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Effect of K_2O on structure–property relationships and phase transformations in $Li_2O–SiO_2$ glasses

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Abstract

Glass compositions with formula $(71.78-x)SiO_2$–$2.63Al_2O_3$–$(2.63+x)K_2O$–$23.7Li_2O$ (mol.%, $x=0$–10) and SiO_2/Li_2O molar ratios far beyond that of stoichiometric lithium disilicate ($Li_2Si_2O_5$) were prepared by conventional melt-quenching technique to investigate the influence of K_2O content on structural transformations and devitrification behaviour of glasses in the $Li_2O–SiO_2$ system. The scanning electron microscopy (SEM) examination of as cast non-annealed glasses revealed the presence of nanosized droplets in glassy matrices suggesting occurrence of liquid–liquid phase separation. An overall trend towards depolymerization of the silicate glass network with increasing K_2O content was demonstrated by employing magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy. The distribution of structural units in the experimental glasses was estimated using ^{29}Si MAS-NMR spectroscopy suggesting the appearance of Q^2, enhancement of Q^3 and diminishing of Q^4 groups with increasing K_2O contents. X-ray diffraction (XRD) and differential thermal analysis (DTA) were used to assess the influence of K_2O on devitrification process and formation of lithium disilicate ($Li_2Si_2O_5$) and/or lithium metasilicate (Li_2SiO_3) crystalline phases.

Keywords: Glass; Glass ceramics; Lithium disilicate; Thermo-physical properties

1. Introduction

The immiscible region between the $Li_2O–2SiO_2$ and SiO_2 end members is an important feature in the $Li_2O–SiO_2$ system. The synthesis of glass-ceramic (GC) materials in the $Li_2O–SiO_2$ system is based on controlled nucleation and crystallization of lithium metasilicate and/or lithium disilicate phases which govern the properties for the final product. The glasses with SiO_2 contents higher than the stoichiometric $Li_2O\cdot 2SiO_2$ (33.33 mol.% Li_2O–66.66 mol.% SiO_2) tend to separate into a matrix phase with a composition almost similar to that of lithium disilicate along with an isolated droplet SiO_2 rich phase,[1] while glasses with Li_2O contents <30 mol.% usually turn out to be opalescent or opaque on cooling owing to phase separation.[1–3] Although, nucleation of base glass with stoichiometric composition of lithium disilicate has been widely investigated for GC manufacture,[4] the GCs derived from this parent binary system exhibit some unfavourable characteristics in terms of their mechanical and chemical properties which hinder their potential applications in several technological areas.

On the other hand, lithium disilicate GCs derived from non-stoichiometric compositions have proven themselves to be potential candidates for different functional applications, for example: dental restorations,[5–8] metal-glass seals,[9,10] etc. Fundamental research on certain non-stoichiometric lithium disilicate based glass compositions was carried out by Stookey (1959).[11] It is noteworthy that according to Höland and Beal,[4] the term 'non-stoichiometric' implies that SiO_2/Li_2O molar ratio deviates greatly from 2:1 and the system in rendered considerably more complex with numerous additional components and nucleating agents. However, the present investigation aims towards investigating a relatively simpler non-stoichiometric lithium disilicate based GC system in the glass forming region of $Li_2O–K_2O–Al_2O_3–SiO_2$ with its SiO_2/Li_2O molar ratio varying between 2.69 and 3.13. The simultaneous incorporating of K_2O and Al_2O_3 is known to significantly improve the chemical

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Table 1
Compositions of the experimental glasses.

	Oxides (mol.%)				SiO_2/Li_2O	SiO_2/K_2O	K_2O/Al_2O_3
	Li_2O	K_2O	Al_2O_3	SiO_2			
GK_0	22.96	2.63	2.63	71.78	3.13	27.29	1.00
$GK_{0.5}$	22.96	3.13	2.63	71.28	3.10	22.77	1.19
GK_1	22.96	3.63	2.63	70.78	3.08	19.50	1.38
$GK_{1.5}$	22.96	4.13	2.63	70.28	3.06	17.02	1.57
GK_2	22.96	4.63	2.63	69.78	3.04	15.07	1.76
$GK_{2.5}$	22.96	5.13	2.63	69.28	3.02	13.50	1.95
GK_5	22.96	7.63	2.63	66.78	2.91	8.75	2.90
GK_{10}	22.96	12.63	2.63	61.78	2.69	4.89	4.80

durability of lithium disilicate GCs,[1,12,13] therefore justifying the choice of these two oxides in the present study. One of the main objectives of this study was to investigate the influence of replacing increasing amounts of SiO_2 by equimolar amounts of K_2O on the structural transformations occurring in the non-stoichiometric lithium disilicate glasses, and on their crystallization mechanism.

