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# Crystallization and properties of a spodumene-willemite glass ceramic

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## Abstract

Spodumene-willemite glass ceramics were produced by replacement of $Al_2O_3$ in lithium aluminium silicate by ZnO. With replacement of $Al_2O_3$ by ZnO, the batch melting temperature, glass transition temperature ($T_g$) and crystallization temperature ($T_p$) all decreased. The main crystalline phases precipitated were eucriptite, β-spodumene and willemite ($Zn_2SiO_4$). All compositions of glass ceramics showed bulk crystallization. As ZnO content increased, the grain sizes and thermal expansion coefficients increased, while the flexural strength and fracture toughness of the glass-ceramics increased first, and then decreased. The mechanical properties were correlated with crystallization and morphology of glass ceramics.

*Keywords:* Glass; Glass-ceramics; Crystallization; Spodumene; Willemite

## 1. Introduction

Glass-ceramics open a wide range of possibilities for designing new materials. The properties of glass-ceramics are determined by the crystallization phases precipitated from the glasses and their microstructures, which depended on composition of the parent glass as well as thermal treatment and addition of nucleating agents [1–3].

Lithium aluminosilicate (LAS) glass-ceramics have low, zero, or even negative thermal expansion coefficient as well as excellent thermal shock resistance and chemical durability [1–3]. But they have high melting temperatures ($\geq$1600 °C). In LAS glass-ceramics, the main crystalline phases are β-quartz solid solution ($Li_2O–Al_2O_3–2SiO_2$) and β-spodumene ($Li_2O–Al_2O_3–4SiO_2$). In commercial LAS glass-ceramics, $Li_2O:Al_2O_3:SiO_2$ is usually 1:1:6–8. For many years, ZnO has been used in LAS glass ceramics to lower the melting point[4–15]. Willemite has a low thermal expansion of $15 \times 10^{-7}\,K^{-1}$, similar to β-quartz solid solution ($0–1 \times 10^{-7}\,K^{-1}$) and β-spodumene ($3–9 \times 10^{-7}\,K^{-1}$)[7,9,10]. Attempts to add ZnO to make glass ceramics with spodumene and willemite have failed [16–20]. In this work, Spodumene-willemite glass-ceramics were produced by replacement of $Al_2O_3$ by ZnO, and the crystallization behaviour and properties of the glass-ceramics investigated.

## 2. Experimental procedures

The starting materials were analytical grade: $SiO_2$, $Al_2O_3$, $Li_2CO_3$, $TiO_2$, $ZrO_2$ and ZnO. The detailed proportions of the glasses are given in Table 1. Glass batches were melted in alumina crucibles at 1500–1600 °C for 2 h, and then annealed at 600 °C for 1 h. Homogeneous, transparent glasses were obtained from all compositions.

Differential thermal analysis (DTA) of annealed glass specimens was carried out in a Dupont 2100 Thermal Analyzer. After crushing annealed glasses to about 100–200 μm, non-isothermal experiments were performed by heating 30 mg samples in a Pt crucible with $Al_2O_3$ as the reference material in the temperature range between 20 and 1200 °C at 5-20 °C $min^{-1}$.

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Table 1
Composition of the glasses (wt.%)

| Sample | $Li_2O$ | $Al_2O_3$ | $SiO_2$ | $TiO_2$ | $ZrO_2$ | ZnO | E/kJ mol$^{-1}$ | *n* |
|---|---|---|---|---|---|---|---|---|
| Z0 | 6 | 22 | 67 | 3.5 | 1.5 | 0 | 415 ± 3 | 2.8 ± 0.2 |
| Z5 | 6 | 17 | 67 | 3.5 | 1.5 | 5 | 395 ± 4 | 3.1 ± 0.3 |
| Z10 | 6 | 12 | 67 | 3.5 | 1.5 | 10 | 381 ± 2 | 3.3 ± 0.2 |
| Z15 | 6 | 7 | 67 | 3.5 | 1.5 | 15 | 368 ± 3 | 3.5 ± 0.3 |

X-ray diffraction (XRD) investigations were made with a D-max-RB diffractometer with Cu Ka radiation in the $2\theta$ range from 10° to 70° at 0.02° steps.

Scanning electron microscopy (SEM) was conducted with a JSM-6301F. Specimens were prepared with standard metallographic techniques followed by chemical etching in an HF solution (5%) for 1.5 min. Etched glass–ceramic samples were coated with a thin layer of gold.

