Nanocrystalline glass-ceramics formation

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The atomic scale mechanism of the transition of the glass structure into the structure of a compound crystallizing in it has been studied. It has been demonstrated that near the glass transformation temperature T_g the crystallization by direct ordering of the amorphous glass structure through local displacements of its elements can take place. TiO_2 nucleated crystallization of SiO_2-Al_2O_3-MgO glass-ceramics is the example. Up to now, it has been thought that amorphous phase separation is an indispensable step in the glass-ceramization. Crystallization with the direct ordering mechanism creates the compounds whose chemical composition and structure are close to those of glass network or to the domains and clusters in it. The (Mg, Al)-titanate, and high quartz structure solid solutions appearence are here the example.

1. Introduction

Glass-ceramic materials with their microstructure formed by uniformly dispersed nanocrystals which are 100 nm in size or smaller (nanocrystalline glass-ceramics) have lately become again the subject of interest in many laboratories.

An object of special interest is transparent, nanocrystalline glass-ceramics of luminescent properties. Many new types of such materials have been developed on purpose to be applied in photonics, solar energetics and in other fields. Another type of nanocrystalline materials is the tough, high-modulus glass ceramics which allows to obtain products with precisely engineered surface, such as magnetic memory disk substrates [1].

A condition of good transparency of the material is that it demonstrates low optical scattering and low ionic and atomic absorption. Low scattering can be obtained when all the crystalline phases and glassy matrices closely match indexes of refraction and when crystals possess low birefringence. Glass-ceramics containing crystals of Zn-stuffed, high quartz structure solid solution (s.s.), which are optical nearly isotropic, has good transparency, despite the crystal size up to 10 μm [2].

So far the widest practical application has found the nanocrystalline glass-ceramics containing Li-stuffed high quartz s.s. [3]. A typical commercial composition may comprise 60 mol% SiO_2 and 40 mol% $LiAlSiO_4$ (eucriptite) with partial substitution

of Li_2O by MgO and ZnO. Schott transparent Zerodur® glass-ceramics also contains $AlPO_4$ substituting part of SiO_2. It possesses an ultra low coefficient of thermal expansion and high thermal stability. It has found application in precision optics as telescope mirror blanks [4]. This material as well as other materials of this type (VISIONS®) have current commercial applications as a radiant cooktop for electric stoves, cookwares, fire doors and other technical devices [5], [6].

Nanocrystalline components of these materials are formed by way of hetero-geneous crystallization with the application of TiO_2 and ZrO_2 as nucleators. $ZrTiO_4$ precipitates, and on its crystals of prismatic habit, the high-quartz s.s. and other crystalline components are crystallized. TiO_2 becomes part of the composition of high-quartz s.s. These nucleators are thus introduced in the proportions of 2/3 TiO_2 and 1/3 ZrO_2.

Transparent nanocrystalline glass-ceramics has been examined lately as a host medium for luminescent, transition metal ions, particularly Cr^{3+} ion. The Cr^{3+} is considered for use as a luminescent ion in tunable lasers and solar condensers. In certain crystalline ligand field environments the Cr^{3+} ions absorb broadly in the visible wavelength range and exhibit luminescence of high quantum efficiency in the near infrared. Thus, a suitable crystal field environment is provided when Cr^{3+} substitutes Al^{3+} or Mg^{2+} in their sites in several silicate structures. Mullite, spinel and mixed high -quartz s.s., as well as spinel and Mg-petalite systems, belong to this group. Moreover, glass-ceramics can be manufactured in large sheets required for solar collectors. This is not possible in the case of crystalline Cr^{3+} hosts ($AlPO_4$, Be_2O_4) in spite of their high (about 90%) luminescent effectiveness [1], [7].

