Ceramics International 43 (2017) 9769–9777

Contents lists available at ScienceDirect

Ceramics International

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

Phase formation during crystallization of a Li_2O-Al_2O_3-SiO_2 glass with ZrO_2 as nucleating agent – An X-ray diffraction and (S)TEM-study

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:
Electron microscopy
X-ray methods
Thermal properties
Microstructure-final
Glass ceramics
ZrO2

ABSTRACT

Glass ceramics based on the system $Li_2O/Al_2O_3/SiO_2$ (LAS) often show a coefficient of thermal expansion close to zero. Although these glass-ceramics are of high economic importance, the fundamentals of the crystallization process are still not fully understood. In this paper, the effect of ZrO_2 addition as a sole nucleation agent on the crystallization of the LAS glass is described predominantly using transmission electron microscopy and X-ray diffraction. The composition of the studied green glass was close to that of the commercially available Robax™ glass (Schott AG), which, however, contained both, ZrO_2 and TiO_2 as nucleating agents. It was found that during thermal treatment, in a first step, already at temperatures around 10–20 K below the glass transition temperature, T_g, ZrO_2 nanocrystals with sizes in the range from 5 to 15 nm were precipitated. The next crystalline phase that forms during the crystallization process was LAS with a structure similar to the hexagonal high temperature phase of quartz. These crystals were much larger than the ZrO_2 crystals. If thermal treatment was carried out at higher temperatures, a dense network of LAS crystals was formed. Differently shaped crystals in samples with different thermal history were visualized, and an enrichment of Ba and Sb in the residual glass phase in the late stages of thermal treatment was found. Also, an enrichment of aluminum around the ZrO_2 crystals was evident, which is a hint at a preceding droplet phase separation from which the ZrO_2 crystals were precipitated. The crystallization is notably different from that of mixed ZrO_2/TiO_2 nucleating agents used in commercial lithium alumosilicate glass ceramics.

1. Introduction

Up to now, industrially produced materials with low, i.e. near to zero thermal expansion are exclusively glass-ceramics based on the Li_2O-Al_2O_3-SiO_2 system [1]. The main applications are cook top panels, telescope mirrors, high temperature (furnace) windows [2–4] as well as devices for numerous optical applications. The most important physical property is a coefficient of thermal expansion (CTE) close to zero, which is quite essential e.g. for telescope mirrors blanks because it enables to minimize shape changes with temperature. A thermal expansion coefficient close to zero is also necessary to achieve a high resistance against thermal shock, required e.g. for cook top panels and furnace windows [2–4].

In order to achieve a CTE close to zero, a crystalline phase with a negative thermal expansion coefficient [5,6] is necessary. Usually, this phase is embedded in or co-exists with other phases which show a positive coefficient of thermal expansion. By careful choice of the volume fraction of phases with positive and negative thermal expansion coefficient, an overall thermal expansion coefficient close to zero can be achieved. Phases occurring in commercial low expansion glass ceramics are predominantly, spodumene, eucryptite, keatite or high-quartz solid solutions [5,7]. The latter has a hexagonal structure similar to the high temperature phase of quartz (β-quartz). Some of these glass-ceramics exhibit a fairly high volume fraction of crystalline phases that are embedded in the residual glass matrix, nevertheless, they are fully transparent in the visible spectral range [8,9]. This can only be achieved if the crystals possess sizes well-below the wavelength range of visible light, i.e. in the range of a few ten nanometers only, to prevent scattering of light. Although this type of material was commercialized already decades ago, there is still a lack in the fundamental understanding of the nucleation and crystallization process [10].

Low thermal expansion glass ceramics based on the $Li_2O/Al_2O_3/SiO_2$ system allow the crystallization of β-quartz, which as a pure phase, is not thermodynamically stable at room temperature, but transfers during cooling at 573 °C to α-quartz [1,11]. A stabilization of β-quartz is achieved by the substitution of Si^{4+} by Al^{3+} in the crystal

* 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).

http://dx.doi.org/10.1016/j.ceramint.2017.04.153
Received 22 December 2016; Received in revised form 17 March 2017; Accepted 26 April 2017
Available online 27 April 2017

structure; the residual negative charge of the AlO_4^- tetrahedra is compensated by the incorporation of mono- or divalent ions, such as Li^+ [5,12], Mg^{2+} [11] or Zn^{2+} [5,13] into the crystal structure [1]. Usually, the $Li_2O/Al_2O_3/SiO_2$ glass system is modified by additives, such as Na_2O, K_2O, MgO, ZnO, and by fining agents, such as Sb_2O_5 [14].

Another important group of additives are nucleating agents. Without the addition of nucleating agents, surface nucleation is the dominant nucleation process, leading to a crystalline structure that is fairly coarse and by no means nanocrystalline [14]. If, however, nucleating agents are added to the green glass composition, a volume nucleation can be triggered, that can lead to the crystallization of finely dispersed, nanoscaled crystals homogeneously distributed within the whole sample volume [15–17]. Nucleating agents applied in the past to the $Li_2O/Al_2O_3/SiO_2$ system are primarily TiO_2 [5,12–22] and ZrO_2 [14,19–24] or both of them [14,19–22,25]. Recently, the effect of the concentrations of both TiO_2 and ZrO_2 in the glass on the crystallization, especially on the microstructure of the resulting glass ceramics, was reported [26]. It has been shown that the concentration plays an important part which is in analogy to other alumosilicate systems such as $MgO/Al_2O_3/SiO_2$ [13,27–35].