The strength was measured in 10 specimens for each sample (4 × 3 × 36) using a 4-point bending strength with a span of 30 mm at a crosshead speed of 0.5 mm/min. The fracture toughness was measured by an indentation fracture (IF) method using the Evans equation to calculate $K_{IC}$ from the length of the crack and the semi-diagonal of the indentation [21]:

$$K_{IC} = 0.015\left(\frac{c-a}{a}\right)\left(\frac{E}{H}\right)^{2/3}\frac{P}{c^{3/2}} \quad (1)$$

where *c* is the crack length; *a*, the half of the diagonal indentation; *E*, the Young's modulus; *H*, the hardness; *P*, the load applied.

## 3. Results and discussion

### 3.1. DTA results

DTA curves of the four glasses at a heating rate of 10 °C min$^{-1}$ are shown in Fig. 1. The decrease of the glass transition temperature ($T_g$) and the crystallization temperature ($T_p$) can be attributed to the increase ZnO content in the glass. The replacement of 15 wt.% $Al_2O_3$ by ZnO decreased $T_g$ and $T_p$ of the glass by approximately 140–150 °C. The peak height and sharpness increased. The glass transition ($T_g$) and the crystallization temperature ($T_p$) decrease can be attributed mainly to the decrease of the melt viscosity with increasing ZnO content. The peak height and sharpness increase may be related to the increased tendency of bulk crystallization [18].

From Johnson-Mehl-Avrami (JMA) equation [22–25]

$$\ln\frac{T_p^2}{\alpha} = \frac{E}{RT_p} + \text{Const} \quad (2)$$

where $T_p$ is the crystallization peak maximum temperature in a DTA curve, $\alpha$ is the heating rate of DTA, *R* is the gas constant, the effective overall activation energy, *E*, can be evaluated. Values of *E* derived from the plots of $\ln T_p^2/\alpha$ versus $1/T_p$ in Fig. 2 are given in Table 1. With increasing ZnO content, *E* decreases.

The Avrami parameter (*n*) was calculated from the activation energy by the Augis-Bennett equation [26]:

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \quad (3)$$

where $\Delta T$ is the full width of the exothermic peak at the half maximum intensity. The values of *n* are 2.8, 3.1, 3.3, and 3.5 for the glasses are given in Table 1. A value of n close to 1 indicates surface crystallization, n close to 2 indicates two-dimensional crystallization, and $n = 3$ as found, implies bulk crystallization [24].

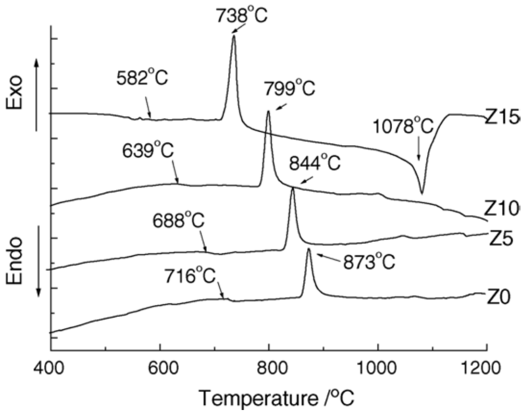

Fig. 1. DTA curves of glass samples, $\alpha = 10$ K/min.

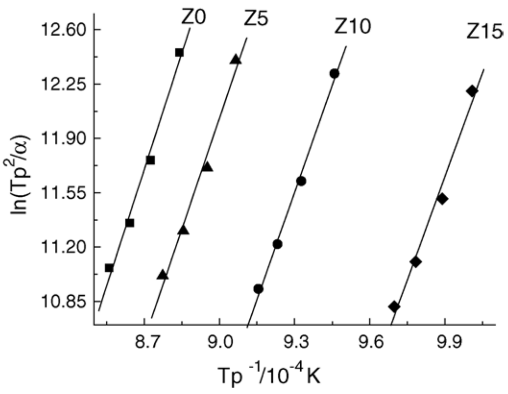

Fig. 2. Plots of $\ln T_p^2/\alpha$ vs. $1/T_p$ for the four glasses.

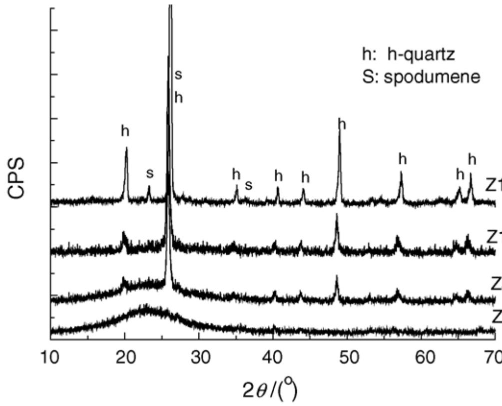

Fig. 3. XRD patterns of the glass-ceramics samples heat-treated at 720 °C/2 h.

