



Crystallization of lithium disilicate-based multicomponent glasses – effect of silica/lithia ratio

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Abstract

Two glass compositions were prepared from the system $\text{SiO}_2\text{-Li}_2\text{O-K}_2\text{O-ZrO}_2\text{-P}_2\text{O}_5$ with different $\text{SiO}_2/\text{Li}_2\text{O}$ ratio (2.39 and 3.39) and the crystallization behavior was investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallization kinetic parameters (activation energy of crystallization and Avrami exponent) were evaluated by different methods from the data obtained by DTA performed at different heating rates. For both glasses, two exothermic peaks were observed in the DTA curves, and the crystallization peak temperatures increased with $\text{SiO}_2/\text{Li}_2\text{O}$ ratio. XRD analysis revealed that the first peak corresponds to the crystallization of lithium metasilicate (Li_2SiO_3) and the second to the formation of lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$). After heating the glasses at a temperature above the second crystallization peak (900 °C), both $\text{Li}_2\text{Si}_2\text{O}_5$ and Li_2SiO_3 were found in samples having the lowest $\text{SiO}_2/\text{Li}_2\text{O}$ ratio, whereas no Li_2SiO_3 was detected in samples with the highest $\text{SiO}_2/\text{Li}_2\text{O}$ ratio. For both glasses, the value obtained by different methods for the activation energy of crystallization was in the range of 225–275 kJ mol^{-1} for the first exothermic peak and in the range of 425–500 kJ mol^{-1} for the second peak. The estimated Avrami exponent was close to 1 for the first exothermic peak, indicating surface crystallization, and close to 3 for the second exothermic peak, suggesting volume crystallization. This was confirmed by the morphological study made by SEM that showed needle-like crystals in the microstructure of samples with lithium metasilicate and granular crystals in the microstructure of samples having lithium disilicate.

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1. Introduction

The $\text{Li}_2\text{O-SiO}_2$ system has attracted great interest since Stookey developed the first glass-ceramic based on the stoichiometric composition of lithium disilicate (LiSi_2O_5 , $\text{SiO}_2/\text{Li}_2\text{O}=2$) [1], and the nucleation and crystallization in the binary $\text{Li}_2\text{O-SiO}_2$ system has been extensively investigated [2–7]. In multicomponent lithium disilicate (LD) glasses, the crystal phase formation is more complicated than in the binary $\text{Li}_2\text{O-SiO}_2$ system and is largely affected by the nature and amount of oxides added to glasses, including the nucleating agents (e.g. P_2O_5 , ZrO_2 , TiO_2) [8–12].

Concerning the crystallization process for non-stoichiometric LD glass compositions, several references [10–13] suggest that the formation of LD is preceded by the crystallization of lithium metasilicate (Li_2SiO_3 , $\text{SiO}_2/\text{Li}_2\text{O}=1$) in contrast to what is observed in stoichiometric glasses [2,11]. First, lithium metasilicate (LS) crystallizes in the glass at temperatures in the range of 650–700 °C and then reacts with SiO_2 to form LD at higher temperatures [10–13].

Glass-ceramics derived from non-stoichiometric LD with addition of several oxides, including nucleating oxides, exhibit good chemical, mechanical and thermal properties and have been recognized as potential candidates for various structural and functional applications, such as ceramic composites, ceramic-metal sealing and all-ceramic dental restorations [10,14–17]. The properties of the glass-ceramics depend upon composition of the parent glass as well as thermal treatment and addition of

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nucleating agents, which control the type of phases precipitated from the glasses, the extent of crystallization, crystal morphology, crystal size and aspect ratio [18–20]. Parameters that should be known for converting glasses into glass-ceramics for specific technological applications include the kinetic parameters, which provide the possibility to determine the mechanisms of nucleation and growth processes [18,19]. Kinetic aspects of crystal growth have been extensively investigated in the simple non-stoichiometric $\text{Li}_2\text{O}-\text{SiO}_2$ binary system [20–22], but investigations on the crystallization kinetics in non-stoichiometric multi-component LD glasses are still needed.

The aim of the present work was to investigate the influence of $\text{SiO}_2/\text{Li}_2\text{O}$ molar ratio (2.39 and 3.39) on the crystallization behavior under non-isothermal conditions of LD glasses based on the system $\text{SiO}_2-\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{ZrO}_2-\text{P}_2\text{O}_5$, namely the crystallization kinetic parameters, phase assemblage and final microstructure. The crystallization parameters, activation energy of crystallization (E_c) and the Avrami exponent (n) in Johnson-Mehl-Avrami (JMA) equation [23–26], were determined from DTA results using non-isothermal methods. The variations of E_c and of n with the fraction of crystallization were evaluated. XRD was employed to identify the crystalline phases that precipitated in heat-treated glass samples. SEM was used to analyze the evolution of microstructural features during the non-isothermal treatment, the results being discussed together with the values calculated for the Avrami exponent to analyze the mechanisms of crystallization.

