Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

The roles of P_2O_5 and SiO_2/Li_2O ratio on the network structure and crystallization kinetics of non-stoichiometric lithium disilicate based glasses

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ARTICLE INFO

Keywords:
Glass
Lithium disilicate
Nucleation
Crystallization kinetics

ABSTRACT

During the last decades, the nucleation and crystallization of the Li_2O-SiO_2 system has been widely investigated and its particular theoretical features disclosed. However, multicomponent lithium disilicate systems, being of higher technological interest, still require further studies aiming at better tailoring their relevant mechanical and chemical properties. Here we report on the effects of SiO_2/Li_2O molar ratio and the addition of P_2O_5 on the structure and crystallization behaviour of multicomponent lithium disilicate based glasses. Two non-stoichiometric P_2O_5-free lithium disilicate based glasses featuring equimolar contents of K_2O and Al_2O_3 and with SiO_2/Li_2O molar ratios of 2.62 and 2.92 were synthesized in the Li_2O-SiO_2 system through the melt-quench technique. The influence of partially replacing (K_2O + Al_2O_3) by P_2O_5 while keeping the same SiO_2/Li_2O molar ratios of P_2O_5-free glasses was investigated. The structural features of glasses were assessed by nuclear magnetic resonance. Differential thermal analysis was used to study crystallization kinetics and the crystalline phase evolution was followed by X-ray diffraction. The results showed that an increase in SiO_2/Li_2O molar ratio decreased the overall crystallization rate, preventing the formation of lithium disilicate. However, adding P_2O_5 had an opposite effect, enhancing the formation of fine lithium disilicate crystals. The nucleating role of P_2O_5 is discussed.

1. Introduction

Glass-ceramics can be produced by melting glasses and converting the vitreous substances into fine-grained materials through controlled nucleation and growth of crystalline phases via heat treatment [1,2]. In particular, the Li_2O-SiO_2 system has attracted great interest since Stookey developed the first glass-ceramic material on the near stoichiometric lithium disilicate composition ($Li_2Si_2O_5$, hereafter named LS_2) [3]. After this, and during the last decades, the nucleation and crystallization in the binary Li_2O-SiO_2 system has been widely investigated [4–7].

However, glass-ceramics derived from the binary system exhibit some unfavourable characteristics in terms of their mechanical and chemical properties which hinder their potential applications in several technological areas. Therefore, nonstoichiometric multicomponent compositions have been developed in order to improve the properties of LS_2 glass-ceramics. For instance, the addition of Al_2O_3 and K_2O to the stoichiometric composition enhanced the chemical durability of the glasses [8–11]. Several other constituents such as ZnO, ZrO_2, CaO, V_2O_5, etc., have also been added to improve the properties of the final materials [1,12,13]. Several compounds such as CaF_2, ZrO_2, TiO_2 and P_2O_5 have been added as nucleating agents [14,15]. Among all of them, P_2O_5 revealed to be most effective, playing an important role in phase formation and crystallization of LS_2 glass-ceramics [15,16,17]. In addition, Beall and Echeverria [18,19] suggested that the SiO_2/Li_2O ratio is also a key success factor in the formation of the main crystal phase in a LS_2 glass ceramic system.

The multicomponent LS_2 based glass-ceramics exhibit promising thermal, chemical and mechanical properties and have been pointed out as potential candidates for various structural and functional applications (e.g. all-ceramic dental restorations, ceramic composites or ceramic-metal sealing) [1,20,21]. But the crystal phase formation from multicomponent glasses is more complex than in the binary Li_2O-SiO_2 system. Moreover, the crystalline nature of the glass-ceramic products is greatly affected by the type and amount of other oxides present in the glass composition, including the nucleating agents [14,15,22–24].