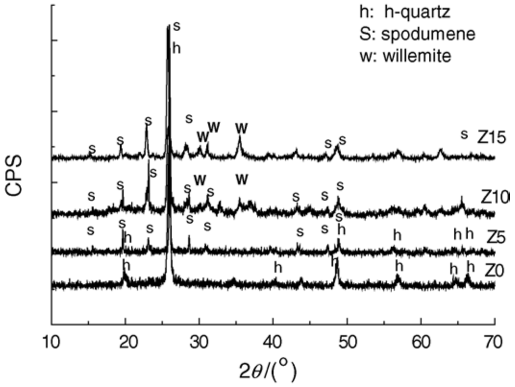

Fig. 4. XRD patterns of the glass-ceramics samples heat-treated at 820 °C/2 h.

### 3.2. XRD results

Fig. 3 illustrates the powder XRD patterns of the glasses heat-treated at 720 °C for 2 h. Sample Z0 heat-treated at 720 °C is still amorphous. In sample Z5, a small amount of β-quartz type structure appeared. In sample Z10, β-quartz solid solution increased, and in Z15, β-spodumene appeared.

The powder XRD patterns of the glasses heat-treated at 820 °C for 2 h are shown in Fig. 4. β-Quartz solid solution appeared in sample Z0. In sample Z5, β-quartz solid solution transformed to β-spodumene. In sample Z10, the main phase was β-spodumene and willemite, and in sample Z15, the amount of willemite increased.

It is clear that with replacement of $Al_2O_3$ by ZnO, the transformations of glass to β-quartz solid solutions and β-quartz solid solutions to β-spodumene are all accelerated. With increasing ZnO content, in high temperature, besides β-spodumene, a willemite phase precipitates.