Similarly, fluoride crystals and glasses are good hosts for optically active rare -earth cations, due to their low phonon energies and broad transparency in the infrared region, to the spectrum used for amplification of light in telecommunication. However, fluoride crystals and glasses have low chemical durability, low mechanical stability and are difficult to obtain and handle. Transparent nanocrystalline oxyfluoride glass-ceramics based on fluoride crystals dispersed in alumino-silicate glassy matrix is free from these disadvantages. The glass-ceramics with LaF_3 crystals doped with Er^{3+} ions shows much better fluorescence effectiveness than ZrF_4 based ZBLAN glass [8].

2. Mechanism of nanocrystallization

The essential factor determining the transparency of glass-ceramics is a sufficiently small size of crystallites, according to Rayleigh–Gauss relation for light dispersion. Their size depends on the crystallizing ability of the glass, in particular on the mechanism of crystallization, to which the parameters of this process, *i.e.*, temperature and time, must be adjusted. The maximal rate of nucleation should be reached at a possibly lowest temperature, if possible near the temperature of the transformation of the glassy state T_g when the glass viscosity is high, about $10^{13.3}$ dPa·s, and it limits the growth rate of the crystals which can obtain only nanometric dimensions. To obtain such a result, the difference between the temperature of the maximal nucleation and the temperature of the maximal growth rate of the crystals should be 50–100 °C.

So far the knowledge of the mechanism of nucleation which is the initial stage of crystals formation has been very general, although it is decisive for obtaining glass-ceramic materials of nanocrystalline structure. The available data on this subject are listed below.

Transparent glass-ceramics:

– *Glass-ceramics based upon metastable, high-quartz s.s.* Li-stuffed high-quartz s.s.: $Li_{2-2(x+y)}Mg_xZn_yAl_2O_3 \cdot zSiO_2$, eucriptite ($LiAlSiO_4$), SiO_2-$AlPO_4$ s.s. Heterogeneous nucleation, TiO_2, ZrO_2–nucleating agents [6].

– *Mullite glass-ceramics.* Mullite: $3Al_2O_3$ $2SiO_2$-$2Al_2O_3 \cdot SiO_2$ s.s., with $9Al_2O_3 \cdot 2B_2O_3$ and ZnO substitutions, up to $5Al_2O_3 \cdot B_2O_3$ and $7Al_2O_3 \cdot 2ZnO \cdot 8$ SiO_2 Self nucleation by amorphous phase separation [9].

– *Spinel glass-ceramics.* Spinel (MgO Al_2O_3)–gahnite (ZnO Al_2O_3) s.s. Heterogeneous nucleation, TiO_2, ZrO_2–nucleating agents [1], [10].

– *Forsterite glass-ceramics.* Forsterite Mg_2SiO_4 in SiO_2-Al_2O_3-MgO-K_2O glass [11]. Self nucleation by amorphous phase separation.

– *Willemite glass-ceramics.* Willemite Zn_2SiO_4 in SiO_2-Al_2O_3-ZnO-K_2O-Na_2O glass [12]. Self nucleation by amorphous phase separation.

– *Oxyfluoride glass-ceramics.* $ReF_3(YbF_3)$-CdF_2-PbF_2 crystals in SiO_2-Al_2O_3 glass, LaF_3 crystals in SiO_2-Al_2O_3-Na_2O glass. Selfnucleated precipitation of fluorides [8].

Tough glass-ceramics: Mg, Al stuffed high quartz s.s., enstatite $MgSiO_3$, spinel $MgO(ZnO) \cdot Al_2O_3$, $(Mg, Al)Ti_2O_5$. Heterogeneous nucleation, TiO_2 as nucleator in SiO_2-Al_2O_3-MgO-ZnO glass [7].

The aim of present work is to study the mechanism of the transformation of the amorphous structure of glass into the crystalline structure of the nucleating compound. As the object of investigations there has been chosen the tough glass-ceramics formation by the heterogeneously nucleated crystallization of Mg-petalite, compound of the structure of Mg-stuffed high quratz, and enstatite. Atomic scale action of TiO_2 as nucleator, and the nucleation through amorphous phase preparation and formation of $AlPO_4$ and next $Mg_3(PO)_4$ in Na_2O-MgO-Al_2O_7-P_2O_5-SiO_2 glass were studied.

