range interactions in oxide glasses

In nanocrystallization by the reorganization of the existing middle range ordering can participate those components of glass, which at given temperature are free enough and mobile to change their position in the parent amorphous structure and build the crystal lattice of a new compound. Consequently, one of the factors limiting the kinetics and order of a new phase formation should be the rate and progress of a brake down of the parent glass structure dependent on the strength of oxygen and electropositive element bond or oxide bridges strength.

The term “bond strength” was introduced into the structural chemistry of glass by DIETZEL [4, 5]. The cation field strength $F = z/a^2$ (z – cation charge, a – anion–cation distance) is the measure of the chemical bond strength. This parameter is derived from a lattice energy formula, where the main parameters are the ions electric charge and anion–cation distance ratio; lattice energy is the energy required to decompose the solid into atoms and separate the atoms by infinite distance. Value F allows to predict numerous properties of glasses.

The ionic potential $f_i = z/r$ possesses similar applications. For network formers $f_i > 10$ but for modifier $f_i < 2$.

Cations disturb the uniform charge distribution of neighbouring oxygene atoms (polarizing effect) relatively to their field strength value. The oxygen volume in

Si–O–Si bridge is $6.16 \times 10^{-10} \text{ m}^{-3}$, in Si–O–Ca; $7.49 \times 10^{-10} \text{ m}^{-3}$ but for weaker cation Na^+ is Si–O–Na; $7.92 \times 10^{-10} \text{ m}^{-3}$ [19].

The heat of formation of oxides and some salts, plotted against ionic potential z/r , is located along two crossing lines. Two crossing branches are also encountered in fusion temperatures of oxides, latent heat (enthalpy) of fusion of oxides in correlation with field force z/a^2 . This peculiarity has been noticed by VOLF [20] and termed "V-phenomenon".

The V-phenomenon is distinctly manifested in thermal expansion, surface tension, viscosity, modulus of elasticity, thermal expansion, and several other properties of glass.

The lowering of the fusion point of pure SiO_2 as a solvent for MeO oxides, indicated by liquidus lines in SiO_2 –MeO phase diagrams and expressed as $\Delta T/n_2$, where $\Delta T = T_s - T$, and T_s – fusion point temperature of SiO_2 , T binary eutectics temperature and n_2 – the molar fraction of the dissolved component MeO related to the ionic potential $f_i = z/r_i$ of its cation. The plot consists of two branches, the first one for oxides chemically more basic than SiO_2 ($z/r_i > z/r_{\text{Si}}$) and the second one for more acidic than SiO_2 ($z/r_i < z/r_{\text{Si}}$) (Fig. 2) [20, 21].

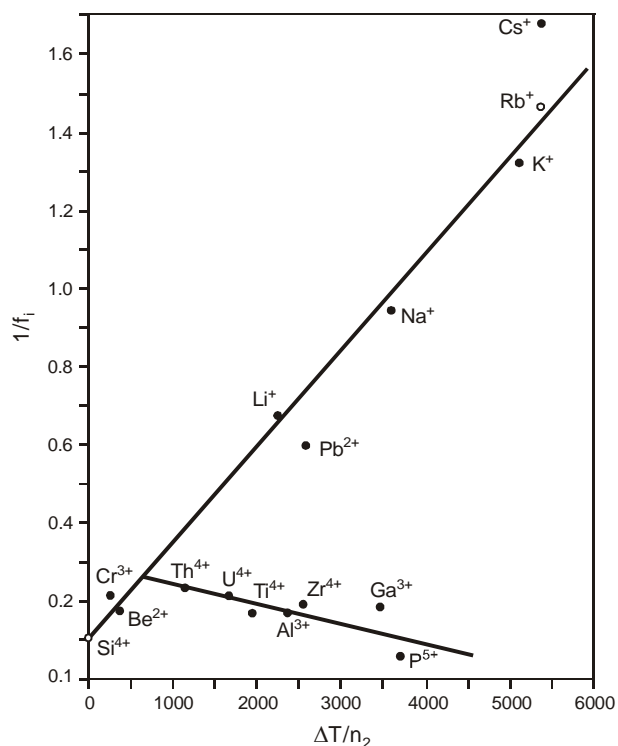


Fig. 2. The V shape dependence of liquidus temperatures in SiO_2 –MeO phase equilibria diagrams and ionic potential of cations (f_{Me}).

