

# Real glass crystallization high resolution electron microscopy (HREM) study and classic nucleation theory concept

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Formation of crystal phases in glass and the kinetics of the crystal growth are commonly interpreted on the basis of classical nucleation theory (CNT), a thermodynamic description of the formation and growth of clusters of atoms (nuclei) of a new phase in heterogeneous system. The high resolution electron microscopy (HREM) has been used to recognize this clusters (nuclei) formation, their nature and structure. The atomic scale mechanism of the formation of the crystal phase structure within the disordered structure of glass near the temperature  $T_g$  was studied. HREM and other methods of the early stages of crystallization of the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  glass studies, with  $\text{TiO}_2$  as a crystallization activator, revealed that glass crystallization can be realized directly through rearrangement of the parent glass structure elements as disorder-order transformation. Its mechanism is similar to the solid solution decomposition or polymorphic transformation. However in the glass with  $\text{ZrO}_2$  admixture, crystallizing in a liquid state, the mechanism of crystal phase formation is different. Zirconia  $\text{ZrO}_2$  particles precipitate and cordierite crystals are growing on them. Validity of CNT for describing the near glass transformation temperature  $T_g$  crystallization and nano glass ceramics formation appears disputable. Alternative way of explaining this process is proposed.

Keywords: glass, glass crystallization, nucleation mechanism, glass-ceramics.

## 1. Introduction

The knowledge of the transition process of amorphous, disordered structure of glass into crystalline structure is important as the basis for obtaining glass-ceramic materials. It is traditionally accepted that glass crystallization proceeds as the crystallization of a liquid through nucleation and crystals growth, preceded by glassy state phase separation [1, 2]. The investigations of several kinds of glasses (silicate, borate, phosphate and of mixed network) have shown that such a mechanism is true when crystallization occurs near the temperature of liquidus when the viscosity is low. However, near the temperature of the glassy state transformation ( $T_g$ ), the glass properties and its structure are close to those characteristic of glass as a rigid solid body, the mobility of chemical components is low and it is greatly differentiated,

among others, depending on the cation size and the strength of the chemical bonds between the cation of the given component and the glass framework. This changes the crystals formation mode [3–5].

The atomic mechanism of crystallization in the range of low temperatures is not sufficiently recognized. Investigations of the crystallization of various glasses with increasing temperature suggest that low temperature crystallization of glasses may take place also through the rearrangement of the glass structure elements [5]. Metastable, intermediate phases of defected structure are then formed and next their composition and structure are rebuilt with the temperature increase. Glass crystallization as such a process can be considered as disorder-order transition, analogous to the mechanism of the decomposition of solid solutions in the crystal phases or the polymorphic transition of solids [5].

Demonstration of the formation of the crystalline phases within the glassy matrix, the mode of the ordering of its structure, especially in the initial stages of crystallization of nanocrystalline glass-ceramic materials is the subject of the present study.

The study was based on the model glass crystallization processes; they are: heterogeneous crystallization in glass from  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$  system, activated with  $\text{TiO}_2$  and  $\text{ZrO}_2$  admixture and homogeneous crystallization in  $\text{SiO}_2\text{·BPO}_4$  glass. Their crystallization is not preceded by an amorphous phase separation.

Near  $T_g$  temperature crystallization of some glasses allows us to obtain materials containing nanosize crystalline phases, what creates new important properties, particularly optical transparency. Important representative of this group is ZERODUR (Schott Company), transparent material of zero value of thermal expansion coefficient, used among others for large telescopes mirrors and colored by  $\text{V}_2\text{O}_5$  for infrared absorption as ceramic plates in kitchen electric heaters. In these materials a nanocrystalline phase is  $\text{SiO}_2$  solid solution (s.s.) of high temperature quartz structure, stuffed with Li and Al atoms. Transparent glass-ceramics is considered as a perspective group of materials possessing specific optical, magnetic and electric properties. Recent publications report that nanometric glass-ceramics is of interest as an ultra transparent, optically active material for photonics and also for magnetic and ferroelectrics applications, as well as materials of high mechanical and chemical resistance for data storages and other applications [1–3, 5].

