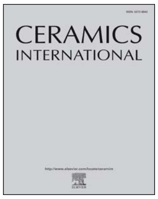
Ceramics International 44 (2018) 2919–2926

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



The evidence of phase separation droplets in the crystallization process of a Li_2O-Al_2O_3-SiO_2 glass with TiO_2 as nucleating agent – An X-ray diffraction and (S)TEM-study supported by EDX-analysis

Enrico Kleebusch[a,*], Christian Patzig[b], Thomas Höche[b], Christian Rüssel[a]

[a] Otto Schott Institut, Jena University, Fraunhoferstraße 6, D-07743 Jena, Germany
[b] Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Walter-Huelse-Straße 1, 06120 Halle (Saale), Germany

ARTICLE INFO

Keywords:
B: Electron microscopy
B: Microstructure-final
B: X-ray methods
D: TiO_2
D: Glass ceramics
D: Glass

ABSTRACT

Lithiumalumosilicate glasses are of great importance for industrial applications, because they enable the preparation of glass ceramics with coefficients of thermal expansion close to zero. While detailed studies of the effect of ZrO_2 on nucleation and crystal growth have already been performed in recent years, the effect of TiO_2 was up to now not reported in detail. It is shown for the first time, that liquid/liquid phase separation is the initial step of nucleation in lithiumalumosilicate glasses containing TiO_2. During temperature treatment above the glass transition temperature, at 740 °C for 0.25–24 h, in the formed droplets, TiO_2 nanocrystals precipitate. The formed phases were investigated by XRD- and TEM and STEM-EDX to illustrate the phase developments as well as the resulting microstructures and the local enrichments of the respective components as a function of time.

Longer crystallization times resulted in the formation of crystalline lithiumalumosilicate (LAS) with a high-quartz structure. These crystals are notably larger than the TiO_2 crystals and are growing with increasing treatment time and temperature. The evidence of anatase formation was obtained from high resolution TEM from the lattice spacings because it cannot be distinguished from the high quartz structure using XRD.

1. Introduction

Glass-ceramics based on the system $Li_2O/Al_2O_3/SiO_2$ are highly interesting because of their wide range of applications [1–7]. Although they were commercialized more than 60 years ago and are widely used today, up to now the nucleation and crystallization mechanisms are still not fully understood [8]. Recently, some detailed studies using electron microscopy and X-ray absorption spectroscopy have been published for glasses doped with zirconia as nucleating agent [9,10]. By contrast, detailed studies on TiO_2 doped lithium aluminosilicate glasses have not been performed up to now to the best of our knowledge. To study the effect of TiO_2 on the nucleation mechanism, a glass composition similar to that of the commercially available ROBAX™ glass (Schott AG), which, however, contains both, TiO_2 and ZrO_2 as nucleating agents, was used.

Commercially successful materials with low, i.e. near to zero coefficients of thermal expansion (CTE) are up to know solely glass-ceramics based on the Li_2O-Al_2O_3-SiO_2 system [1,8,11–13]. There are numerous applications, among them daily life products such as cook top panels and high temperature (furnace) windows as well as devices for numerous optical applications, e.g. telescope mirror blanks [1,14]. For the latter, the coefficient of thermal expansion (CTE) must be very close to zero in order to minimize the change of shape as an effect of temperature [14]. For cook top panels and furnace windows, a CTE close to zero is also necessary in order to achieve the required high thermal shock resistance [3,5,6].

A material with a CTE close to zero, is composed of a crystalline phase with a negative CTE, which is embedded in or co-exists with other crystalline or amorphous phases with a (slightly) positive CTE [15,16]. The CTE can be tailored by adjusting the volume concentrations of the phases with positive and negative CTE [17] as well as their chemical compositions [18]. In commercial low CTE glass ceramics as phases with negative CTE, mainly, high-quartz solid solutions, eucryptite, spodumene or keatite occur [7,12,19–26]. High-quartz solid solutions have a hexagonal crystal structure, similar to that of the high temperature phase of quartz (β-quartz) [27]. In many glass-ceramics, these negative thermal expansion phases possess high volume fractions in the range of 75–85% [28,29]. They can, nevertheless, be completely transparent for visible light [30–33]. This means, the crystals should