The position in the diagram indicates the degree of weakening of the oxide bridges by a given cation and depolymerizing of SiO₂ network activity. The slope of the lines in the diagram indicates that it is higher for basic as compared with acidic cations.

In the case of crystallization of glasses, especially near T_g , it is helpful to consider the influence of factors of the structural-chemical nature characterizing short distance interactions. It would make it possible to anticipate the middle range ordering formation course of the destruction of the primary structure of the glass, which determines the order of formation of the crystal structures.

In the present study, the usability of structural-chemical modelling in the investigations of the middle range ordering of polycomponent glasses and its role in the nanocrystallization are demonstrated on the example of the studied TiO₂ activated glass.

A simple chemical-structural parameter, defining the character and the strength of the cation-oxygen chemical bonds, is the ionicity of these bonds.

Oxygen atoms in glasses behave like Lewis bases and the transfer of part of their negative charge to cations [22] takes place. The ability of an oxygen atom to transfer the negative charges is the highest when it is situated in the surroundings of weak cations as, *e.g.*, the alkalis. If it is combined with the cation by a strong bond, as in the [SiO₄] tetrahedra or other tetrahedra of the network forming components, the acidity of oxygen is smaller and the possibility of transferring part of the charge to the mutual cation is also smaller. The acid-base interactions determine simultaneously the mutual chemical affinity between the components, which is the greater, the more different is their basicity. According to BALTA [23], a difference in ionicity of oxides is a measure of the strength of acid–base interaction between them.

Pauling's electronegativity X_p [2], as a measure of the ability of an atom to attract electrons, is generally used in structural chemistry. The X_p value is calculated from ionization energy (in eV), it is the energy required to detach an electron from an atom or an ion and transfer it to infinite distance. Ionization energy corresponds to the energy of the attraction of the nuclear charge. It helps to estimate the strength of the cation-oxygen chemical bond and the degree of ionicity of the bonds. For example, the ionicity value of Si–O and Na–O calculated from X_p are 41% and 70%, respectively.

In the presented study, Görlich's ionicity i_G as based on *a recent concept of chemical bonds*, was used [24]. Görlich's ionicity i_G is calculated from the effective nuclear charge of an atomic core, defined as $Z_{\text{eff}} = \sqrt{I'_\nu}$, where I'_ν is the ionization energy in the Rydberg units, needed to remove the ν valence electrons from an atom. Its values are closely related to Pauling's electronegativity. The relative difference of the nuclear charge of the two bonding atoms constitutes the factor determining the ionicity of the heteropolar bond. The ionicity i_G or the asymmetry of the chemical bonds between different atomic cores or ions, as a cation–oxygen bond, is defined by the relation $i_G = (1 - Z_{\text{eff}1}/Z_{\text{eff}2})$, where $Z_{\text{eff}1} < Z_{\text{eff}2}$. The intrinsic affinity between two different atoms forming a heteronuclear compound is directly connected with the value of ionicity of a chemical bond.

Another parameter is the “localisation of the bonding electron” $L = \bar{Z}_{\text{eff}} = \sqrt{Z_{\text{eff}1} \cdot Z_{\text{eff}2}}$. Its value increases with the covalence of the bonds with oxygen. This parameter has been accepted as a measure of rigidity of the bonds.

The increase in the proportion of the non-directional ionic bonds makes the structure flexible. The increase in the covalence of chemical bonds makes the structure more rigid, but simultaneously increases its strength. Ionicity of modifiers of the silicate glasses decreases in the following order $K > Na > Ca > Mg$. Network formers have ionicity below 0.500 and it decreases in the direction $Al > B > Si > P$.

As a measure of the strength of oxygen bonds, it is proposed to accept the difference in the value of i_G of the bonds with the oxygen of the cations joined by this oxygen (Δi_G). The difference in the value L between these bonds (ΔL) is here a measure of the internal strains in the oxygen bridges with the predominance of nonflexible, covalent bonds. The difference in the i_G values (Δi_G) also supplies information in this case.

