Journal of the European Ceramic Society 38 (2018) 263–269

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Full Length Article

Controlled precipitation of lithium disilicate ($Li_2Si_2O_5$) and lithium niobate ($LiNbO_3$) or lithium tantalate ($LiTaO_3$) in glass-ceramics

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ARTICLE INFO

Keywords:
Lithium disilicate
Lithium niobate
Lithium tantalate
Glass-ceramics
Twofold crystallization

ABSTRACT

In the present study, the crystallization principles and phenomena of base glasses from the system of SiO_2-Li_2O-P_2O_5-Al_2O_3-K_2O-Nb_2O_5 or Ta_2O_5 were investigated. Annealing parameters such as temperature and time were varied. Annealing the base glasses 10 min at temperatures < 850 °C for Nb_2O_5 or Ta_2O_5 containing samples lead to the crystallization of Li_2SiO_3. At higher annealing temperatures or longer annealing times, Li_2SiO_3 disappeared and $Li_2Si_2O_5$ was the main crystal phase in all glass-ceramics. After the dissolution of Li_2SiO_3, the minor crystal phases of $LiNbO_3$ or $LiTaO_3$ were precipitated. Increasing the annealing temperatures as well as the annealing times lead to higher bending strengths up to about 676 MPa and CR-values of up to 100. Increasing the contents of Nb_2O_5 or Ta_2O_5 lead to higher CR-values. The radiopacities increased up to 355% compared to aluminum.

1. Introduction

Lithium disilicate glass-ceramics were the first glass-ceramic materials to be discovered by Dr. Donald Stookey [1] in the 1950s. Since that time, the precipitation of $Li_2Si_2O_5$ crystals from many different base glass systems as well as applying a number of different mechanisms and techniques for nucleation and crystallization were investigated [2–23]. The microstructure of glass-ceramics can be controlled by the chemistry of the base glass and by the particular nucleation and crystallization process. This ongoing research created a large width of different microstructures and hence disclosed a large width of achievable properties for $Li_2Si_2O_5$ glass-ceramics. The properties of the lithium disilicate glass-ceramics made the material useful for technical applications such as hard disk substrates [24] and sealing applications for SOFCs [25]. For instance, being able to combine properties such as strength and translucency opened the field for applications in prosthodontics [2]. Twofold crystallization, which is the parallel precipitation of two crystalline phases within a specific chemical glass-ceramic composition and a specific temperature range by means of separate nucleation and crystallization mechanisms, has been currently applied to create new sets of material properties [26–28]. Crystals of $Ca_5(PO_4)_3F$, $CsAlSi_5O_{12}$ or $CaMgSi_2O_6$ were precipitated as minor phases in $Li_2Si_2O_5$ glass-ceramics to control properties such as opalescence, thermal expansion or translucency.

Besides the exclusive combination of specific properties, the advantageous methods for production and processing via conventional glass technology routes as well as the machinability of glass-ceramics can display crucial pros in the competition with other materials. Especially with sintered ceramics, where issues as powder processing, debinding, sintering and machining are challenging. One typical field of application for technical ceramics is electronic packaging where most exclusively the dielectric properties are important. MacDowell and Beall, 1990 [29], as well as Tummala (1991) [30] and Knickerbocker (1992) [31] investigated cordierite glass-ceramics as an alternative to Al_2O_3 ceramics for electronic packaging [2]. With the fast growing importance of digital technologies including the transfer, storage and processing of data, preferably in handheld devices, also the requirements for materials used in this field strongly increased and specified. Engineering glass-ceramics helps to achieve some of the new requirements. For instance a mechanically strong and black opaque glass-ceramic, still being transparent for microwave and radio radiation, and therefore ideal for the application as backs for electronic devices has been developed by Dejneka et. al (2014) [32]. The glass-ceramics investigated in their study comprise magnetite, pseudobrookite and ε-Fe_2O_3 crystals of approximately 10–20 nm.