2. Experimental procedure

2.1. Glass preparation

The investigated glass compositions were designed according to the general formula $(71.78 - x)$ SiO_2–$2.63Al_2O_3$–$(2.63 + x)$ K_2O–$23.7Li_2O$ (mol.%), where x changed from 0 to 10, with SiO_2/Li_2O ratios far from lithium disilicate stoichiometry ($SiO_2/Li_2O = 2$). Accordingly, the glasses have been labelled as GK_x depending on the amount of K_2O being substituted for SiO_2 in the glass compositions. For example: GK_0 corresponds to the parent composition, i.e. $x = 0$ and $K_2O/Al_2O_3 = 1$. Table 1 presents the detailed composition of the glasses along with their corresponding SiO_2/Li_2O, SiO_2/K_2O and K_2O/Al_2O_3 ratios.

A total of eight glasses were prepared in Pt-crucibles using melt quenching technique. The powders of technical grade SiO_2 (purity >99.5%) and of reactive grade Al_2O_3, Li_2CO_3, and K_2CO_3 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. The glasses were produced in bulk (monolithic) form by pouring glass melts on bronze mould in two different sets. The glasses of one set were immediately annealed at 450 °C for 1 h; the other set of glasses was preserved in the non-annealed condition.

2.2. Thermo-physical properties of glasses

The coefficient of thermal expansion (CTE) of the annealed glasses was measured by dilatometry using prismatic samples of bulk glasses with cross section of $3 \times 4\ \mathrm{mm}^2$ (Bahr Thermo Analyse DIL 801 L, Germany; heating rate $5\ \mathrm{K\,min}^{-1}$). The differential thermal analysis (DTA, Setaram Labsys, Setaram Instrumentation, Caluire, France) of glasses was carried out in air from room temperature to 1000 °C at heating rate (β) of $20\ \mathrm{K\,min}^{-1}$. The glass powders with sizes in the range of 500–1000 μm (collected by sieving of crushed non-annealed glass blocks) and weighing 50 mg were contained in an alumina crucible and the reference material was α-alumina powder. The value of the glass transition temperature T_g, crystallization onset temperature, T_c and peak temperature of crystallization, T_p were obtained from the DTA scans.

Archimedes' method (i.e. immersion in ethylene glycol) was employed to measure the apparent density of the bulk annealed glasses which was further applied along with compositions of glasses to calculate their excess volume (V_e) according to a procedure described elsewhere.[3]

2.3. Structural characterization of glasses

^{29}Si MAS-NMR spectra were recorded on a Bruker ASX 400 spectrometer operating at 79.52 MHz (9.4 T) using a 7 mm probe at a spinning rate of 5 kHz. The pulse length was 2 μs and 60 s delay time was used. Kaolinite was used as the chemical shift reference. ^{27}Al MAS-NMR spectra were recorded on a Bruker ASX 400 spectrometer operating at 104.28 MHz (9.4 T) using a 4 mm probe at a spinning rate of 15 kHz. The pulse length was 0.6 μs and 4 s delay time was used. $Al(NO_3)_3$ was used as the chemical shift reference. The Q^n distributions were obtained by curve fitting and spectral deconvolution using DMFIT program (version 2011).[14]

2.4. Crystalline phase analysis and microstructural evolution in glass-ceramics

Bulk parallelepiped glass samples were heat treated non-isothermaly at 600, 700, 800 and 900 °C for 1 h, respectively, at a heating rate of $2\ \mathrm{K\,min}^{-1}$. The amorphous nature of the parent glasses and the nature of crystalline phases present in the GCs were determined by X-ray diffraction (XRD) analysis (Rigaku Geigerflex D/Mac, C Series, Japan; Cu Kα radiation, 2θ between 10° and 60° with a 2θ-step of $0.02\ ^\circ\ \mathrm{s}^{-1}$). The crystalline phases were identified by comparing the obtained diffractograms with patterns of standards complied by the International Centre for Diffraction Data (ICDD).

Microstructure observations were done at polished (mirror finishing) and then etched surfaces of samples (by immersion in 2 vol.% HF solution for 1–2 min) by field emission