## 2. Experimental

Glass elaborated by PINCKNEY and BEALL [6] of well described crystallization process was selected as a model glass for heterogeneous crystallization investigations. This glass allows us to obtain tough nanocrystalline glass-ceramics; it is of the composition (wt%): 47.1  $\text{SiO}_2$ , 22.0  $\text{Al}_2\text{O}_3$ , 16.9  $\text{MgO}$ , 1.7  $\text{ZnO}$  and 12.3  $\text{TiO}_2$ . Crystallization activating component  $\text{TiO}_2$  was substituted by  $\text{ZrO}_2$  and  $\text{ZrO}_2 + \text{TiO}_2$  mixture. Chemical composition of these glasses was as follows (wt%): 47  $\text{SiO}_2$ , 22  $\text{Al}_2\text{O}_3$ , 17  $\text{MgO}$ , 2  $\text{ZnO}$ , 12  $\text{TiO}_2$  (glass G-“0”), 51.0  $\text{SiO}_2$ , 24.0  $\text{Al}_2\text{O}_3$ , 18.0  $\text{MgO}$ , 2.0  $\text{ZnO}$ , 5.0  $\text{ZrO}_2$  (glass G- $\text{ZrO}_2$ ) and 47  $\text{SiO}_2$ , 22  $\text{Al}_2\text{O}_3$ , 17  $\text{MgO}$ , 2  $\text{ZnO}$ , 7  $\text{TiO}_2$ , 5  $\text{ZrO}_2$  (glass G- $\text{TiO}_2 + \text{ZrO}_2$ ).

Glass of the composition corresponding to the formula  $BPO_4 \cdot SiO_2$  was the model for homogeneous crystallization investigation.

Glasses were obtained by melting mixtures of chemical grade purity oxides in Pt20Rh crucibles at  $1520^\circ C$ . The melt was cast on a steel plate of 6 mm thickness to vitrify. Crystallization was studied using samples of these glasses heat treated at different temperatures for 4 hours.

Crystal phase formation was investigated by the differential scanning calorimetry (DSC) and differential thermal analysis (DTA) at the heating rate of 10 K/min, temperature measurement accuracy 1 K. The phase composition of crystallized glass was investigated using X-ray diffraction (XRD), and scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) as well as transmission electron microscopy (TEM). The observations were carried out at the Institute of Metallurgy and Materials Science of the Polish Academy of Science in Kraków. The early stages of crystallization were investigated using high resolution transmission electron microscopy (HREM) in order to determine the character and size of nuclei, followed by studies of later stages using SEM, TEM, and EDS. HREM observations were carried out at Eidgenössische Technische Hochschule in Zürich and in Silesian University in Katowice. The thin foils of heat treated glass samples were prepared by dimpling followed by ion milling.

### 3. Results

The DTA measurements of G-“0” glass indicate that the dense, bulk crystallization starts at the temperature of  $820^\circ C$ , what is marked by the beginning of the exothermic effect of crystallization, and reaches the maximum at  $869^\circ C$ ; the second stage of crystallization takes place at  $935^\circ C$  and a third at  $1204^\circ C$  (Fig. 1).

XRD investigations have revealed that first crystals are formed at  $T_g$  ( $725^\circ C$ ), where the lines of the (Mg, Al)-titanate and high temperature quartz solid solution containing Mg, Al, Ti substitutions (high quartz s.s.) appear. The higher the heating temperature of the glass, the stronger is the characteristic line of high quartz s.s.

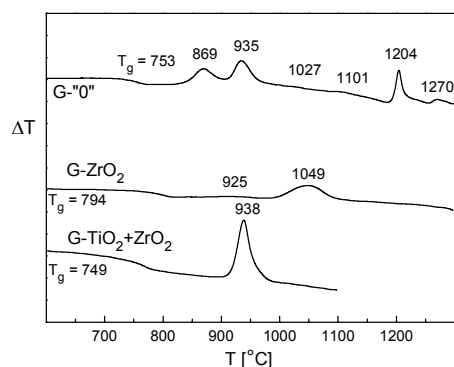


Fig. 1. DTA curves of  $SiO_2-Al_2O_3-MgO-(TiO_2, ZrO_2)$  glasses.

(3.44 Å), and above 825°C, there is the main crystal phase. Above 1000°C, cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) crystallizes.

Investigations of the initial stage of glass crystallization by TEM and electron diffraction, earlier described [5, 7], have confirmed the formation of dendrite aggregates about 10–100 nm in size at 725°C. Moreover, irregular areas indicating the beginning of the formation of another crystalline phase could be observed around them. At 750°C they are much better developed and reach dimensions up to 100 nm. Prismatic crystals have been formed from the irregular areas [5].

Based on the chemical composition determined by EDS method, it has been stated that the prismatic crystals formed at 725° are phases with increased Mg and Al and small Ti (about 5 atom% and less) concentration in comparison with the surrounding glassy matrix. The Si concentration in them is changing with the temperature increase, reaching up to 70 atom%, which is accompanied by the reduction of Mg and Al content. This is an indication that they are crystals of a solid solution having the structure of high temperature quartz, containing varying amounts of Mg and Al and a small amount of Ti. It has been confirmed by XRD investigations. Formation of the high-quartz of similar composition in the  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--TiO}_2$  glass and its transition into low-quartz during cooling has been also described in [8].