High dielectric constants or optoelectronic effects of crystals of the perovskite-type and ilmenite-type such as $LiNbO_3$ and $LiTaO_3$ are interesting properties for the electronics industry [2]. Kokubo et al. (1973) [33] developed a perovskite-type glass-ceramic with the main crystal phase of $K(Ta,Nb)O_3$ in the $SiO_2 – Al_2O_3 – K_2O – Nb_2O_5 – Ta_2O_5$

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.08.032
Received 19 May 2017; Received in revised form 28 August 2017; Accepted 30 August 2017
Available online 01 September 2017
0955-2219/

system. Beall [2] succeeded in precipitating $LiTaO_3$ crystals in the chemical SiO_2 – Li_2O – Ta_2O_5 system. This crystal of $LiTaO_3$ is not an ilmenite crystal but the crystal structure is similar to that of ilmenite, $FeTiO_3$.

The controlled precipitation of $LiNbO_3$ crystals in different types of glass-ceramics was also established. Komatsu et al. [34,35] demonstrated the controlled crystallization of $LiNbO_3$ by laser initiation in glasses derived from the SiO_2 – Li_2O − Nb_2O_5 system.

Gerth et al. (1999) studied controlled, oriented crystallization in the 35 SiO_2 – 45 Li_2O − 20 Nb_2O_5 system. Therefore, a platinum wire was dipped into the melt to initiate the nucleation process. Due to the high content of Nb_2O_5 in the base glass, $LiNbO_3$ precipitated as main crystal phase. Only minor contents of $Li_2Si_2O_5$ and Li_2SiO_3 could be detected [36].

The present study investigates the precipitation of $LiNbO_3$ or $LiTaO_3$ crystals as minor phases in $Li_2Si_2O_5$ glass-ceramics. Extending the base-glass system SiO_2-Li_2O-P_2O_5-K_2O-Al_2O_3 by Nb_2O_5 or Ta_2O_5 was mandatory. Glass-ceramics with high mechanical strength, based on the interlocking network of lathlike $Li_2Si_2O_5$ crystals, were developed. The investigation of the dielectric properties of the new glass-ceramic materials could be a promising subject of further research in the field.

2. Materials and methods

Glasses of the SiO_2-Li_2O-P_2O_5-Al_2O_3-K_2O system extended by Nb_2O_5 or Ta_2O_5 were melted from the raw materials quartz, lithium carbonate, aluminium metaphosphate, aluminium oxyhydroxyhydrate, potassium carbonate and niobium oxide or tantalum oxide in batches of 100–200 g in an uncovered Pt-Rh10 crucible. Table 1 summarizes the base glass compositions.

After one hour at 1500 °C, the melts were casted into water, crushed and subsequently dried at 150 °C for approximately one hour. Thermal analysis of the dried glass frits was conducted by means of differential scanning calorimetry (DSC) in nitrogen atmosphere with a heating rate of 10 K/min until 1200 °C (STA 449 Jupiter F3, Netzsch, Selb, Germany). Afterwards, the glass frits were melted again for one hour at 1500 °C and cast into a graphite mold of the dimensions 13 mm × 13 mm × 30 mm. The monolithic blocks were transferred to a furnace preheated to temperatures between 490 and 520 °C immediately after casting. After a dwell time of 10 min, the furnace was switched off and cooled to room temperature with approximately 2–3 K/min.

Small plates with dimensions of 13 mm × 14 mm × 2 mm were cut from glass blocks and crystallized in a Programat® furnace (Ivoclar Vivadent AG, Schaan, Liechtenstein) applying different heat treatment schedules. The heat treatment schedules are summarized in Table 2.