2. Experimental procedure

The glasses were prepared from SiO_2 (BDH), Li_2CO_3 (Sigma-Aldrich), K_2CO_3 (BDH), ZrO_2 (BDH) and P_2O_5 (Sigma-Aldrich) powders, all of them with a purity higher than 99%. Table 1 presents the nominal glass compositions with the corresponding $\text{SiO}_2/\text{Li}_2\text{O}$ ratio. An homogeneous mixture of a 30 g batch was prepared by weighing the right amounts of the starting materials, mixing for 30 min in a PTFE jar, using a laboratory powder mixer (model T2F, WAB, Switzerland), and then melting in alumina crucible in an electric furnace at 1250 °C for 2 h in air. The molten glass was quenched into cold distilled water to form a glass frit. The glass frit was dried, milled with absolute ethanol for 2 h in an agate ball mill (model Pulverizette, Fritsch, Germany), dried again, and sieved to obtain a glass powder with a particle size smaller than 65 μm .

Differential thermal analysis (DTA) was performed in an equipment (model STA PT1600, Linseis, Germany), where 50 mg glass powder samples were heated in alumina crucible

from room temperature to 900 °C, at various heating rates (2, 5, 10, 15, 20, 25 and 30 K/min) in static air and using an empty crucible as reference. From the DTA curves, the glass transition temperature (T_g), the onset crystallization temperature (T_c) and the peak crystallization temperature (T_p) were determined using the software associated with the equipment, and the measurement error is assumed as 1%.

The heat-treated samples used in this study were prepared by uniaxial pressing the glass powder under a compressive stress of 110 MPa and firing the resulting compacts (≈ 3 mm height, 13 mm diameter) in an electric tubular furnace from room temperature up to a selected temperature suggested by the DTA results. The samples were heated at a heating rate of 5 °C min^{-1} , held during 1 h at that temperature and then were left to cool inside the furnace.

The amorphous nature of the as-prepared glass powder and the crystalline phases formed in heat-treated glass samples were identified by X-ray diffraction analysis (XRD), using a diffractometer (model DMAX-IIIIC, Rigaku Industrial Corporation, Japan), with $\text{CuK}\alpha$ radiation (40 kV, 30 mA), 2θ angle range of 10–60°, a scanning rate of 2° min^{-1} and a sampling interval of 0.01° (2θ). The phases were identified by comparing the experimental X-ray patterns to standards compiled by the International Centre for Diffraction Data (ICDD). The microstructure of sintered glass samples was observed using a scanning electron microscope, SEM (model DSM 960, ZEISS, Germany). SEM observations were carried out in polished surfaces (mirror finishing) that were etched by immersion in 2 vol. % HF solution for 7 min. To reduce charge effects, as the samples are nonconductive, they were fixed to the holder with a carbon tape and coated with carbon before SEM observation.

3. Results and discussion

3.1. Differential thermal analysis

DTA curves for both glass compositions exhibited an endothermic step associated with glass transition and two crystallization exothermic peaks. Typical scans at heating rates of 10 and 20 K min^{-1} are shown in Fig. 1, where temperatures of glass transition (T_g), first crystallization peak (T_{p1}) and second crystallization peak (T_{p2}) are indicated.

To study the non-isothermal crystallization kinetics, DTA thermographs at various heating rates were recorded. The peak crystallization temperatures (T_{p1} and T_{p2}) at the different heating rates for each glass composition are summarized in Table 2. It is observed that for each glass composition the values of T_{p1} and T_{p2} increase with the heating rate. It is also observed that peak crystallization temperatures are higher for composition S2, having the highest $\text{SiO}_2/\text{Li}_2\text{O}$ ratio. This may be attributed to the fact that the higher content of modifier oxide (LiO_2) in composition S1 comparatively to that in S2 can facilitate the breakdown of the silicate glass network favoring the occurrence of crystallization at lower temperature [27].

Table 1
Glass compositions (mol %).

Composition	SiO_2	Li_2O	K_2O	ZrO_2	P_2O_5	$R=(\text{SiO}_2/\text{Li}_2\text{O})$
S1	67.70	28.29	1.89	1.40	0.72	2.39
S2	74.12	21.86	1.89	1.40	0.72	3.39

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