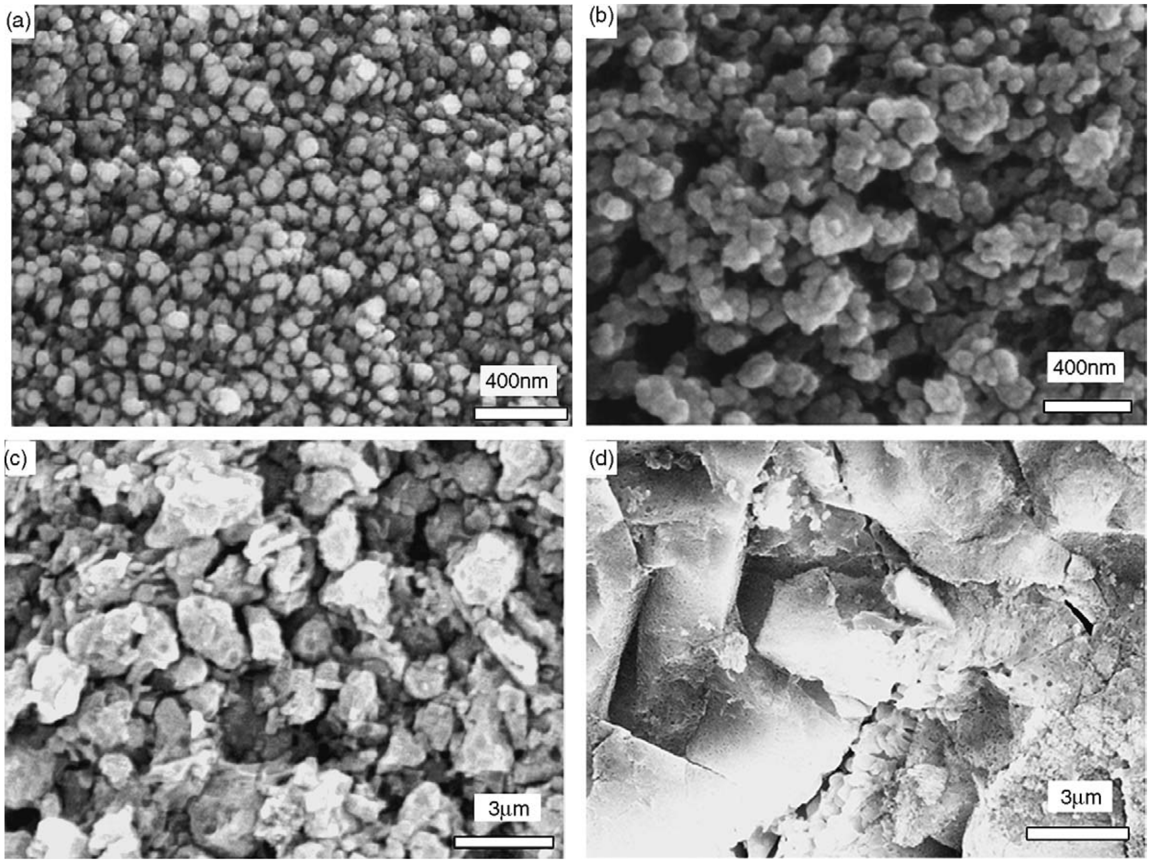

Fig. 5. SEM photographs of Z0, Z5, Z10 and Z15 samples heat-treated at 820 °C for 2 h.

Table 2
Crystallized phases, thermal expansion coefficient, bending strength and fracture toughness of glass-ceramics

| Sample | Applied heat treatment/°C/h | Crystallized phases | Thermal expansion coefficient/K | Bending strength/MPa | Fracture toughness/MPa m$^{1/2}$ |
|---|---|---|---|---|---|
| Z0 | 720/1 + 820/2 | β-Quartz | $0.4 \times 10^{-7}$ | 118 | 1.6 |
| Z5 | 690/1 + 820/2 | β-Quartz, β-Spodumene | $0.9 \times 10^{-7}$ | 124 | 1.9 |
| Z10 | 660/1 + 820/2 | β-Quartz, β-spodumene, willemite | $3.8 \times 10^{-7}$ | 135 | 2.1 |
| Z15 | 620/1 + 820/2 | β-Spodumene, willemite | $5.3 \times 10^{-7}$ | 125 | 1.9 |

### 3.3. Microstructures

Fig. 5 shows SEM micrographs of the glass–ceramic samples heat-treated at 820 °C for 2 h. All samples showed homogeneous dispersion of crystallites. Samples Z0 and Z5 had homogeneous dispersion of tiny spherical crystallites; the grain sizes were 100–200 nm (Fig. 5a and Fig. 5b). With increasing ZnO content, the grains sizes increased too, as in samples Z10, the grains sizes were 1–2 μm (Fig. 5c), and in sample Z15, the sizes were increased to 3–5 μm (Fig. 5d).

### 3.4. Thermal expansion and bending strengths

After crystallization, the glass-ceramics consist of β-quartz solid solution, β-spodumene and willemite. It is well known that β-quartz possesses negative or slightly positive expansion coefficient, willemite has low coefficient of expansion of $15 \times 10^{-7}\,\mathrm{K}^{-1}$, and β-spodumene has slightly positive expansion coefficient of about $9 \times 10^{-7}\,\mathrm{K}^{-1}$.

The thermal expansion coefficient, bending strength and fracture toughness of glass-ceramics are given in Table 2 together with the crystalline phases. It is known that in glass-ceramics, the coefficient of expansion could be associated with the expansion characteristics of the crystalline phases. In Z0 samples, the major crystalline phases were β-quartz. As β-quartz possesses negative or slightly positive expansion coefficient ($0–1 \times 10^{-7}\,\mathrm{K}^{-1}$), the glass-ceramics possess very low expansion coefficient. Meanwhile, high internal stresses can be caused by mismatches in the thermal expansion coefficients of β-quartz solid solution and the glass matrix, and it can be expected to reduce the strength of the glass-ceramics. With increasing ZnO content, the coefficient of expansion increased. This can be attributed to the appearance of willemite and spodumene phase. β-spodumene has an expansion coefficient of about $9 \times 10^{-7}\,\mathrm{K}^{-1}$, and willemite, $15 \times 10^{-7}\,\mathrm{K}^{-1}$[15,17]. Precipitation of β-spodumene and willemite can lower internal stresses in glass-ceramics, so the bending strengths and fracture toughness increased. However, as the ZnO content increased to 15 wt.%, the microstructures coarsen and the space between the grains becomes larger, lowering the bending strengths and fracture toughness.

## 4. Conclusions

From the experimental results, the following conclusions can be drawn:

1. The replacement of $Al_2O_3$ by ZnO causes a decrease in the glass transition temperature.
2. All glasses exhibit bulk nucleation.
3. Spodumene-willemite were obtained.

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