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https://doi.org/10.1016/j.jnoncrysol.2017.11.034
Received 20 December 2016; Received in revised form 13 November 2017; Accepted 18 November 2017

Please cite this article as: Gaddam, A., Journal of Non-Crystalline Solids (2017), https://doi.org/10.1016/j.jnoncrysol.2017.11.034

During the crystallization process of non-stoichiometric LS_2 glass compositions, several authors suggested that lithium metasilicate ($LiSi_2O_3$, hereafter named LS) precedes LS_2 formation [15,25,26] in contrast to what was observed in the stoichiometric composition [5,15]. In particular, the crystallization process of non-stoichiometric LS_2 glass compositions occurs in two stages: (1) LS crystallizes in the glass at lower temperatures (in the range of 650–700 °C), and (2) LS reacts with SiO_2 to form LS_2 at higher temperatures [27,25]. The mechanism of this behaviour was explained in our previous paper [23].

The properties of the glass-ceramics depend upon the type of phases precipitated from the glasses, the extent of crystallization, crystal morphology, crystal size and aspect ratio. All these features are, in turn, dependent upon the composition of the parent glass (including the addition of nucleating agents) and thermal treatment [1,28]. Therefore, determining the parameters that control the mechanisms of nucleation and growth processes (e.g. kinetic parameters) is of major importance to obtain materials with the desired properties [1,28]. Although kinetic aspects of crystal growth have been extensively investigated in the simple non-stoichiometric Li_2O-SiO_2 binary system [29,30], the crystallization kinetics in non-stoichiometric multicomponent LS_2 glasses still needs to be studied.

The aim of the present work was to investigate the influences of SiO_2/Li_2O molar ratio (2.62 and 2.92) and of the added amount of P_2O_5 (1 mol%) on the structure and crystallization behaviour of non-stoichiometric multicomponent lithium silicate glasses based on the system $Li_2O-K_2O-Al_2O_3-SiO_2$.

2. Experimental procedure

2.1. Synthesis

Four experimental compositions (Table 1) belonging to Li_2O–K_2O–Al_2O_3–SiO_2–(P_2O_5) system were prepared. Potassium from K_2O was used for charge compensating when Al_2O_3 partially replaces SiO_2 in the binary Li_2O–SiO_2 system, while P_2O_5 was incorporated as a nucleating agent. Powders of technical grade SiO_2 and reagent grade Li_2CO_3, K_2CO_3, Al_2O_3 and $(NH_4)_2HPO_4$ were used as precursors; all having a purity of > 99%. Batch compositions of 100 g were prepared by homogenously mixing the powdered raw materials in a ball mill, followed by calcination at 1073 K (800 °C) for 1 h. Pt crucibles were used to melt the compositions at 1823 K (1550 °C) for 1 h in air. Bulk (monolithic) glasses were prepared by pouring the melt on a bronze mould and allowed to cool at ambient temperature. Glasses were not subjected to annealing to avoid any pre-nucleation and crystallization. The glass-ceramics (*GCs*) were prepared from small pieces of the bulk glasses by heating them first to a temperature of 823 K (550 °C) for 1 h at 10 K min^{-1} in air (for nucleation) followed by heat treatment to temperatures between 873 K (600 °C), and 1173 K (900 °C) for 1 h at intervals of 100 K.

2.2. Characterization

The network structure of the glasses was investigated by magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR, Bruker ASX 400). All samples were crushed to fine powders and characterized in a 400 MHz (9.4 T) spectrometer working at Larmor frequencies of 79.5, 104.3 and 161.9 MHz and were excited by 90°, 45° and 10° pulses for ^{29}Si, ^{27}Al and ^{31}P nuclei, respectively. The spin-lattice relaxation times for ^{29}Si, ^{27}Al and ^{31}P were 60, 1 and 60 s, respectively, which were optimized from the previous glass compositions. 4 mm rotors for ^{27}Al and ^{31}P nuclei, and 7 mm rotors for ^{29}Si, were used. The MAS frequencies were 5, 14 and 12 kHz for ^{29}Si, ^{27}Al and ^{31}P nuclei, respectively. The obtained spectra were deconvoluted using DMFIT program [31]. Fourier transform infrared spectroscopy (FTIR, model Mattson Galaxy S-7000) was carried out in the range of 300–1400 cm^{-1} with a resolution of 4 cm^{-1} on glass powders prepared by crushing the bulk glass. Samples for FTIR were prepared by mixing 1/150 (by weight) portion of the sample with KBr and hand pressed to obtain pellets.