Using these parameters, it is possible to draw up a scheme of the local interatomic interactions in the structure of the particular glass and to indicate the weakest

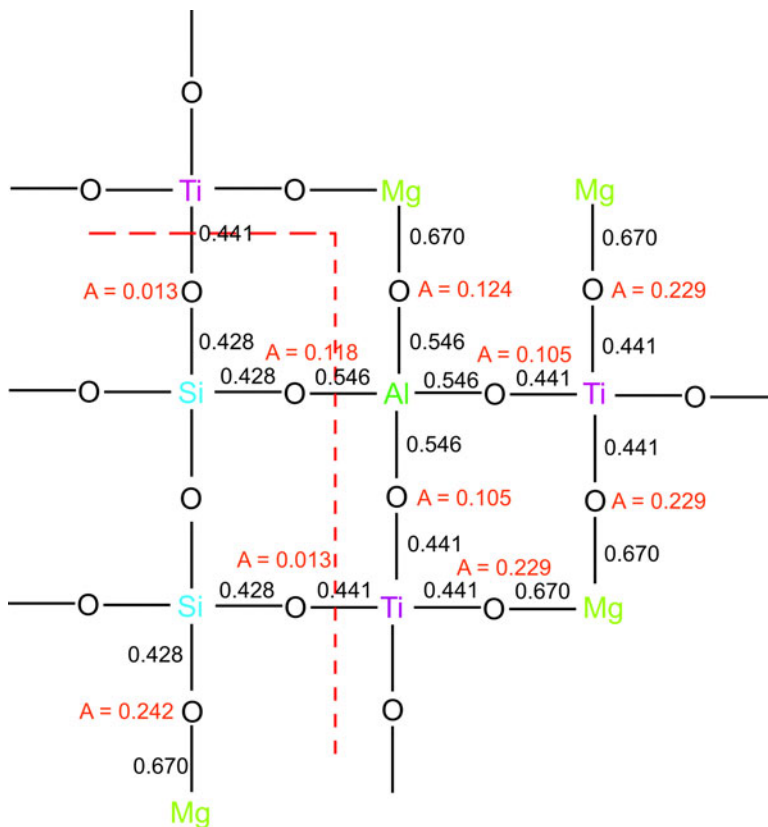


Fig. 3. Scheme of short distance interactions in the structure of $SiO_2-Al_2O_3-MgO-TiO_2$ glass (after [25] actualized). Explanation in the text.

oxygen bonds in the solidified glass, through the cracking of which in molten glass there can be formed clusters or middle range order groups. They can be initiators of the nuclei of the crystal phases formation (Fig. 3). The difference in the ionicity of Δi_G of the cation–oxygen bonds, composing a definite bridge, is simultaneously the measure of the local chemical affinity A of the cations to the bridging oxide and the measure of the acid-base interactions within the area of the bridge. In the case of Me–O–Si bridge, $A = \Delta i = i_{\text{Me-O}} - i_{\text{Si-O}}$.

In the case of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--TiO}_2(\text{ZrO}_2)$ glass, it can be assumed that the oxygen bridges binding with each other the cations whose bonds with oxygen have a large proportion of covalency, thus high acidity, such as Ti–O–Si, $\Delta i = 0.013$, Zr–O–Si, $\Delta i = 0.075$, make the bridge rigid and induce stresses in it, which reduces its strength. This may be responsible for their cracking and the release of Ti already at the temperature T_g , which thanks to it can participate in the formation of its own compounds. The bond Mg–O–Ti has $\Delta i = 0.229$ and it is higher than that for the bridge Mg–O–Si, $\Delta i = 0.179$, at the same time it means a larger affinity of MgO to TiO_2 than to SiO_2 which is strongly bound in the framework, causing thereby that magnesium titanate and high quartz s.s. are formed at a lower temperature, prior to magnesium silicate. It confirms and explains the nanocrystallization mechanism suggested by HRTEM and EDAX results.

4. Final remarks

In the modern structure controlled technology of nano-materials, based on the modifying of short distance interactions, crystallochemical parameters are a useful tool for new materials designing.

The analysis of the value and distribution of the ionicity/covalency of chemical bonds, as a measure of local chemical affinity of components joined by oxygen, and the strength of bridges, has made it possible to predict the middle range grouping in the structure of oxide glass and its influence on the crystal phase formation.

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