The dendrites are characterized by a considerable amount of Ti (about 15 atom% larger than in the amorphous matrix) and Mg (about 20 to 30 atom% larger than in the amorphous matrix) with a rather small increase in Al concentration, which corresponds to titanate with the structure of a pseudobrookite ( $\text{Fe}_2^{3+}\text{TiO}_5$ ), containing Mg and Al substitutions instead of  $\text{Fe}^{3+}$ . The results of EDS point analyses are as follows (atom%): Si 29.9, Ti 15.3, Al 22.5, Mg 31.5, Zn 0.5. They are far from the theoretical compositions of Mg-titanate. The crystal phases emerging from the glassy matrix contain incorporated components forming the glassy matrix and may differ from their ideal composition.

Observation of the transition of the amorphous structure of the glass into a crystalline one was made possible by HREM study at  $10^6$  magnification. Figure 2 demonstrates the crystal phase formation by amorphous structure of glass rebuilding.

The formation of areas measuring up to  $5\times 20$  nm with ordered arrangement of atoms in the disordered structure of glass is visible there (Fig. 2a). The degree of the organization of the newly formed crystal structures is various, from low organized grouping of atoms (Fig. 2a) to fully ordered crystal lattice (Fig. 2b). There can be distinguished lattice planes with the distance of about 0.5 nm, corresponding to [020] plane of  $\text{MgTi}_2\text{O}_5$  phase. The phenomenon of immiscibility and drop-like liquation as the glass crystallization initiator, suggested in [2, 6, 8, 9] was not observed.

The two stage crystallization (800°C/2 h and 900–1000°C/4 h) leads to the fine-crystalline material with the grains of about 60–100 nm Mg, Al-titanate and high quartz s.s. containing Mg, Al, Ti substitutions. In the HREM image of this material, well developed grains of the titanate phase can be distinguished. They were formed by recrystallization of the aggregates of dendritic structure, which developed below 800°C at the initial crystallization stage. According to EDS they contain more Ti and

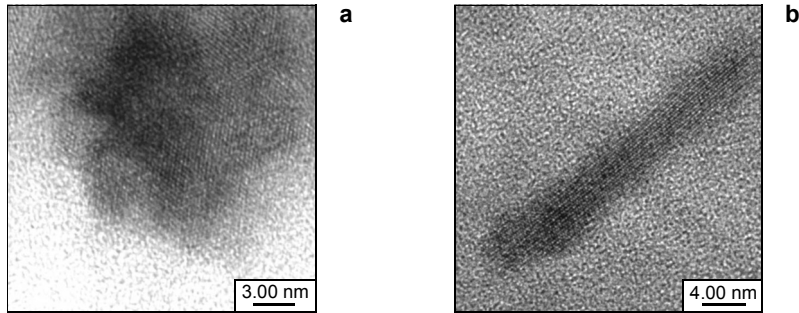


Fig. 2. Early stage of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$  glass crystallization (HREM image): ordering of the amorphous structure components and beginning of the crystal lattice formation, 725°C (a) and well shaped high quartz s.s. micro crystal, of well order lattice, 750°C (b).

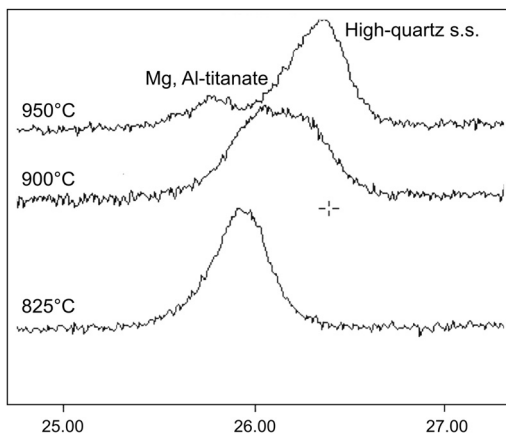


Fig. 3. Evolution of high quartz s.s. Change of XRD line with temperature, indicating recrystallization and Mg, Al-titanate component separation.

their composition is closer to the theoretical one in comparison with those formed at the earlier crystallization stage. They occur between the grains of the high quartz s.s.

The growth of the crystals occurs through incorporation of the atoms of the components from the surrounding glassy matrix. At the same time an exchange of components between crystals and glass is going. As a result with the temperature increase the chemical composition of crystals is closer and closer to the theoretical one. In titanates increasing Ti content, accompanied by decrease in Al and Si admixtures, is observed. In high quartz s.s.  $\text{SiO}_2$  content increases, Mg, Al and Ti are removed and participate in titanate recrystallization (Fig. 3).

