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The crystallization and microstructure evolution of lithium disilicate-based glass-ceramic

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ABSTRACT

In this work, transformation of crystalline phases and development of microstructure of two kinds of glass-ceramics, SiO_2–Li_2O–P_2O_5 and SiO_2–Li_2O–K_2O–Al_2O_3–ZrO_2–P_2O_5, have been studied by X-ray diffraction and scanning electron microscopy analysis.

In the former glass, a small amount of spherical $Li_2Si_2O_5$ crystals precipitated at the usual nucleation temperature, which changed little in size and packing density with the increase of the temperature. These spherical $Li_2Si_2O_5$ also have no effect on the volume crystallization of residual glass or the morphology of subsequently formed plate-like $Li_2Si_2O_5$ crystals. In the latter glass, Li_2SiO_3 crystallized first and then decomposed at higher temperature, forming two kinds of $Li_2Si_2O_5$ crystals with different morphologies. The interlocked rod-like shaped $Li_2Si_2O_5$ crystals were resulted from interaction of Li^+ ions and SiO_2-rich glassy phase and oriented crystal bundles of $Li_2Si_2O_5$ were formed from rearrangement of a silicate framework in Li_2SiO_3.

1. Introduction

Glass-ceramics (GCs) are attractive materials with a unique microstructure obtained by a controlled heat treatment of glass [1–4]. Their wide range of properties can be obtained by changing the composition and the heat treatment process [5]. Among GCs, lithium disilicate ($Li_2Si_2O_5$, hereafter referred to as LD), one of the most thoroughly studied GCs for its good crystallization ability and mechanical properties, has a wide range practical applications, especially for dental restorative applications [6–9].

The nucleation mechanism and crystalline phase formation in both binary SiO_2–Li_2O system [10] and multi-component LD glasses [11] after heat treatment have been extensively investigated. In the binary SiO_2–Li_2O system, one or more metastable phases formed prior to LD did [12–14]. While for multi-component LD glasses, the crystal phase formation is more complicated and largely affected by additives added to glasses [15–17]. A common crystallization process suggested in the literature is this [18]: first lithium metasilicate (Li_2SiO_3, hereafter referred to as LM) crystallizes in the glass and then reacts with SiO_2 to form LD underlying the state reaction $Li_2SiO_3 + SiO_2 \rightarrow Li_2Si_2O_5$ at higher temperature. In the case of P_2O_5 doped glasses, Headley et al. [19] found that silicate phases showed an epitaxial growth on crystallized Li_3PO_4 seeds, but nuclear magnetic resonance (NMR) results obtained by Bischoff et al. [20] negated the epitaxial growth model and instead suggested that the nucleation of LM and LD both initiated at the phase boundary between the amorphous phosphate species and glass matrix. However, more details about relationship between LM and LD and how the microstructure was affected by crystalline phase transformation were not revealed by these researchers. In our present work, a binary system and a multi-component SiO_2–Li_2O system were used as model materials and P_2O_5 was added as nucleating promoter. A multi-stage heat treatment was designed to crystallize these glasses. The main purpose is to study the precipitation and transformation process of crystalline phases and microstructural evolutions in these two systems.

2. Material and methods

Two-component and five-component lithium disilicate glass systems with SiO_2/Li_2O molar ratio of 2.41 and extra addition of P_2O_5 prepared in this work were named as C2 and C5. Table 1 summarizes the composition of those glasses. 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% purity, CNCM, China) were chosen as raw materials. Homogeneous mixtures of

Table 1
Batch compositions of the two glasses; random errors <±3%.

Constituent (mol.%)	SiO_2	Li_2O	P_2O_5	K_2O	Al_2O_3	ZrO_2
C2	70	29	1			
C5	66	27.4	1	1.8	1.8	2

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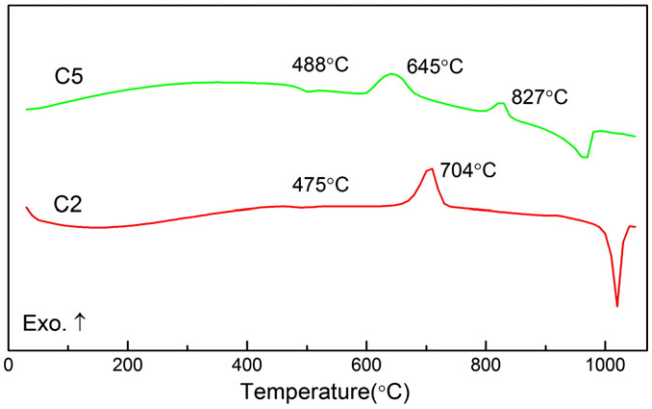

Fig. 1. DSC analysis of the two parent glasses (ramp rate of 10 °C/min in air).

batches, obtained by ball milling, were melted in high-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. The compositions of the prepared glasses were analyzed by X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS). Random errors of single components were smaller than ±3%.

