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Effect of heat treatment on the microstructure and properties of lithium disilicate glass-ceramics

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ABSTRACT

The effect of heat treatment on microstructure and properties of SiO_2–Li_2O–K_2O–Al_2O_3–ZrO_2 glass-ceramics was investigated. The glasses were subjected to a multi-stage heat treatment. At the first stage at 650 °C, Li_2SiO_3 was the main crystalline phase of all samples, which had a dimensional change with prolonging the heating time from 3 h to 72 h. After the second stage treatment at 830 °C for 3 h, all the Li_2SiO_3 crystals decomposed and $Li_2Si_2O_5$ crystals formed with an opposite dimensional change from that of Li_2SiO_3. These $Li_2Si_2O_5$ crystals were small, which could contribute to forming high translucency. The third stage at 550 °C would release the internal strain and improve samples' bending strength, which could reach up to above 560 MPa. The sample treated for 48 h at the first stage had the smallest crystals and also obtained a highest real in-line transmission of 29% at 650 nm with a thickness of 1.45 mm and a bending strength above 581 ± 25 MPa.

1. Introduction

Glass-ceramics (GCs) are polycrystalline materials obtained by crystallization of suitable glasses through an appropriate heat treatment [1–3]. Many properties of GCs are determined by the precipitated crystals and their microstructures [4,5]. Lithium disilicate ($Li_2Si_2O_5$, hereafter referred as LD) GC is one of the most thoroughly studied GCs for its good crystallization ability, translucency and mechanical properties. This glass has a wide range of practical applications [6–9]. The excellent properties depend on the composition of the parent glass and thermal treatment. In the case of the composition, several oxides have been introduced for developing LD GC featuring properties. Hugo R. et al. found that the addition of Al_2O_3 and K_2O could improve the chemical durability, densification and mechanical strength, which can reach up to 201 MPa [10]. TiO_2 and P_2O_5 were used as efficient nucleating agents, contributing to a fine-grained interlocking microstructure in GCs which could lead to a high mechanical strength [11,12].

In the case of heat treatment, the crystallization in the multicomponent glasses took place in two heat-treat stages [13]: first lithium metasilicate (Li_2SiO_3, hereafter referred to as LM) crystallized in the glass then transformed into LD, this transformation was believed to underlie the solid-state reaction of $Li_2SiO_3 + SiO_2 \rightarrow Li_2Si_2O_5$ [14]. The heat treatment at both stages would have a significant influence on final crystal precipitation, crystal species and content. Borom et al. [15] studied the effect of different heating routes on the microstructure of Li_2O–Al_2O_3–SiO_2–B_2O_3–K_2O–P_2O_5 system, and found that LD content and crystal size remained fairly constant with increasing growth time. Zheng et al. [16] studied one-stage and two-stage treatments on Li_2O–SiO_2–ZnO–K_2O–P_2O_5 glass and found that two-stage treatment was favorable for the growth of stable LD crystals. Some researchers also focused on the extended heat-treatment of the glasses, McCollister et al. [17] heat treated the SiO_2–Li_2O–Al_2O_3–K_2O–P_2O_5–B_2O_3 glass for a time period sufficient to cause growth of cristobalite and LM producing a glass-ceramic having a specific thermal expansion coefficient. Burgner et al. [18] heated the $34.5Li_2O$–$65.6SiO_2$ (mol%) glass for over 100 h and found that LM phases did not persist at long times in lithium disilicate glass. But few reports systematically studied the effect of different holding times at the LM precipitation stage on the microstructure, mechanical and optical properties of final LD GCs. In this study, experimental lithium disilicate GCs in the SiO_2–Li_2O–K_2O–Al_2O_3–ZrO_2–P_2O_5 system were prepared by melt-casting and three-stage heat treatment was carried out. Different holding times, especially extending to 72 h at the first stage, were performed to evaluate the developed microstructure, mechanical and optical properties. Furthermore, the interrelation of microstructure, mechanical and the optical properties of the GC was also discussed in detail.

2. Experimental

2.1. Glass preparation

The investigated glass composition was designed as follows: 65.0 SiO_2–27.5 Li_2O–2.2 Al_2O_3–2.3 K_2O–2.0 ZrO_2–1.0 P_2O_5 (mol%). Standard laboratory reagent-grade Li_2CO_3, SiO_2, Al_2O_3, K_2CO_3, ZrO_2 and $NH_4H_2PO_4$ powders (99.99 mass%, CNCM, China) were chosen as raw

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materials. Homogeneous mixtures of batches were obtained by ball milling and melted in high-purity alumina crucibles at 1450 °C for 2 h, in air. The melts were poured into preheated steel molds and annealed at 500 °C for 2 h to relieve stress. Annealed glass samples were cut into 30 mm × 3 mm × 4 mm for bending test and 1.45 mm × 15 mm × 15 mm for translucency evaluation. Small amounts of the glasses were poured into water to obtain glass frits.

2.2. DSC analysis and heat treatment

The glass frits were used for differential scanning calorimetry measurement with DSC-machine (SDT Q600, TA, America). The temperature range was from room temperature to 1150 °C in air and the heating rate amounted to 10 K/min. A three-stage heating cycle was designed in the present work. At the first stage, samples named G3, G6, G12, G24, G48 and G72 were heat treated at 650 °C for 3 h, 6 h, 12 h, 24 h, 48 h and 72 h, respectively. Subsequently, all of them were heated at 830 °C for 3 h at the second stage, and then all the samples were treated at 550 °C for 3 h at the third stage. All treatments were carried out in a muffle furnace with a heating rate of 5 K/min. Finally, all the treated samples were ground on wet silicon carbide papers and then polished to get a smooth surface.