There has been also attained the nanocrystallization of  $\text{BPO}_4$  (grain size 25–80 nm, see Fig. 4) in 50 $\text{SiO}_2$  and 50 $\text{BPO}_4$  (mol%) glasses to obtain glass-ceramics as a solder for corundum materials. Geometry of  $\text{SiO}_2$  and  $\text{BPO}_4$  structures are very similar (isotypic). HREM demonstrated that the initial stage of  $\text{BPO}_4$  crystallization is

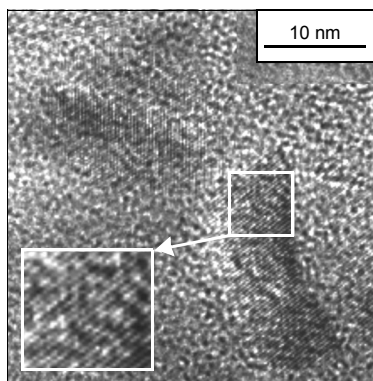


Fig. 4.  $\text{SiO}_2\cdot\text{BPO}_4$  glass crystallization by reassembling of the parent amorphous structure components, and  $\text{BPO}_4$  crystals formation, HREM image.

similar to titanate and high-quartz s.s. formation described above. It consists in local reorganization and ordering of the glass components (disorder-order transition) without the phenomenon of the glassy phase separation, which is usually regarded as indispensable to initiate the crystallization of glass.

To test the effect of the type of the nucleator on the ceramization process,  $\text{ZrO}_2$  was introduced replacing  $\text{TiO}_2$  ( $\text{G-ZrO}_2$ ) glass. Zircon ( $\text{ZrO}_2$ ) forms with  $\text{SiO}_2$  the orthosilicate  $\text{ZrSiO}_4$  (mineral zircon), however, very limited amounts of it can be incorporated into the structure of silicates and the silicate glasses.

It was introduced in the amount of 5 mass%, as in greater amounts it crystallizes as  $\text{ZrSiO}_4$ , already in the course of glass melting. The replacement of  $\text{TiO}_2$  by  $\text{ZrO}_2$  increase the  $T_g$  temperature to  $794^\circ\text{C}$  and crystallization temperature (Fig. 1). There are two stages of crystallization. First stage is poor and shifted to  $925^\circ\text{C}$  and it is mainly surface crystallization. Bulk crystallization does not occur until at the second stage, within the range of  $1000\text{--}1100^\circ\text{C}$ , when glass viscosity is low enough.

At the first crystallization stage  $\text{ZrO}_2$  is formed, and cordierite at the second stage. Zr is not present in the composition of this silicate. The experiments indicate that zirconia crystallization activation is of physical character and consists in the formation of a surface on which there grow up crystals of magnesium alumino-silicate-cordierite. The stage of high-quartz s.s. formation is omitted and the glass ceramisation mechanism is different than in the case when it is activated by  $\text{TiO}_2$  admixture and starts at  $T_g$  temperature. Introducing  $\text{TiO}_2$  and  $\text{ZrO}_2$  diminishes the crystallization temperature, and high quartz s.s. and next cordierite are crystallizing. It means that  $\text{TiO}_2$  is the intrastructural admixture indispensable for the high quartz s.s. formation in  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$  glasses.

#### 4. Discussion

The results of performed investigations and earlier systematic studies have shown that the applicability of the traditional interpretation of crystal phase formation in

the glasses with the increase in temperature from  $T_g$  to liquidus temperature needs a modified approach.

Two terminal structural states of glass must be distinguished, which determine the mechanism of its crystallization. They are the solid body state to the visco-elastic state transition near the transformation temperature  $T_g$ , when the glass structure is close to that in its solidified form, with a short range and middle range ordering and near the liquidus temperature  $T_L$  state of liquid, with the retained near range ordering and only small fragments of the middle range ordering.

The mechanism of near  $T_g$  temperature crystallization thus differs from the mechanism described by classical nucleation theory (CNT) which in fact refers to the state of an ideal liquid when formation of embryos or nuclei of crystals requires supercooling below  $T_L$  temperature, which is necessary for chemical bonds strengthening and crystal structure formation. In spite of this the crystallization of glass in the solidified form requires its overheating above  $T_g$  temperature. It is necessary to break an appropriate amount of the chemical bonds and to make some components of the glass sufficiently mobile to enable their reorientation and reassembling required to form areas of ordered crystal structure to occur.