3. Experimental

3.1. Materials

Glasses of the well-known crystallization process, whose parameters had been published earlier were selected for investigations. This glass allowing to obtain tough nanocrystalline glass-ceramics of the following composition: SiO_2 – 47.1, Al_2O_3 – 22.0, MgO – 16.9, ZnO – 1.7 and TiO_2 – 12.3 wt% [7] was choosen. The nanocrystalline material contains Mg-petalite of high quartz s.s. structure, anastatite, spinel and $MgTi_2O_5$-Al_2TiO_5 s.s. as the first crystallizing phase. Crystallization begins with the amorphous phase separation with precipitation of the glassy phase enriched with titanium from which Mg, Al-titanates crystallize [7]. Mg-petalite and next the other crystalline phases are formed around them [13].

Crystallization of phospho-alumino-silicate glass of the composition SiO_2 – 43, Al_2O_3 – 16, P_2O_5 – 13, MgO – 20, Na_2O – 8 mol% begins with the amorphous separation accompanied by the formation of glass drops enriched with Al and P. At higher temperatures $AlPO_4$ crystallizes in these drops and next $MgPO_4$ [14] is formed on their surface.

3.2. Methods

Glasses were melted in an electric furnace at the temperature of 1450 °C. The obtained melt was vitrified by pouring a layer, 5 mm thick, on a steel plate. In order to induce volume crystallization, the glass samples were heated at selected temperatures for 4 hours. Surface-nucleated crystallization was investigated on glass grained to 0.1–0.3 nm by the differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermal mechanical analysis (TMA) methods (Perkin–Elmer apparatus) at the heating rate 10 °C/min.

The structure of crystallized glass was investigated using the following techniques: X-ray diffraction (XRD), DRON-1.5 apparatus and scanning electron microscope (SEM) Philips XL30 with Oxford Instruments energy dispersive spectroscopy (EDS) system, transmission electron microscopes (TEM) and analytical electron microscopy (AEM) CM30 Ultra TWIN and CM20 TWIN with energy dispersive X-ray (EDAX) Phoenix system, respectively. Thin foils were prepared by dimpling followed by ion milling.

The early stages of crystallization were investigated using high resolution electron microscopy (HREM) in order to determine the character and size of nuclei, followed by studies of later stages using SEM, TEM and AEM. HREM observations were carried out at Eidgenörrische Technische Hochschule in Zurich [15].

4. Results and discussion

4.1. SiO_2-Al_2O_3-MgO-TiO_2 glass

It is seen on the DTA curve (Fig. 1) that the examined glass shows a jump-like change in molar heat capacity C_p value connected with the transition of glassy state in the interval 726–784 °C; the temperature of this transition has been estimated as 760 °C. The change in C_p is large and it is retained up to 820 °C. Hence, it can be concluded that the effect of this transformation comprises the rearrangement of the glass structure which precedes crystallization. The temperature 820 °C marks the beginning of the exothermic effect of crystallization which reaches the maximum at 879 °C; the second stage of crystallization takes place at 950 °C.

Changes in the glass colour preceding its bulk crystallization are visible already at 650 °C. They are manifested by the change of yellow colouring of the glass, caused by the presence of TiO_2, into grey-blue and then starting from 725 °C, into deep blue. These changes are induced by the change of the position and/or Ti valence in the glass structure, and they always occur when titanium is used as a catalyser of crystallization of silicate glasses. From 725 °C the opalescence can be observed, indicating the
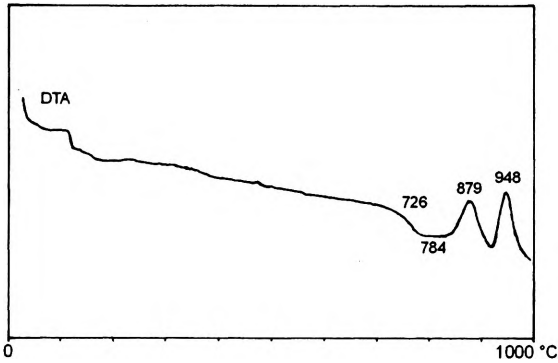
Fig. 1. DTA curve of glass.

