

Quartz crystallization in soda-lime-silica glass

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The tribochemical treatment of glass and grains surface area as a crystallization activating factor and its influence on the crystal phase formation is a subject of the study. Sheet glass SiO_2 -CaO- Na_2O as a material of extremely small crystallization ability has been used in the investigations. Tribochemical activating glass powder, pressed and heated at 750°C makes it possible to obtain glass-ceramic material containing quartz, devitrite and wollastonite crystals. During a prolonged heating time, up to 500 hours, devitrite and wollastonite content is diminishing and quartz becomes a main component of the material. Structural mechanism of tribochemical activated glass crystallization in its viscoelastic state as compared with liquid glass crystallization is considered.

Keywords: glass, quartz crystallization, tribochemical activation, glass-ceramics.

1. Introduction

Silica (SiO_2) is a compound with the highest glass-forming ability from among the oxides. It forms glass in its pure form (silica glass) as well as in combination with most of chemical elements. The structure of silica glass as well as of multicomponent silicate glasses possesses a polymeric character. Its essence is a structural framework built of SiO_4 tetrahedra joined together by common oxygen atom situated at the corners of the tetrahedra (Si-O-Si oxygen bridges). The Si-O bond has the ionic-atomic character and it belongs to strong bonds. The angles of this bond can be changed in a wide range from 132° to 180°, which makes the silicate framework flexible. The flexibility of the structure is the indispensable condition of the existence of the glassy state [1]. It accounts for the specific glass-forming properties of SiO_2 and for the exceptionally low crystallization ability of silica glass. The flexibility of the chemical bonds is responsible for the fact that SiO_2 can form many polymorphic varieties, among them three low-pressure ones: quartz, tridymite, and cristobalite, each having two high- and low-temperature forms. Silica glass and its natural analogue – lechatelirite are amorphous, high temperature, low pressure forms. Opal, amorphous

SiO_2 and its synthetic analogue, silica gel, are precipitated from solutions. High temperature and high pressure varieties of silica are: coesite, kaetite, stishovite, minerals of dens structure [2].

The crystal forms of SiO_2 are relatively chemically pure. They accept in their structure rather small amounts of admixtures. An exception here is tridymite tolerating greater amounts of Na and Ca which stabilize its structure. The structure of low-temperature quartz accepts exceptionally few admixtures. Natural quartz contains admixtures of Al and alkalis in the total amount of some tens of ppm, up to 0.1 wt% [2].

In glass-ceramic materials from the systems $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ there has been observed the formation of a crystal phase with the structure of high temperature modification of quartz which contains in its structure considerable amounts of Al^{3+} replacing Si^{4+} in the tetrahedra. The presence of aluminium is coupled with the presence of Li^+ or Mg^{2+} which supplement the missing positive charge of $[\text{AlO}_4]$ tetrahedra in the silicate framework. The total content of these admixtures varies and it may be considerable, reaching up to 40 wt% of the composition of the substance, which is defined as high-quartz solid solution. This is an unstable variety, formed by way of rebuilding the glass structure. With increasing temperature which causes the increase in the mobility of the admixtures atoms there takes place their removal and ordering of the quartz structure [3–6].

Present-day sheet glass $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ has its chemical components selected so as to make its ability to crystallize as small as possible. This is attained, among others, by the addition of the small quantities of MgO and Al_2O_3 . If sheet glass crystallization occurs, it consists in the formation of devitrite ($\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$) and wollastonite ($\text{CaO}\cdot \text{SiO}_2$). Occasionally SiO_2 polymorphs tridymite or cristobalite can be observed. They are formed, however, due to the inclusions of refractory silica materials which have dropped into the glass melt.

At present, in the technology of the glass-ceramic materials the crystallization, by heating the solidified glass, is utilized. The crystals of nanometric size are already formed when glass reaches the viscoelastic state [7]. The comparison of crystallization realized in this way with the crystallization of a melt of low viscosity is the subject of the present study. Its aim is also to determine the effect of the tribochemical treatment and the grains surface area as a factor influencing the crystallization of glass. A long time of the glass heat treatment from 24 up to 500 hours has been applied to attain the state of recrystallization close to the equilibrium state.