It should be expected that near the  $T_L$  temperature it will be a mechanism proper for the crystallization of a liquid with modifications resulting from the fact that the molten glass is a remote approximation of an ideal liquid, whereas crystallization near  $T_g$  temperature proceeds in the way similar to that of phase transitions in solid bodies (polymorphic transitions, decomposition of solid solutions) by means of rearrangement of the amorphous disordered structure into the ordered one (disorder-order transformation).

HREM images proved that in this case the first appearance of new phase grains, of a few nanometer size, have a determined crystallographic structure from the very beginning, and a habit dictated by its geometry. Middle range order domains, existing in the parent glass, can be nucleating centers for the crystalline embryos formation. This mechanism enables the structure inheritance.

This is why the first product of the bulk crystallization of glass are the crystal phase, whose chemical composition and structure are close to those of the glass network or its clusters. They are usually transitional, metastable phases. At higher temperatures, when the diffusional transport is intensive enough, the decomposition of transitional phase, redistribution of chemical components and formation of crystal phase proper for the thermodynamic equilibrium state of the melt takes place.

The obtained results show that  $\text{TiO}_2$  activated crystallization of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  glasses, beginning near the temperature of glass transformation  $T_g$ , proceeds directly by way of successive displacement and ordering of atoms of the amorphous structure of glass as a transition disorder-order type, similar to changes in the crystalline solid bodies, as it has been postulated earlier [3–5]. Then, the glass retains still the properties of a rigid body and thus the rate of the crystals growth is limited and the titanate grains do not exceed the nanometric dimensions. Homogeneous crystallization can have

the same mechanism.  $\text{BPO}_4$  crystallization into  $\text{SiO}_2$  matrix is an example. This mechanism promotes the nanocrystalline phase formation.

A component most weakly combined with silicate network as  $\text{TiO}_2$  already at  $T_g$  temperature is mobile enough to form new crystal phases and Mg, Al-titanates are crystallizing first. Silicates are crystallizing successively at higher temperatures around them. Structural mechanism of glass structure decomposition, proceeding with temperature increase and making particular components mobile, is determining the composition and order of the formation compounds crystallizing next [3, 4, 10].

At higher temperature high quartz s.s. containing Mg, Al and Ti disappears, and above  $1000^\circ\text{C}$  cordierite crystallizes. Cordierite is a phase corresponding to the state of thermodynamic equilibrium, since the parent glass composition lies within the field of its primary crystallization in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  phase composition diagram.

Crystallization of nanocrystalline glass-ceramics should take place at a temperature close to the  $T_g$  when the glass structure has properties similar to properties of rigid solid body and mechanism of crystallization consist in the ordering of the components inside the primary structure of glass. It is also convenient to use such a crystallization activating component, which has the ability to incorporate into the newly forming main crystal phases.  $\text{TiO}_2$  in magnesium aluminosilicate glass is an example. Replacing it by  $\text{ZrO}_2$ , which has not this property, makes that the crystallization occurs above the glass softening temperature and its mechanism is changing. This is a liquid state; zirconia particles nucleated crystallization and coarse crystals of cordierite are growing on them.

## 5. Conclusions

The results of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$  glasses crystallization study demonstrated that near  $T_g$ , at the temperatures of transition from solid body state to visco-elastic state, when parent glass structure is still preserved in a considerable degree, crystallization can proceed by successive displacement and local ordering of atoms in the amorphous structure, similarly to disorder-order transformations in crystalline solid bodies. Middle range order domains, existing in the parent glass, can be nucleating centers for the crystalline embryos formation. This mechanism enables thus the structure inheritance during glass crystallization process.

The mechanism of near  $T_g$  temperature crystallization thus differs from the mechanism described by CNT which in fact refers to the state of an ideal liquid when formation of embryos or nuclei of crystals requires supercooling below liquidus temperature, which is necessary for chemical bonds strengthening and crystal structure formation.

Near  $T_g$  crystallization begins with the formation of simple compounds, made up of chemical elements which are weakly bonded in the structure and are most mobile at the given temperature (compounds of simple composition, crystallization activating admixtures). Their crystallisation is succeeded by the formation of the compounds of a more complex structure.



The first product of the bulk crystallization of glass are the crystal phases, whose chemical composition and structure are close to those of the glass network or its clusters. High quartz s.s. is an example. They are usually transitional, metastable phases. At higher temperatures, when the diffusional transport is intensive enough, the decomposition of a transitional phase, redistribution of chemical components and formation of a crystal phase proper for the thermodynamic equilibrium state of the melt takes place.

The proposed mechanism explains the nanocrystalline glass-ceramic materials formation. It can be also valid for amorphous metallic alloys crystallization.

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