---

[*] Corresponding author.
E-mail addresses: enrico.kleebusch@uni-jena.de (E. Kleebusch), christian.patzig@imws.fraunhofer.de (C. Patzig), thomas.hoeche@imws.fraunhofer.de (T. Höche), ccr@uni-jena.de (C. Rüssel).

https://doi.org/10.1016/j.ceramint.2017.11.040
Received 24 September 2017; Received in revised form 30 October 2017; Accepted 7 November 2017

have sizes below roughly one fifth of the wavelength of visible light, i.e. below approximately 100 nm. Since the crystals have a certain size distribution, the mean crystallite size should not exceed a few ten nanometers, otherwise, light scattering occurs [13,32,33].

From glasses in the system $Li_2O/Al_2O_3/SiO_2$, β-quartz can be crystallized. The pure β-quartz phase, transfers during cooling at 573 °C to α-quartz [14,34], which is the phase thermodynamically stable at room temperature. However, in the high temperature phase β-quartz, Si^{4+} can be substituted by Al^{3+} and, the negative charge of the AlO_4^- tetrahedra is then compensated by mono- or divalent comparatively small ions, such as Li^+ [26,35], Mg^{2+} [34] or Zn^{2+} [26,36]. The glass system $Li_2O/Al_2O_3/SiO_2$ is further modified by the addition of, Na_2O, K_2O, MgO or ZnO [37–40], and, as fining agent, Sb_2O_5 [32].

Furthermore, nucleating agents are added, which are necessary because otherwise, predominantly surface nucleation occurs [13]. In that case, the resulting microstructure is quite coarse and not at all nanocrystalline. By contrast, the addition of nucleating agents results in volume or bulk nucleation [12,13,41–43] and nanoscaled crystals can be precipitated, which are, if a proper composition and heat treatment is chosen, homogeneously dispersed in the glass matrix. The most frequently used nucleating agents for the $Li_2O/Al_2O_3/SiO_2$ system are ZrO_2 [11,44–48], TiO_2 [3,11,26,35,36,44–47,49–54] or both of these additives [11,44–47,55,56]. The concentration of these nucleation agents plays a major part for the crystallization process and the development of the microstructure, just like in other alumosilicate systems, e.g., in the $MgO/Al_2O_3/SiO_2$ system.

In this paper, TiO_2 as the sole nucleating agent is reported and the effect of the temperature/time schedule on the microstructure is studied.

2. Experimental

The glass was melted in batches of 300 g in an inductive furnace in a platinum/rhodium crucible. As raw materials Li_2CO_3 (UCB), $LiNO_3$ (Honeywell Riedel de Haën AG), Na_2CO_3 (Carl Roth GmbH & Co. KG), 4 $MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (Merck KGaA), $Al(OH)_3$ (Sumitomo Chemical), SiO_2 (Carl Roth GmbH & Co. KG), K_2CO_3 (Carl Roth GmbH & Co. KG), TiO_2 (Germed DDR), ZnO (Vertriebsgemeinschaft für Harzer Zinkoxide GmbH (VHZ), Heubach), ZrO_2 (Tosoh), Sb_2O_3 (Ferak Berlin GmbH) and $BaCO_3$ (SABED) were used. The chemical composition of the glass is summarized in Table 1.

In a first step, the glass was melted at a temperature of 1615 °C kept for 2 h. Then, the crucible with the melt was removed from the inductive furnace and placed in another furnace with $MoSi_2$ heating elements at a temperature of 1680 °C which was kept for 3 h. The initially used middle frequency furnace enables to fill the raw materials stepwise into the crucible which is hardly possible using a superkanthal furnace. The latter is, however, required to reach the necessary high melting temperature of 1680 °C.

Finally, the glass melt was cast into a mould (brass) and later transferred to a preheated muffle furnace (680 °C). Then, the furnace was switched off to allow a slow cooling of the glass to room temperature (rate: approximately 2 K/min). As described above, the composition of the glass for this study was similar to that of industrially produced Robax™ (SCHOTT AG) glass. The only exception is that Robax™ contains both ZrO_2 and TiO_2 while in our study, only 5 mol% TiO_2 was added.

