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Crystallization of a high-strength lithium disilicate glass-ceramic: An XRD and solid-state NMR investigation

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ABSTRACT

The phase evolution of a high flexural strength lithium disilicate ($Li_2Si_2O_5$: LS_2) glass-ceramic in a complex SiO_2–Li_2O–Al_2O_3–MgO–P_2O_5–ZrO_2 glass system has been investigated as a function of temperature using in situ and ex situ X-ray diffraction (XRD) and ^{31}P and ^{29}Si solid-state nuclear magnetic resonance (SSNMR) spectroscopy. In the base glass, lithium metasilicate (Li_2SiO_3: LS) crystallizes (at 525 °C) before LS_2 (at 675 °C). ^{29}Si NMR shows that LS is not only formed from the $Q^{(2)}_{glass}$ species, but also by disproportionation of the $Q^{(3)}_{glass}$ units. The XRD data demonstrate the formation of a minor phase of $MgAl_2Si_4O_{12}$ from the reaction of SiO_2 with minor components of Al_2O_3 and MgO. Diffraction peaks of Li_3PO_4 are firstly detected at 675 °C, and they become evident at 750 °C and above. The evolution of phosphorus species in the glass as a function of temperature has been revealed by ^{31}P NMR spectroscopy. Two ^{29}Si T_1 relaxation components were observed in samples across all temperatures, suggesting the presence of glass-in-glass phase separation in the base glass. A plot of ^{29}Si T_1 relaxation measurements shows discontinuity at 750 °C, indicating microstructural changes. A detailed crystallization mechanism of high-strength LS_2 glass–ceramics is proposed.

1. Introduction

Lithium disilicate ($Li_2Si_2O_5$, LS_2) glass-ceramics, as an outstanding candidate for dental restorative material [1,2], have been intensively studied because of their biocompatibility, ease of fabrication, chemical stability, optical aesthetics, and excellent mechanical qualities [3–10]. Base glasses of the LS_2 type glass-ceramics for dental applications are usually comprised of multiple components. They consist of Li_2O and SiO_2 as dominant components, with some minor additions such as nucleants, fluxing agents and colorants. It is essential to understand the nucleation mechanism and the process of structural transformation to obtain glass-ceramics with desirable microstructure and physico-chemical properties. P_2O_5 has been used as a nucleating agent to achieve controllable nucleation and crystal growth of LS_2 [9–12]. However, phosphate-related species at early stages of nucleation, being mainly amorphous, cannot be investigated by X-ray diffraction (XRD) until lithium orthophosphate (Li_3PO_4, LP) has crystallized.

Solid-state nuclear magnetic resonance (SSNMR) is capable of monitoring the changes occurring between one state of structural disorder and another [13]. This makes SSNMR a unique multinuclear technique for studying the conversion of glasses to glass-ceramics. Because of the enhanced resolution it provides, magic-angle-spinning (MAS)-NMR has been used for probing the local structure, $Q^{(n)}$, of silicate glasses [14–17]. Q denotes a silicon atom bonded to four oxygen atoms and the superscript $n = 0$ to 4 indicates the number of bridging oxygen atoms [14,18]. ^{29}Si and ^{31}P NMR was used to investigate the early stages of crystallization in LS_2 glasses [19,20]. Holland et al. [19] reported that crystalline LP was not detected before the formation of LS_2. They implied that somehow greater linewidth of the crystalline $Q^{(3)}$ resonance, compared to the crystalline LS_2 peak, could be due to a local disorder and the formation of *metastable* LS_2 phases which were precursors to a *stable* one. Based on chemical shift information and experiments with increased delays between pulses, the authors have also suggested the presence of a glass-in-glass phase separation in the $Q^{(4)}$ species. Iqbal et al. indicated that multiple polymorphs (or a disordered phase) coexisted with crystalline LS_2 in a glass nucleated for longer than 228 h at 454 °C [20]. Bischoff et al. suggested that the nucleation of LS_2 glasses was triggered by the steep compositional gradients, highlighting the role of the disordered/amorphous phosphate species at early stages in the crystallization of glasses [21]. Such a mechanism for the nucleation of LS_2 glasses has been recently supported by in situ synchrotron XRD investigations [22].