precipitation of fine grains of the crystalline phase in the glassy matrix. Above 775 °C with increasing temperature, the material loses transparency assuming white-grey colour as a result of progressing crystallization, the growth of crystalline grains and the decay of the glassy matrix. Above 925 °C the material is completely recrystallized and it takes on white colour.

The XRD investigations have revealed that at 725 °C the lines of Mg-petalite and of the (Mg, Al)-titanate appear. The higher the heating temperature of the glass, the stronger is the characteristic line of Mg-petalite (3.44 Å), and at 825 °C it is the main, detectable crystalline phase. About 925 °C lines which can be ascribed to clinoestatite appear. Investigations of the initial stage of glass crystallization by the TEM method and electron diffraction have confirmed the formation of crystalline phases already at the temperature of 725 °C. In the glass, the dendrite aggergates about 10–100 nm in size appeared. Moreover, irregular areas indicating the beginning of the formation of another crystalline phase could be observed around them. At higher temperature (750 °C) they are much better developed and reach the dimensions up to 100 nm. Prismastic crystals and crystals of isometric shape, some of them characterized by lamellar structure, have been developed from the irregular areas. At the temperature of 825 °C they are already well developed (Fig. 2) and allow to obtain distinct electron diffraction.
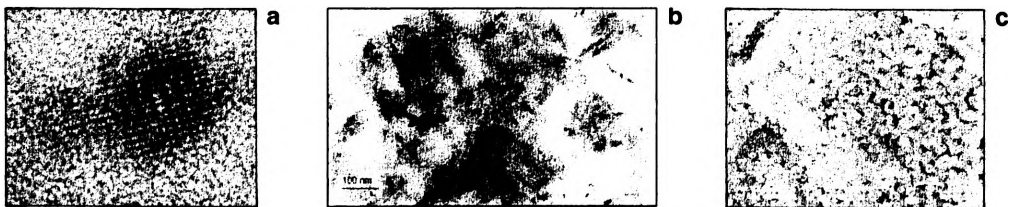

Fig. 2. Transition of the amorphous structure of glass into crystalline by structure components rearrangement and ordering in SiO_2-Al_2O_3-MgO-TiO_2 glass; **a** – HREM micrograph of glass heated at 725 °C for 4 h; **b** – TEM image of glass heated at 825 °C for 4 h; **c** – SEM micrograph of glass heated at 850 °C.

Quantitative local chemical analysis has shown that the crystalline phase developed in the form of dendrites (Fig. 2b, black crystals) is characterized by a considerable increase in Ti content, from about 5 to 15 atom%, in relation to the amorphous matrix, and an increase in Mg content, from 20 to 30 atom%, and a rather small increase in Al content, which corresponds to titanate with the structure of pseudobroockite $(Fe_2^{+3}TiO_5)$ and Mg and Al replacing Fe^{3+}. The results of performed investigations indicate that these crystals contain an admixture of Si.

The crystalline phase forming around the dendrites, in comparison with the surrounding glass, shows increased concentration of Mg and Al and a small content of Ti (about 5 atom% and less). The content of Si varies and reaches up to 70 atom%. This indicates the high-temperature quartz structure s.s., containing varying amounts of Mg and Al and a rather small amount of Ti. This means that the crystalline phases originating from the glassy matrix still contain the components present in the matrix and their composition does not exactly corresponds to the theoretical one.