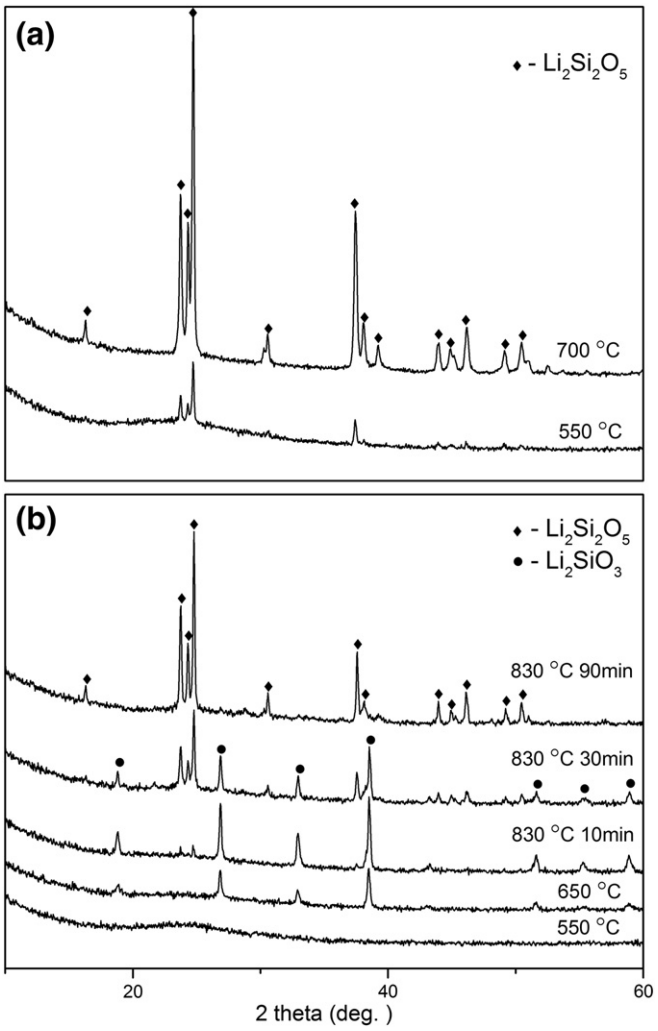

Fig. 2. X-ray diffractograms of bulk glasses heat treated at different temperatures for different time: (a) C2 glass, (b) C5 glass.

Small amounts of glass were used for differential scanning calorimetry (DSC) measurements 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. Based on the DSC results, multi-stage heat treatments were designed. The two glasses were annealed at 550 °C for crystal nucleation, then C2 was treated at 700 °C for 2 h with a heating rate of 20 K/min, while C5 was heated at 650 °C for 2 h with the same heating rate, then quickly heated to 830 °C in 2 min and hold for 10, 30, and 90 min, respectively. The fast heating was employed to minimize the additional nucleation or crystal growth during the heating process. The crystalline phases were determined by X-ray diffraction (XRD) analysis (Empyrean, PANalytical, Netherlands) with Cu Kα radiation and scanning from 10° to 60°. A microstructure analysis in a field emission scanning electron microscope (SEM, FE-SEMVEGAII XMU, Tescan, Czech Republic) was employed to detect the crystal transformations. The samples were polished and etched by 5 vol.% HF solution for 15 s, then subsequently sputtered with Au.

3. Results

The DSC trace of the investigated glasses is shown in Fig. 1. The glass transition temperature (*Tg*) of two studied systems is about 480 °C. For C2, DSC trace reveals a single crystallization event at 704 °C, while C5 shows two exothermic crystallization peaks at 645 °C and 827 °C.

Fig. 2 presents XRD patterns of glasses subjected to sequential heat treatment. The characteristic peaks of LD crystals can be observed in C2 after annealed at 550 °C for 2 h while no crystallographic peaks can be defined in C5. The sequential heat treatment at 700 °C for 2 h causes

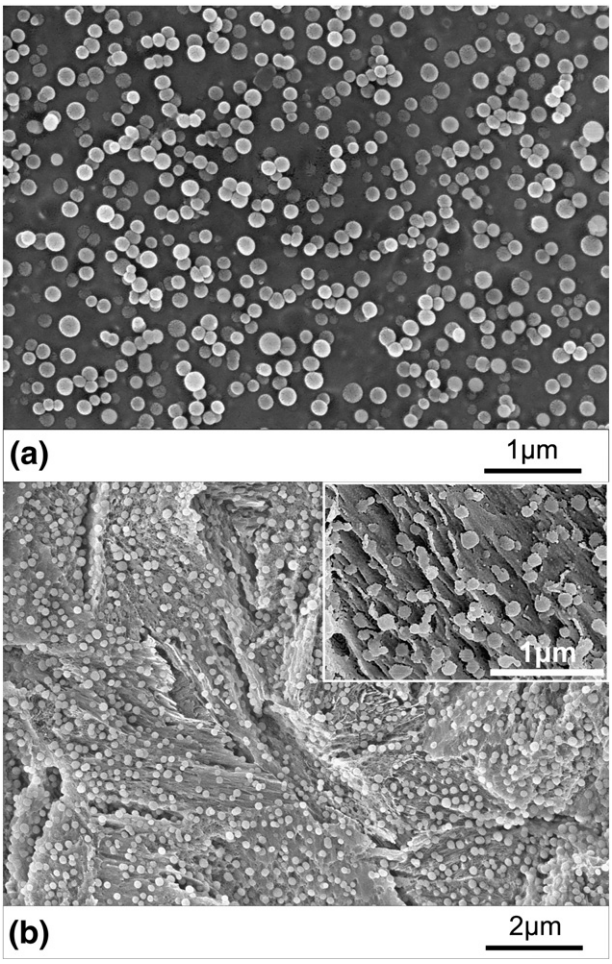

Fig. 3. SEM images of C2 glass, heat treated at different temperatures: (a) 550 °C, (b) 700 °C. The inset is the enlarged image.