2. Experimental and materials

Soda-lime-silica sheet glass produced in Libya Aziza Glass Factory having the composition (wt%): 70.30 SiO_2 , 17.32 Na_2O , 0.96 Al_2O_3 , 0.08 Fe_2O_3 , 7.0 CaO, 3.50 MgO has been used in the study. The influence of heat treatment and tribological activation by long time grinding of glass on the crystallization of glass has been studied.

Differential thermal analysis (DTA) at 10°C/min heating rate and thermomechanical analysis (TMA) have been used in the investigations. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) have been used for crystals in a glass formation study. Crystallization progress was controlled by X-ray diffraction analysis (XRD).

Glass transformation temperature T_g measured by DTA is 560°C and 555°C, according to TMA measurements. Glass softening temperature measured by TMA is 589°C.

The glass was refined to the grain size below 0.063 mm; part of the powdered sample was pelletized by compression in a press with the pressure of 36 tons. Pieces of glass, powdered glass samples and compacted powdered samples were placed side by side in an electric furnace and heated. At the beginning they were heated at the rate of 200°C/h up to 600°C and held for 2 hours to nucleate. The temperature was increased then at the same rate up to 750°C for crystallization. The samples were kept at this temperature for various time periods: 24, 48, 72, 96, 120, 144, 168 and 500 hours and allowed to cool. The kind of crystallizing phases and their chemical composition as well as the size and the habit of the crystals were examined by the above mentioned methods.

3. Results

After 24 hours of heat treatment at 750°C of pieces of glass, the only crystallizing phase is devitrite ($\text{Na}_2\text{O}_3 \cdot 3\text{CaO} \cdot 6\text{SiO}_2$). Its crystallization is a surface crystallization and as it was determined by optical measurements of a length of the crystals, they are growing at the rate of 0.1 mm for 10 hours and no other crystal phases are appearing with prolonged heating time. In powdered glass samples besides devitrite there appears quartz in the amount detectable by XRD method. Their amounts increase with heat treatment. In the samples of glass powdered and compacted by pressing, quartz becomes the main crystal phase.

As it follows from XRD patterns, the main (011) crystallographic line of quartz, formed in the examined glass has the d_{011} (distance between crystal lattice (011) planes) equal to 3.355 Å, whereas the d_{011} of typical quartz is 3.219 Å. Such difference in the value of d_{011} indicates the presence of isomorphic substitutions in the structure of quartz from glass, which increase the unit cell volume (Fig. 1).

The presence of quartz as a product of crystallization was confirmed by DTA study of samples glass powdered, compressed and heated for 500 hours. They contain the greatest amount of quartz and it is best shaped. Quartz shows reversible polymorphic transformation at about 580°C, which distinguishes it from among other crystal forms. On the DTA curve of this sample the peak of the polymorphic transformation of quartz is marked by a weak, scattered thermal effect. In order to make it well visible, the heating rate has been increased from 10 to 40°C/min. Such a procedure is used in the investigations of reversible polymorphic transformations

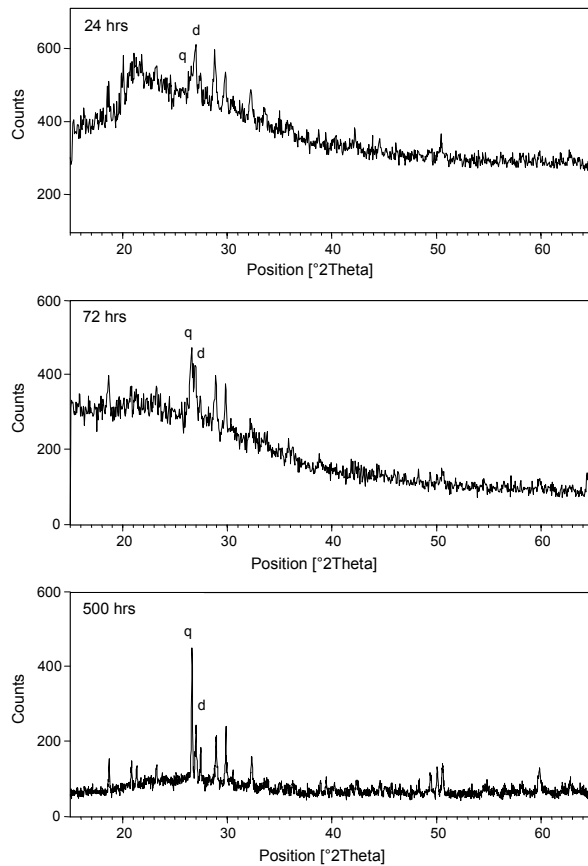


Fig. 1. XRD patterns of glass crystallized at 750°C, for the differential periods of time (*q* – quartz, and *d* – devitrite characteristic lines); powdered and compacted samples.

when their thermal effects are weak and extended in time. To confirm the reversibility of the transition, the same sample was several times heated and cooled in a DTA apparatus. Each time, on DTA curve, the peak of the quartz transition at the temperature 575–577°C was recorded (Fig. 2).