This paper provides a study on glasses containing solely ZrO_2 as nucleating agent. The effect of thermal treatment on the phase composition and the microstructure is studied.

2. Experimental

The following raw materials were used for the preparation of the glasses: 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).

Approximately 300 g of glass were melted in a middle frequency furnace using a platinum/rhodium crucible. In the first melting step, a temperature of 1615 °C was applied and kept for 2 h. Then the crucible with the melt was transferred to a furnace with $MoSi_2$ heating elements. The crucible with the melt was then heated to a temperature of 1680 °C and kept for 3 h. Then, the glass melt was cast into a cuboid brass mold and transferred to a muffle furnace, preheated to 700 °C. Finally, the furnace was switched off and the glass was cooled to room temperature with a rate of approximately 2 K/min. The studied glass has a composition similar to that of the commercially available Robax™ glass, except the nucleating agent, which was only ZrO_2, i.e. without TiO_2 while in Robax™, both ZrO_2 and TiO_2 are added. The concentration of ZrO_2 was 3.0 mol%.

In Table 1, the chemical composition of the glass is given. The glasses were cut into pieces with a size of around 0.5×0.5 and 0.5 cm^3. For glass crystallization, the specimens were heated to temperatures in the range from 680 to 750 °C, kept for 24 h. For X-ray diffraction (XRD), the samples were powdered and investigated using a Siemens D5000 diffractometer with Cu-K_α radiation (λ=0.154 nm) in a 2θ range from 10° to 60°.

The dilatometric measurements were performed using a Netzsch Dil 402-PC dilatometer. For this purpose, specimens with a diameter of 8 mm and a length of 25 mm were used; the employed heating rate was 10 K/min. Differential scanning calorimetry (DSC, Linseis Pt-1600) with a heating rate of 10 K/min was used to determine the glass transition as well as the crystallization temperatures. In addition, Vickers hardness (microhardness) was measured; the load used was 1.96 N (microhardness tester Duramin 1, Struers). For this purpose, coplanar samples were polished and 10 indentations were made all over the sample. The microhardness was calculated using Eq. (1)

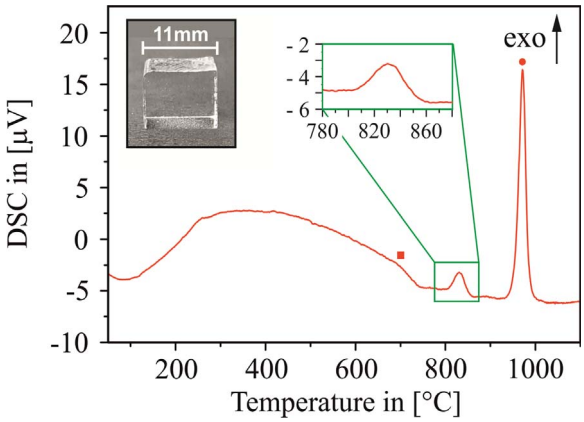

Fig. 1. In the left corner of the DSC-profile, a photo of the melted, as-casted, transparent glass is shown. The inset shows a narrow temperature range in a higher magnification. The glass transition temperature T_g (■), the onset of crystallization and the crystallization temperature T_c (•) are shown.

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

with H_V - the Vickers hardness in GPa, F - the supplied force in N and d - the mean length of the indentation diagonals in m. The density was measured using a helium pycnometer (AccuPyc 1330). Some of the samples were selected for analytical studies to investigate the microstructure by XRD, and (Scanning) Transmission Electron Microscopy (S)TEM combined with Energy-Dispersive X-Ray Spectroscopy EDXS. The transmission electron microscopy analysis was performed with a c_s-aberration corrected FEI TITAN^3 80-300 electron microscope using 80 kV acceleration voltage. The instrument is equipped with a high-angle annular dark field detector (Fischione Model 3000) to perform scanning TEM. For some samples, STEM was combined with energy-dispersive X-Ray spectroscopy analysis (EDXS), using a Super-X EDX detector that is equipped with four SDD detectors (FEI company). Element distribution analyses and element mappings of different elements of chosen samples were obtained that way, 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*- (in case of Zr) or *L*- (in case of Sb and Ba) edges of the analyzed elements, with an automatic, software-provided routine.

As the first step, 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). Using this tool, every sample was formed into a wedge-like shape, whose edge tip is thin enough for TEM to be applied. Each sample underwent a final Ar^+ ion broad-beam milling step (precision ion polishing system PIPS, Gatan company) to remove polishing residues and to reach electron transparency. Finally, the samples were selectively carbon coated using a specific coating mask (CoatMaster, 3D- Micromac AG) [36].

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	ZrO_2	Sb_2O_3
Glass	7.6	0.2	0.1	1.9	0.3	1.2	12.7	72.6	0.0	3.0	0.4