For the glass crystallization, pieces with a size of around 0.5 × 0.5 and 0.5 cm^3 were cut and heated to temperatures in the range from 680 to 750 °C, kept for 24 h. In order to perform X-ray diffraction (XRD), the powdered samples were studied using a Siemens D5000 diffractometer for the temperature series, while the time series was measured at bulk samples using a Rigaku MiniFlex 300. Both series of measurement were recorded with Cu-K_α radiation ($\lambda = 0.154$ nm) in a 2θ range from 10° to 60°.

Table 1
Chemical composition of the glass in mol%.

	Li_2O	Na_2O	K_2O	MgO	BaO	ZnO	Al_2O_3	SiO_2	TiO_2	Sb_2O_3
Glass	7.6	0.2	0.1	1.9	0.3	1.2	12.7	70.6	5.0	0.4

The coefficients of thermal expansion and the glass transition temperatures were determined with a Netzsch Dil 402-PC dilatometer. The studied specimens were cylinders with a length of 25 mm and a diameter of 8 mm; the supplied heating rate was 10 K/min. Differential scanning calorimetry (DSC, Linseis Pt-1600) was used to determine the glass transition and the crystallization temperatures (heating rate: 10 K/min). Vickers hardness (microhardness) was determined using the microhardness tester Duramin 1, Struers with a load of 981.2 mN. The coplanar samples were ground and polished; 10 indentations were generated in the sample. Eq. (1) was used to calculate the microhardness from the indentations.

$$H_V = 1.854 \cdot \frac{F}{d^2}, \tag{1}$$

with H_V - Vickers hardness (GPa), F - the applied force (N) and d - the mean length of the indentation diagonals (m). The density was determined with a helium pycnometer (AccuPyc 1330). Selected specimens were studied by XRD, and (Scanning) Transmission Electron Microscopy (*S*)TEM. The latter was done with a c_s-aberration corrected FEI $TITAN^3$ 80–300 electron microscope with 80 kV acceleration voltage. A high-angle annular dark field detector (Fischione Model 3000) was used to perform scanning TEM. For selected specimens, STEM was combined with energy-dispersive X-Ray spectroscopy (EDXS), using a Super-X EDX detector equipped with four SDD detectors (FEI company). Element distribution analyses and element mappings were performed using the commercially available software *Esprit* (Bruker company). Element mappings were derived by evaluating the lateral distribution of the peak intensity, i.e., the area underlying the *K*- edges of the respective elements, with an automatic, software-provided routine.

Sample preparation for (S)TEM was done using a purely mechanical wedge-polishing approach with a dedicated sample grinding and polishing tool (Multiprep, Allied company), followed by an Ar^+ ion broad-beam milling step (precision ion polishing system PIPS, Gatan company) to clean the sample from polishing residues and to reach electron transparency. Finally, the samples were selectively carbon coated using a specific coating mask (CoatMaster, 3D- Micromac AG) [57].

3. Results and discussion

The casted glass has a brown color due to an Fe^{3+}-O-Ti^{4+} charge transfer formed by trace quantities of iron. This coloration is well-known from literature and is frequently denoted as “ilmenite coloration” [58,59]. Fig. 1 presents a DSC profile and additionally an image of the brownish glass in the left corner of this figure. From the DSC profile, the glass transition temperature, T_g, (663 °C), was determined by the tangent method. Furthermore, the profile shows a pre-crystallization peak at 754 °C, a sharp exothermic peak at 867 °C, which is due to the crystallization of the sample, and a further exothermic peak at 1022 °C. The broad peak between 100 and 700 °C is device-specific and occurs because no baseline correction was done. Due to the crystallization of the glass, as a not thermodynamically stable phase, the crystallization peaks are exothermic. The determination of T_g by dilatometry resulted in a value of 666 °C. The comparison of both values show that the different methods lead to nearly the same results. Dilatometry was also used to determine the CTEs; in the temperature ranges from 100 to 300 °C and from 100 to 500 °C, the CTEs of the glass were 3.84 and 4.04 × 10^{-6} K^{-1}, respectively. The density of the glass is 2.47 g/cm^3 and is almost equal to that of a glass containing 2.1 mol% TiO_2 and 0.9 mol% ZrO_2 and somewhat higher than for a glass containing 4.2 TiO_2 and 1.8 mol% ZrO_2, as reported in a previous study [56]. It should be noted