The broad thermal effect of the transition is an indication of the defective structure of quartz crystallizing in glass. It may consist in the wrongly developed structural framework, the presence of admixtures in the structure and very small size of crystal grains.

The SEM image of the sample heated 168 hours, shows the crystallization of crystals of devitrite as well as wollastonite admixture. There are also visible grains of quartz (Fig. 3). It is surrounded by a homogeneous glassy matrix. The composition of this glass is impoverished in the components which became part of the composition of the crystal phases, *i.e.*, Na₂O, CaO, and thereby it became enriched with SiO₂.

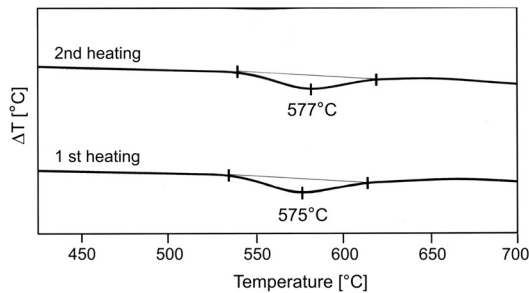


Fig. 2. DTA peak of the reversible quartz polymorphic transformation; glass crystallized at 750°C for 500 hours; powdered and compacted sample.

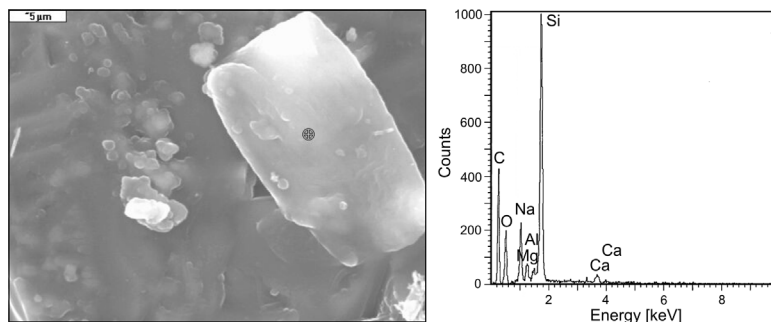


Fig. 3. SEM image and EDS spectrum of the quartz prismatic crystal; glass heated 168 hours at 750°C; powdered and compacted sample.

Samples of glass powdered, compacted and crystallized at 750°C demonstrate a granular texture. They contain mainly crystal grains of a uniform size and strictly regular form. There can be observed quartz grains of a prismatic habit with a rectangular transverse section (Fig. 3). As it is shown by the EDS spectrum it contains admixtures of Na₂O and smaller amounts of Al₂O₃, CaO and MgO in the proportions similar to those in the primary glass. Among the grains, irregular crystal forms of devitrite and wollastonite as well as quartz, there have been observed also the grains of sodium silicate Na₂Si₂O₅, which generally does not crystallize in glass.

The prismatic forms of large dimensions are formed by devitrite and wollastonite, the space between them is filled with irregular crystal grains. Well developed crystal forms are thus specific of the crystal phases formed as the first, thanks to their great ability to crystallize, and in this way the chemical composition becomes changed as a result of binding some of the components, *i.e.*, Na₂O and CaO in the structure of devitrite and wollastonite.