The transition of the amorphous structure of glass into the crystalline structure could be observed on HREM photos at 10^6 magnification of the glass crystallized for 4 hours at 725 °C (Fig. 2a), i.e., just at the beginning of the glassy state transformation T_g when the glass possess still the properties of a solid body. There could be observed on the photographs the formation of zones with an ordered arrangement of atoms in the disordered structure of glass through the displacement of its components. The degree of organization of the newly formed crystalline structure changes, leading to the development of phases of prismatic or isometric habit. On the other hand, the phenomenon of glassy drops formed by amorphous phase separation was not observed.

It shows the direct formation of the nuclei of a crystalline structure, measuring 5 nm in width and 20 nm in length in the amorphous matrix. The lattice planes with the distance of about 0.5 nm corresponding to [020] plane of $MgTi_2O_5$ [15] could be distinguished on it.

The degree of recrystallization of the glass heated at 850 °C is considerable (Fig. 2c). The SEM image shows grains about 1 μm in size of columnar habit. They form characteristic conglomerates, made up of prisms grown in their corners and surrounded by a glassy matrix. At the temperature of 920 °C the structure is already completely crystalline, formed of prismatic closely packed crystals, a few to 10 μm in length. It follows from the EDS spectra that both the crystals and the surrounding amorphous matrix do not differ in their chemical composition, containing similar amounts of Si, Al, Mg, Ti. On the other hand, (Mg, Al)-titanate as a separate phase disappeared.

4.2. SiO_2-Al_2O_3-P_2O_5-MgO-Na_2O glass

Phase transition in glass follows the transformation of the glassy state (T_g about 624 °C) and consists in the amorphous phase separation. Drops are formed with their surface distinctly separated from the surrounding matrix (Fig. 3a). The electron diffraction have confirmed the amorphous nature of both phases. The drops are enriched with Al_2O_3 and P_2O_5. The crystallization of $AlPO_4$ grains takes place at the
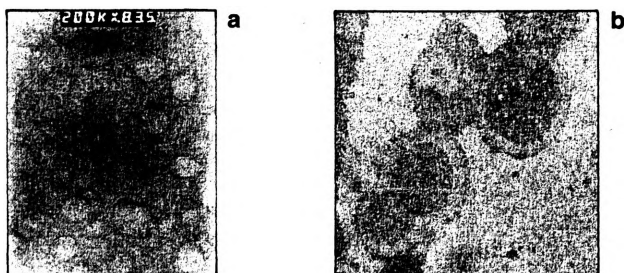
Fig. 3. Amorphous phase separation in SiO_2-Al_2O_3-P_2O_5-MgO-Na_2O glass, TEM image, magnification 10 000× (a); $AlPO_4$ crystallization inside and $Mg_3(PO_4)_2$ arround the droplets of separated glassy phase, SEM micrograph, magnification 150× (b).

temperature 700–750 °C in the drops. Their surface nucleates the formation of fibrous crystals of $Mg_3(PO_4)_2$ (Fig. 3b). Near the liquidus temperature both these phases become dissolved in glass. The second generation of $AlPO_4$ crystallizes from glass in the shape of columnar crystals forming the dendrites.

5. Mechanism of the transition of amorphous glass structure into crystalline

The obtained results show that TiO_2 nucleated crystallization of SiO_2-Al_2O_3-MgO glasses takes place directly, by way of local displacements and ordering of the atoms of the amorphous structure of glass, thus, similarly to the polymorphic transitions, diorder–order type in the crystalline solid bodies. The possibility of such mechanism of the crystal phases formation in glass, when the temperature of crystallization is close to T_g, was suggested by the author earlier [16], [17]. So far it has been thought that the beginning of crystallization of such glass is the amorphous phase separation with the formation of drops of the glass rich in Ti, from which crystals of (Mg, Al)-titanate are formed [7]. Crystallization through local ordering of the amorphous structure without the separation of the amorphous phases presented here has been found to be a frequent phenomenon. It has been also observed in glass from SiO_2–BPO_4 system [18].