After annealing, the surfaces of the samples were ground with a 125 µm diamond grit grinding disk. From those samples, XRD-patterns were recorded with $Cu_{K\alpha}$ radiation (λ = 0.154 nm) from 10° to 60° 2θ applying a step size of 0.014° with a D8-Advance diffractometer (Bruker, Karlsruhe, Germany). Furthermore, a quantification of the phases was conducted for samples Nio-2 annealed at 800 °C for 60 min and Tan-3 annealed at 900 °C for 10 min applying Rietveld refinement with the TOPAS software from Bruker. Therefore, the glass-ceramics were crushed and milled using a mortar grinder (Mortar Grinder RM 200, Retsch, Haan, Germany) and subsequently sieved. The pulverized samples with a particle size < 45 µm were mixed with approximately 20 wt% of α-Al_2O_3 (Alfa Aesar, 99,9%, 20–50 µm//ICSD number: 31548) as internal standard and elutriated with acetone. The suspensions were dried in an oven at 80 °C before recording XRD patterns from 10° to 100° 2θ in 0.014° steps.

Table 1
composition of the glasses in mol%.

oxide composition	SiO_2	Li_2O	P_2O_5	Nb_2O_5	Ta_2O_5	K_2O	Al_2O_3
Reference [37,38]	66.70	27.85	1.28	–	–	2.30	1.87
Nio-1	66.03	27.57	1.27	1.00	–	2.28	1.85
Nio-2	65.53	27.36	1.26	1.75	–	2.26	1.84
Nio-3	65.04	27.15	1.25	2.50	–	2.24	1.82
Tan-1	66.03	27.57	1.27	–	1.00	2.28	1.85
Tan-2	65.53	27.36	1.26	–	1.75	2.26	1.84
Tan-3	65.04	27.15	1.25	–	2.50	2.24	1.82

Table 2
temperature/time schedules for the heat treatment of the base glasses.

sample	temperature/time schedule
Ref. (BN030)	600 °C/10 min 850 °C/60 min
Nio-1	850 °C/60 min 850 °C/24 h
Nio-2	800 °C/20 min 800 °C/60 min
Nio-3	600 °C/10 min 750 °C/10 min 850 °C/10 min
Tan-1	850 °C/60 min 900 °C/24 h
Tan-2	850 °C/1 min 850 °C/10 min 850 °C/60 min
Tan-3	600 °C/10 min 750 °C/10 min 820 °C/10 min 850 °C/10 min 900 °C/10 min

The biaxial fracture strength was determined according to ISO 6872:2015 including a surface finishing with a 15 µm diamond grit grinding disc. The specimens were milled from glass blocks using a CEREC® InLab milling machine (Sirona, Bensheim, Germany). The biaxial strengths are given as the means of ten to twelve data sets with standard deviation.

Micrographs of the glass-ceramics were taken by means of scanning electron microscopy (SEM) using backscattered electrons. Therefore, the surface of the glass-ceramic samples were polished using a 0.5 µm diamond grit grinding disc and subsequently etched with 40% hydrofluoric acid vapor for 10 s. After drying, the edged samples were coated with a 1–2 nm Au-Pd layer.

The contrast ratios (CR) of the glass-ceramic discs were determined with a spectrometer of the type CM-3700d (Konica-Minolta, Tokyo, Japan). The glass-ceramic discs were prepared according to BS5612.

The radiopacity was characterized for glass and glass-ceramic samples with dimensions of 13 mm × 14 mm and a thickness of 1 or 2 mm. The specific radiopacity was analyzed according to EN ISO 4049. The radiopacity values were calculated based on the grey shade of the radiograph in comparison to an aluminum standard. The radiographs were detected with a HeliodentPlus X-ray system (Sirona, Bensheim, Germany) on a Carestream CS7600 No.2. imaging plate (Carestream Dental, Atlanta, USA). The specific grey shades were evaluated with the Adobe® Photoshop software (Adobe® Systems, San José, USA).

3. Results

All prepared glasses were transparent. The Ta_2O_5 containing compositions were colorless. Increasing the content of Nb_2O_5 lead to glasses with a slightly yellow to green color.

Figs. 1 and 2 present the results of the DSC measurements. Table 3 summarizes the glass transition temperatures as well as exothermic and endothermic peaks of all samples in comparison to the reference. The glass transition temperatures and the first exothermic peak increase with increasing the content of Nb_2O_5 from zero in the reference sample to 2.5 mol% in Nio-3. All other peak temperatures decrease with