2.3. Crystalline phase analysis and performance test

The crystalline phases were determined by X-ray diffraction (XRD) analysis (Empyrean, PANalytical, Netherlands) with Cu K_α radiation and scanning from 10° to 60° at a scanning speed of 5°/min. The polished samples were etched by immersing in 5 vol.% HF solution for 15 s and coated with a very thin Au layer. A microstructure analysis in a field emission scanning electron microscope (FE-SEMVEGAII XMU, Tescan, Czech Republic) then followed. The crystallinities of lithium disilicate GCs could be estimated by Eq. (1), where I_a is the integrated intensity of the non-crystalline phase and I_c is the integrated intensity of the crystalline phase.

$$X_c = \frac{\sum I_c}{\sum I_c + \sum I_a} \times 100\%. \quad (1)$$

The SEM results were also used for measuring the crystal length using Nano-Measuring image analysis software. Three-point bending strength was tested with a universal testing apparatus (Instron-1195, Shimadzu, Japan), at a span length of 16 mm and a crosshead speed of 0.5 mm/min. Translucent values were expressed by real in-line transmission, which was measured in 300–1100 nm range by ultraviolet/visible spectrum spectrometer (UV-1800; Mapada, Shanghai, China).

3. Results

3.1. Phase formation

DSC trace of the investigated glass is shown in Fig. 1. The glass transition temperature (Tg) is about 480 °C. Two exothermic crystallization peaks at 645 °C and 827 °C could be associated to the formation of LM and LD, respectively.

Fig. 2 presents the XRD patterns of the glass samples subjected to sequential heat treatments. At 650 °C, LM dominated in all samples and there was no significant change in crystalline composition until the heating time reached 72 h, at which a few of silica and LD emerged in G72. Fig. 2b indicates that LM had completely disappeared and LD formed, acting as principal crystalline phase in all samples after treated at 830 °C for 3 h. A few SiO_2 as minor phase appeared in all samples. Crystallinities of all samples after treated at the first stage are summarized in Table 1. According to the table, all samples' crystallinities did not change obviously with prolonging the heating time except that of G72, which was relatively higher. The total crystallinities of all samples were similar after the second stage.

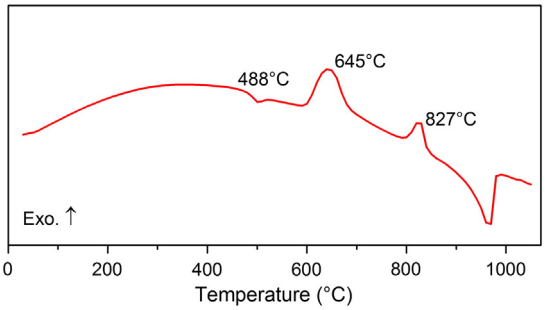

Fig. 1. DSC analysis of parent glass (ramp rate of 20 K/min in air).

3.2. Microstructural features

The microstructural features of glass heated at 650 °C for different holding times are illustrated in Fig. 3. As LM is more easily dissolved in HF than silica glass matrix, when the glass is etched by HF, left pits reflect the microstructure of LM crystals. The LM crystals of all samples were in dendritic shape and had a dimensional change with prolonging the holding time. Fig. 4 represents the microstructure of samples under same treatment at 830 °C for 3 h at the second stage. Fig. 4(a) shows rod-like shape LD crystals of G3 in a closely packed and multi directionally interlocking microstructure. The other samples had the same microstructure with a gentle variation of the mean size of LD crystals. Some LD crystals in G72 were relatively coarser and in an irregular

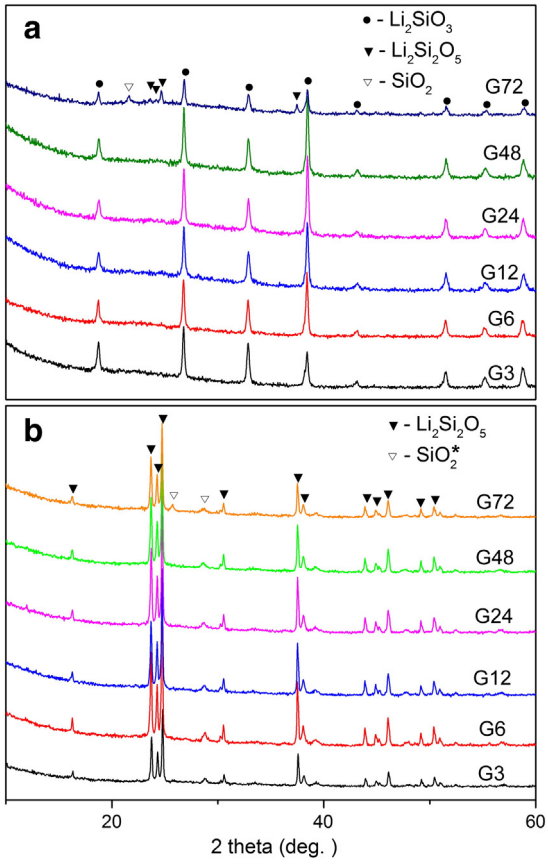

Fig. 2. XRD patterns of lithium disilicate glass ceramics underwent two-stage heat treatment. (a) glasses treated at first stage, at 650 °C for different time, (b) all glasses treated at second stage, at 830 °C for 3 h: Li_2SiO_3, ICCD card 29-0829; $Li_2Si_2O_5$, ICCD card 40-0376; SiO_2, ICCD card 42-1401, Tridymite; SiO_2*: ICCD card 12-0711, Coesite.