According to Bischoff et al. [21], crystallization proceeds in two steps: (i) $Q^{(3)}$ units yield the crystalline LS and $Q^{(4)}$ units (at ca. 650 °C) and (ii) the crystalline LS reacts with the $Q^{(4)}$ units yielding crystalline LS_2 (at ca. 850 °C). ^{31}P NMR revealed the formation of pyrophosphate and orthophosphate groups at the same time. These findings

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suggest that the disordered LP and crystalline LS form simultaneously as intermediate phases, while the well-ordered LP and LS_2 crystallize at higher annealing temperatures. Such a process represents one of the three crystallization sequences categorised in our previous study [23]. Nevertheless, in the sealing application of LS_2 glass-ceramics, the nucleation process can initiate on preferential facets of pre-existing LP crystallites [24], implying that glass-ceramics can crystallize by epitaxial growth on species obtained from a specifically introduced nucleating agent.

It is reported that a transition between $Q^{(3)}$ and $Q^{(4)} + Q^{(2)}$ species occurs in silicate glasses [3,21]. Mortuza et al. indicated that the disproportionation of $Q^{(3)}$ occurs only with the preexistence of $Q^{(2)}$ in partially devitrified LS_2 glasses [14]. Very recently, we have developed an LS_2 glass-ceramic material with an exceptionally high flexural strength of 562 ± 107 MPa [25]. In that work, we focused primarily on the strengthening of glass-ceramics via a step-by-step optimization from a novel glass composition. We also showed that the highly intertwined microstructure formed in these glass-ceramics contributed effectively to the high flexural strength. However, the mechanism that drives the microstructure evolution, and the structural transformation at the atomic level during the glass crystallization process is as yet unclear.

Hence, there is an obvious requirement for additional investigations of the crystallization process from bulk glasses to high-strength LS_2 glass-ceramics. To get a better insight into the structural evolution, both crystalline and amorphous phases have to be examined. To extend this investigation to precursors, i.e. amorphous phases present at the beginning of the annealing process, we investigate the nucleation and crystallization of the LS_2 glass-ceramic using ^{29}Si and ^{31}P MAS-NMR experiments. Microstructural changes were further explored by measuring the ^{29}Si spin-lattice relaxation time (T_1).

2. Experimental section

2.1. Materials

The complex LS_2 glass demonstrating high-strength properties in its glass-ceramic products was designed in the $SiO_2 - Li_2O - MgO - Al_2O_3 - P_2O_5 - ZrO_2$ system [25], and melted in a corundum crucible at 1350 °C for 18 h at Gaffer Coloured Glass Ltd., Auckland, New Zealand. The main glass composition was 63.27 SiO_2, 24.77 Li_2O, 2.49 MgO, 2.48 Al_2O_3, 1.63 P_2O_5, and 0.90 ZrO_2 in molar percentages. Some minor additives were added to the composition as well, including the flux agents (2.47 CaO, 1.18 K_2O and 0.80 Na_2O) and 0.1 mol% MnO which was introduced to reduce the relaxation time for ^{29}Si NMR experiments.

2.2. High-temperature X-ray diffraction

High-temperature X-ray diffraction (HT-XRD) measurements were performed using Cu Kα radiation produced at 40 kV and 30 mA in a diffractometer (D8 Advance, Bruker AXS, Germany) with a high-temperature chamber (Anton Paar HTK 1200). Continuous XRD patterns were recorded in the temperature range of 500– 925 °C with step intervals of 25 °C (a total of 18 measurements), in the 2θ range of 10–40° with a step size of 0.02° and a step time of 1 s. The average heating rate in the temperature range of 480–930 °C was 1 K/min.

