

Effect of Al₂O₃ and K₂O content on structure, properties and devitrification of glasses in the Li₂O–SiO₂ system

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Abstract

The effect of Al₂O₃ and K₂O content on structure, sintering and devitrification behaviour of glasses in the Li₂O–SiO₂ system along with the properties of the resultant glass–ceramics (GCs) was investigated. Glasses containing Al₂O₃ and K₂O and featuring SiO₂/Li₂O molar ratios (3.13–4.88) far beyond that of lithium disilicate (Li₂Si₂O₅) stoichiometry were produced by conventional melt-quenching technique along with a bicomponent glass with a composition 23Li₂O–77SiO₂ (mol.%) (L₂₃S₇₇). The GCs were produced through two different methods: (a) nucleation and crystallization of monolithic bulk glass, (b) sintering and crystallization of glass powder compacts.

Scanning electron microscopy (SEM) examination of as cast non-annealed monolithic glasses revealed precipitation of nanosize droplet phase in glassy matrices suggesting the occurrence of phase separation in all investigated compositions. The extent of segregation, as judged from the mean droplet diameter and the packing density of droplet phase, decreased with increasing Al₂O₃ and K₂O content in the glasses. The crystallization of glasses richer in Al₂O₃ and K₂O was dominated by surface nucleation leading to crystallization of lithium metasilicate (Li₂SiO₃) within the temperature range of 550–900 °C. On the other hand, the glass with lowest amount of Al₂O₃ and K₂O and glass L₂₃S₇₇ were prone to volume nucleation and crystallization, resulting in formation of Li₂Si₂O₅ within the temperature interval of 650–800 °C.

Sintering and crystallization behaviour of glass powders was followed by hot stage microscopy (HSM) and differential thermal analysis (DTA), respectively. GCs from composition L₂₃S₇₇ demonstrated high fragility along with low flexural strength and density. The addition of Al₂O₃ and K₂O to Li₂O–SiO₂ system resulted in improved densification and mechanical strength.

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1. Introduction

Phase separation, nucleation and crystallization of glasses in the Li₂O–SiO₂ system have been the subject of many theoretical studies.^{1–9} According to Vogel,⁹ Li₂O–SiO₂ liquids containing less than 30 mol.% Li₂O lead to opalescent or opaque glasses on cooling owing to phase separation. TEM investigation revealed segregation into droplet like zones of Li-rich phase and SiO₂-rich glass matrix. Moreover, within the Li₂O content range of 14–16 mol.% in the entire glass, Li₂Si₂O₅ (here after referred

as LD) composition was already reached in the droplet phase.⁹ Further increasing the Li₂O content in the entire glass reduced the surface tension of the two phases because Li₂O entered into the SiO₂-rich phase surrounding the droplets and the size of the droplets reduced continuously. Subsequently, with Li₂O content of 33.3 mol.%, corresponding to Li₂Si₂O₅ in the entire glass, the droplet phase and the phase surrounding the droplets had the same composition, with this stoichiometric LD glass composition exhibiting the most homogeneous possible structure.

Generally, slight changes in lithium silicate glass composition may have significant effects on chronology and morphology of phases formed. The addition of P₂O₅ to LD glass was observed to induce amorphous phase separation and to increase the crystal nucleation rate, simultaneously.^{1,2,10–12} The incorporation of

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Table 1
Compositions of the experimental glasses.

	Oxides (mol.%)				
	SiO ₂ /Li ₂ O	Li ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂
G1	4.88	15.23	5.24	5.24	74.30
G2	3.83	19.08	3.94	3.94	73.04
G3	3.13	22.96	2.63	2.63	71.78
L ₂₃ S ₇₇	3.35	22.96	-	-	77.04

TiO₂ in addition to P₂O₅ greatly affected phase evolution, morphology and thereby thermo-physical properties of crystallized glasses in low alumina Li₂O–SiO₂ glasses.¹³ The conventional nucleating agent ZrO₂ in Li₂O–SiO₂ glass enhanced the polymerization of the silicate network, and caused a significant red shift in Raman frequencies for Q² species and amorphous phase separation before crystallization.¹⁴ Recently it was demonstrated that very small amount of MnO₂ and V₂O₅ (less than 1 wt.% in total) might decrease the critical cooling rate of the LD melt and so increase the glass forming tendency.¹⁵ The occurrence of this phenomenon was attributed to the following possible reasons: (a) an increase of melt viscosity and, therefore, of the kinetic barrier against crystallization; (b) an increase of the surface energy difference between the Li-silicate crystals and residual melt, thus enhancing the surface energy barrier against nuclei formation.¹⁵