EDS mapping of the chemical elements distribution in the recrystallized areas as well as the profiles of changes in their concentration, along some definite line, show that the new crystal phases are formed through the redistribution of cations in

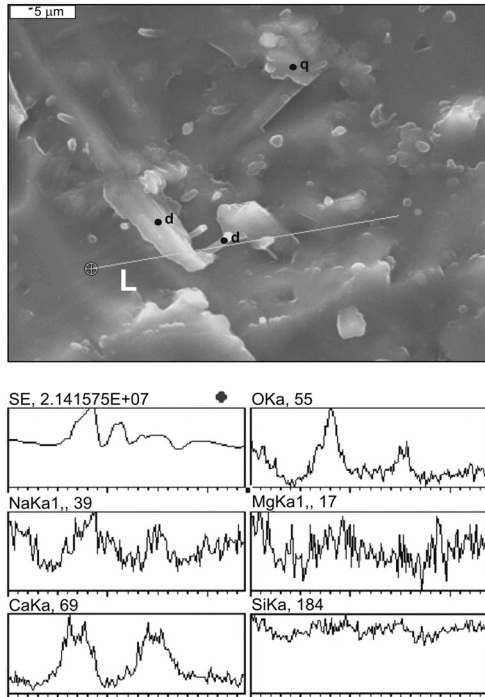


Fig. 4. SEM image of the glass heat treated at 750°C, for 168 hours and pictures of the change in chemical components concentration along the line *L* (*q* – quartz, and *d* – devitrite grains); powdered and compacted sample.

the area of the silicate framework which becomes adjusted to their presence. This is well illustrated by the formation of wollastonite (Fig. 4). Si content is stable along the analyzed line, and only Ca peaks appear at places of cutting the wollastonite crystals.

4. Discussion

From the analysis of the diagrams of phase equilibria $\text{SiO}_2\text{--CaO--Na}_2\text{O}$ it follows that the melt of the composition of the examined glass has the liquidus temperature of about 970°C. Its crystallization begins at this temperature. The point of the glass composition lies on the diagram in the area of crystallization of devitrite ($\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$) and this compound crystallizes with the decrease in temperature. When the temperature reaches 870°C there begins the co-crystallization of high-temperature quartz (double eutectic devitrite – quartz). At the temperature 730°C, there should crystallize as the third the silicate $\text{Na}_2\text{Si}_2\text{O}_5$ (triple eutectic, solidus level) from the melt. This leads to complete recrystallization of the melt. The system attains then the equilibrium phase composition corresponding to the chemical composition of glass. Below the temperature

of 583°C, the structure of high temperature quartz becomes changed into the structure of low temperature quartz [8].

The performed investigations allow to determine the progress of glass crystallization at the temperature of 750°C when it is still in the visco-elastic state of high viscosity and the amorphous structure of the glass is already to a high degree established. In these conditions crystallization has the character of a rearrangement in the internal structure of glass.

The conducted investigations of tribochemically activated glass have shown that isothermal crystallization at a temperature close to the solidus temperature in the system of phase equilibria has a different progress in comparison with the crystallization of a melt, cooled step by step. The crystal phases observed during X-ray examination appear after the induction period, which in this case lasts for about 24 hours. Crystallization proceeds as a co-formation of devitrite, quartz and wollastonite admixture. At first devitrite prevails, afterwards when Ca and Na become bound in the structure of devitrite, and in this way the glassy matrix becomes enriched with SiO₂, the proportions become reversed and more quartz is formed. Occasionally quartz co-exists with the silicate Na₂Si₂O₅ which appears at the final stage of crystallization, after a long period of heating (500 hours). The system is then approaching the state of equilibrium. These transformations are possible due to flexibility of silica structure, described earlier [1].

At 750°C quartz crystallizes as high-quartz structure solid containing Na as an admixture as well as small amounts of Al and Mg. It transforms reversible into low-quartz during cooling. EDS shows that in the case when crystallization takes place at 750°C, it is near the solidus temperature, and its mechanism is different from that of crystallization of a molten glass of low viscosity. At the temperature close to the solidus temperature when the glass structure has already a high degree of polymerization, its crystallization has the mechanism close to the described in [9]: new crystal phases are formed through the redistribution of cations in the area of the silicate framework which next adjusts to their presence. This is well illustrated by the formation of wollastonite (Fig. 4).

Such a mechanism enables also the formation of non-equilibrium phases as a result of limited mobility of cations at relatively low temperature. In this case it is the wollastonite.

5. Conclusions

The investigations have shown that using tribochemical activation it is possible to crystallize glass, even this of very low crystallization ability, such as sheet glass SiO₂-CaO-Na₂O and obtain the material of high degree of crystallinity, comparable to that formed by crystallization with nucleating components additions.

The mechanism of glass crystallization at the temperature close to solidus temperature, differs from that of the crystallization of a melt of low viscosity. It consists

in the redistribution of the cations-modifiers within the silicate framework, already developed, which adjusts its form to their presence.

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