2.3. Sample annealing

To understand the structural changes related to the Si and P in the glass during the annealing process, seven samples were produced for NMR measurements. The base glass (without annealing) was labelled C0 and the samples annealed at 525–850 °C were labelled C1– C6, respectively. Sample annealing was done in the same furnace. Samples were taken out sequentially under the programmed six-step profile at 525, 675, 700, 750, 800 and 850 °C with a holding time of 25 min for each step. All samples were powdered for SSNMR measurements.

2.4. Room-temperature X-ray diffraction

Crystalline phases were identified by laboratory X-ray powder diffraction (XRD; D2-Phaser, Bruker AXS, Germany) with Cu K_α radiation ($\lambda = 1.5418$ Å), which was operated at 30 kV and 10 mA. Data was recorded over the 2θ range of 10°– 90° with a step increment of 0.02° and an interval time of 0.1 s per step.

2.5. Solid-state NMR measurements

All solid-state NMR experiments were carried out on dry powder samples using a Bruker AVANCE 300 standard bore magnet system (7.05 T) operating at 59.62 MHz for ^{29}Si and 121.50 MHz for ^{31}P measurements.

2.5.1. ^{29}Si spectroscopy

Experiments were carried out at ambient temperature using samples enclosed in zirconium oxide (ZrO_2) 7 mm rotors. The ^{29}Si chemical shift scale was referenced to tetramethylsilane (TMS). The 90° pulse length was 4.2 μs. Different recycle delays were used for the samples C0–C6, depending on the T_1 relaxation time. The relaxation delays were from to 800 to 10,000 s. All relaxation delays were determined to enable the complete relaxation of the longest component present in the sample. The spectral width was 50.125 kHz. The saturation recovery method was used for the measurement of ^{29}Si T_1 relaxation times, where a train of fifty 90° pulses was applied followed by an observe pulse. The recycle delay was 1 s and the delay in saturation pulse train was 5 ms. The relaxation data are summarized in the Supplementary Information (SI) section. The spinning speed for ^{29}Si was 5 kHz.

2.5.2. ^{31}P spectroscopy

The spinning speed for all ^{31}P experiments was 7 kHz. The 90° pulse length was 4.6 μs and the spectral width was 50.125 kHz. The ^{31}P chemical shift scale was referenced to 85% H_3PO_4. The inversion recovery method was used for the measurement of the T_1 relaxation times of the ^{31}P species and the relaxation delays were between 40 and 120 s. These delays were sufficient to allow detection of ^{31}P containing phases, although they might not be adequate for the exact quantification of ^{31}P species, which was not the aim of this study. Consequently, the spinning sidebands were not included in the fitting.

Spectral fitting was carried out using MestReNova program (version 8.14 2013). Spectra were deconvoluted with a Gaussian lineshape that reflects the distribution of chemical shifts due to disorder, while a predominantly Lorentzian lineshape was found more suitable for the crystalline phases observed in the glass-ceramic samples.

3. Results

3.1. In situ laboratory high temperature XRD

The HT-XRD patterns of the glass in situ monitored from 500 to 900 °C using laboratory Cu Kα radiation are shown in Fig. 1. At 525 °C, the LS phase is exclusively nucleated at the beginning, via reaction Eq. (1). Subsequently, at 675 °C, both the LS and LS_2 phases appear in the sample. LS_2 is formed from LS and a glassy SiO_2 component via the reaction shown in Eq. (2). From that point, the LS_2 phase dominates in the glass-ceramic. The formation of LP was detected at 725 °C, and it subsequently crystallized well at temperatures above 750 °C (Eq. (3)). Two minor phases, β-quartz (825–900 °C) and $MgAl_2Si_4O_{12}$ (800–875 °C), whose diffraction peaks are very close (Fig. 1), crystallized from the residual glass matrix at high temperatures via Eqs. (4) and (5).

$$Li_2O_{glass} + SiO_{2\ glass} = Li_2SiO_{3cryst} \quad (1)$$

$$Li_2SiO_{3cryst} + SiO_{2\ glass} = Li_2Si_2O_{5cryst} \quad (2)$$