The role of Al₂O₃ and K₂O on crystallization in glasses featuring SiO₂/Li₂O ratios (3.13–4.88) far beyond of LD stoichiometry was recently studied.¹⁶ Glasses in both bulk and frit form were produced by the conventional melt-quenching technique using alumina crucibles. Therefore, an unavoidable alumina uptake from the crucibles cannot be neglected. To eliminate this anomaly leading to uncontrolled compositional variations, Pt crucibles were used in the present work to prepare the same glass compositions along a new bicomponent (23 mol.% Li₂O and 77 mol.% SiO₂) glass denoted as L₂₃S₇₇. The aim of this work was, therefore, to get a deeper insight on phenomena related to a metastable immiscibility and devitrification in Li₂O–SiO₂ glasses in relevance with Al₂O₃ and K₂O content. Particular emphasis was also given to the investigation of sintering behaviour and the properties of the corresponding glass powder compacts. Significant differences between L₂₃S₇₇ composition and its Al₂O₃ and K₂O containing counterparts were encountered in terms of structure, crystallization kinetics, thermal behaviour and properties.

2. Experimental procedure

Table 1 presents the compositions of the glasses investigated in the present study along with the corresponding SiO₂/Li₂O ratios. The addition of Al₂O₃ and K₂O was performed on equimolecular basis and the amount of additives decreased from glass G1 to G3. The glass L₂₃S₇₇ containing the same amount of Li₂O (22.96 mol.%) as glass G3, but richer in SiO₂ (77.04 mol.%) due to complete exclusion of Al₂O₃ and K₂O from its composition was also prepared and investigated for comparison purposes.

Powders of technical grade SiO₂ (purity >99.5%) and of reactive grade Al₂O₃, Li₂CO₃, and K₂CO₃ were used. Homogeneous mixtures of batches (~100 g), obtained by ball milling, were calcined at 800 °C for 1 h and then melted in Pt crucibles at 1550 °C for 1 h, in air. Glasses were produced in bulk (monolithic) and frit form as described below.

2.1. Crystallization behaviour of bulk glasses

Two sets of bulk glasses for each composition were obtained by pouring the glass melt on preheated bronze mould. The first set of glasses was allowed to cool down in the air while second set of glasses was subjected to annealing at 450 °C for 1 h.

The coefficient of thermal expansion (CTE) of the annealed samples was determined by dilatometry using prismatic samples of bulk glasses with cross section of 3 mm × 4 mm (Bahr Thermo Analyse DIL 801 L, Germany; heating rate 5 K min⁻¹).

The onset of crystallization, T_c and peak temperature of crystallization, T_p for the investigated glasses was obtained from DTA thermographs of glass grains with sizes in the range of 415–1000 μm, collected by sieving of grounded non-annealed glass blocks. The DTA was carried out in air (Netzsch 402 EP, Germany) from room temperature to 1000 °C at different heating rates ($\beta = 2, 5, 10$ and 15 K min⁻¹). The kinetics of crystallization was studied using the formal theory of transformation kinetics as developed by Johnson and Mehl¹⁷ and Avrami,^{18–20} for non-isothermal processes:

$$\ln \left(\frac{T_p^2}{\beta} \right) = \frac{E_c}{RT_p} - \ln q = 0 \quad (1)$$

which is the equation of a straight line, whose slope and intercept gives the activation energy, E_c , and the pre-exponential factor, $q = Q^{1/n} K_0$, respectively, and the maximum crystallization rate by the relationship²¹:

$$\left. \frac{d\chi}{dt} \right|_p = 0.37 \beta E_c n \left(RT_p^2 \right)^{-1} \quad (2)$$

which enables obtaining, for each heating rate, a value of the kinetic exponent, n . In Eq. (2), χ corresponds to the crystallization fraction and $\left. \frac{d\chi}{dt} \right|_p$ is the crystallization rate, which may be calculated by the ratio between the ordinates of the DTA curve and the total area of the crystallization curve.

In order to study the evolution of crystallization phases in monolithic glasses, the annealed glasses were cut into cubes (1 cm × 1 cm × 1 cm) and heat treated non-isothermally at 550, 650, 750, 800 and 900 °C for 1 h, respectively, at heating rate of 2 K min⁻¹.

2.2. Sintering and crystallization of glass powder compacts

The glass frits were produced by quenching of melt in cold water. Further, the glass frits were dried and milled in high speed agate mill resulting in fine glass powders with mean particle size of 5–10 μm as determined by light scattering technique (Coulter LS 230, UK, Fraunhofer optical model). Infrared spectra of the

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