The HREM images have shown that formation of the crystal phases by way of such a rearrangement consists in local redistribution and ordering of the components of the glass structure and in the formation in it of the regions of topologically ordered arrangement of the structure elements, according to a definite geometry (Fig. 2). These regions, about 5 nm in size, have an already outlined habit proper to the crystalline form. In this way the dendrites of (Mg, Al)-titanate and grains of Mg-petalite containing Ti admixtures, are formed. The latter forms at the beginning crystals of irregular shape, which with increasing temperature assume a prismatic habit.

At the temperature of 800 °C crystallization has a different character. (Mg, Al)-petalite disappears, and the main crystal phase is Mg-petalite, which besides Mg contains Al and Ti in its structure. The glass sorrounding it becomes impoverished in

Mg and Ti. Crystallization leads in this case to the formation of twin structure aggregates of prismatic crystals, measuring about 1 up to a few μm. This stage of crystallization is registered on the DTA curves as a peak at about 880 °C (Fig. 1). The second stage of crystallization, which gives the next exothermic peak at about 950 °C, is also a spontaneous crystallization of (Mg, Al)-petalite, combined with the growth of its crystals to the size of 10 μm. Then clinoenstatite appears, but in a rather small amount.

As it can be assumed the first stage of crystallization has changed the composition of the residual glassy phase enriching it with SiO_2. Thus its viscosity increased and the increase in temperature, providing an appropriate drop in this viscosity, enabled renewed crystallization of the glass, as well as recrystallization of the earlier formed, fine prismatic crystals into bigger ones.

Crystallization of multicomponent glasses often takes a multi-stage course and proceeds through the formation of metastable phases according to Ostwald rule of stages which subsequently, with temperature increase, making the components of this structure more and more mobile can recrystallize, by exchanging the chemical components and internal structure reconstitution. The phase composition corresponding to the equilibrium state is attained near the liquidus temperature when crystallization takes place in liquid glass melt [16], [17].

Thus the mechanism of glass crystallization at the low and high temperature stage of the process is different. In the temperature not far from T_g point (rigid or viscous -elastic state of glass) the micromechanism of crystallization is determined mainly by the strength of chemical bonds in the structure and mobility of the particular component of glass structure.

Crystallization of glass by the amorphous structure ordering mechanism at its low temperature stage is determined by crystallochemical factors [18]. It begins with the formation of compounds of simple composition, nucleators. They are made up of chemical elements whose bonds in the glass structure are easy broken by thermal vibrations and are the most mobile at given temperature. These are the components bonded to network oxygens with weak ionic bonds (glass modifiers) or whose bonds are weakened by internal strains due to the coexistence of chemically different elements in the network. Si^{4+} and P^{5+} in phospho-silicate glass joined by common oxygen bridges are the example. Their crystallization is succeeded by the formation of compounds of a more complex structure. The first product of the main bulk crystallization of glass is then a crystal phase, the chemical composition and structure of which are close to those of the glass network or its microregions (domains or clusters). Crystallization of quartz-like solid solutions of anomalous chemical composition is an example [16], [19].

6. Conclusions

Nanocrystalline glass-ceramic formation is determined in a considerable degree, by micromechanism of the transition of disordered glass structure into the forming crystal

structure. Crystallization with the direct amorphous structure ordering mechanism, near temperature T_g, makes it possible to obtain well crystallized material, composed of crystals of the nanometric size. SiO_2-Al_2O_3-MgO glass ceramics, nucleated with TiO_2 is the example. Micromechanism of crystal phase formation influences the shape of crystals formed. They are either irregular (structure ordering mechanism) or more equidimensional and uniformly dispersed (nucleation by amorphous phase separation). Nanocrystals shape effects the mechanical properties and/or light scattering of material.

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