Differential thermal analysis (DTA, Netzsch STA 409 EP, Germany) was carried out on all glass compositions obtained by crushing the bulk glass to particle sizes between 500 and 1000 μm (collected by sieving). DTA experiments were carried out in air from ambient temperature to ~1173 K (900 °C) at heating rates α = 10, 15, 20 and 25 K min^{-1} using ~330 mg of sample in an Alumina crucible, with α-Alumina powder as reference material. The DTA-calibration was done using α-alumina pre-calcined at 1600 °C in both crucibles and for all heating rates. The results obtained are then used to calibrate the DTA apparatus by comparison with an internal standard and to make the correction of the DTA-baseline curves using a polynomial function.

Both glass and crystallized samples were polished and etched using 2 vol% hydrofluoric acid for 60 s and their microstructures were recorded using scanning electron microscope (SEM, SU-70, Hitachi, Japan) and stereo microscope (SM, Leica EZ4 HD, Germany). Crystalline phases in the samples were identified by X-ray diffraction (XRD, Rigaku Geigerflex D/Mac, C Series, Japan) using CuKα radiation with 2θ varying from 10 to 60° at steps of 0.02 s^{-1}.

Densities of all bulk glasses were measured employing Archimedes principle by immersing the samples in ethylene glycol solution.

Table 1
Compositions of the experimental glasses and the compositions calculated from the NMR spectra in parenthesis (in mol %).

	Li_2O	K_2O	Al_2O_3	SiO_2	P_2O_5	SiO_2/Li_2O
G24	24.0 (26.0)	3.0 (2.9)	3.0 (2.9)	70.0 (68.1)	0.0 (0.0)	2.9 (2.6)
$G24_P$	24.0 (23.4)	2.5 (2.5)	2.5 (2.5)	70.0 (70.5)	1.0 (1.0)	2.9 (3.0)
G26	26.0 (28.7)	3.0 (2.9)	3.0 (2.9)	68.0 (65.5)	0.0 (0.0)	2.6 (2.3)
$G26_P$	26.0 (26.8)	2.5 (2.5)	2.5 (2.5)	68.0 (67.3)	1.0 (1.0)	2.6 (2.5)

3. Results

All glass compositions were suitable for easy casting after melting for 1 h at 1823 K (1550 °C), resulting in homogeneous and transparent bubble free glasses. The amorphous nature of the as-cast glasses was confirmed by XRD (**S1**). Considering the high melting temperature, at which the lighter elements are prone to volatilization (such as Li in the current compositions), the determined weight losses upon melting the glasses were < 0.2%. Such values are negligible, being within the limits of experimental errors [32].

3.1. MAS-NMR and FTIR spectroscopy

The deconvoluted ^{29}Si NMR spectra into three components of Q_2, Q_3 and Q_4 units are presented in Fig. 1. Similarly, the deconvoluted ^{31}P NMR spectra into two components of $Q_{0(P)}$ and $Q_{1(P)}$ are presented in Fig. 2. The corresponding NMR parameters of simulations and the relative amounts of each species are presented in Table 2. Due to the large amounts of network modifiers available to charge compensate $(AlO_{4/2})^-$ tetrahedra, the ^{27}Al NMR spectra (**S2**) for all the glasses exhibit only a single peak at ~58 ppm, which corresponds to Al^{IV} species. The chemical shift was obtained by fitting a single line shape using Czejeck distribution [33], and the corresponding quadrupolar coupling constant (C_Q) was 4.4 MHz.

The FTIR spectra of the experimental glasses (Fig. 3) show three absorption peaks at positions ~470, ~775 and ~1050 cm^{-1}, which correspond to the TO_1, TO_2 and TO_3 modes of vibrations, respectively [34]. Due to very small variations in the chemical compositions of the studied glasses, there are no noticeable differences in the spectra.