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Short communication

Nearly zero thermal expansion of β-spodumene glass ceramics prepared by sol–gel and hot pressing method

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Abstract

β-Spodumene glass–ceramics were fabricated by sol–gel process followed by hot pressing technique. The microstructure, mechanical properties and thermal expansion behavior of the glass–ceramics were investigated. The glass ceramics hot pressed at 1200 and 1300 °C have relative good mechanical properties and nearly zero coefficient of thermal expansion (CTE). CTE of the specimen sintered at 1200 °C ranges from $-0.03 \times 10^{-7}\,K^{-1}$ to $-0.97 \times 10^{-7}\,K^{-1}$. The thermal expansion behavior characteristics are found to be strongly influenced by crystalline phases, crystallinity and microstructure in the specimens, which depend on the sintering temperatures.

Keywords: A. Sol–gel processes; C. Mechanical properties; C. Thermal expansion

1. Introduction

Lithium–aluminosilicate glass–ceramics (Li_2O–Al_2O_3–SiO_2) system can achieve very low or even negative bulk thermal expansion [1]. Their thermal stability and resistance to thermal shock have led to many applications in domestic cookware, precision optical devices and turbine engine heat exchangers [2]. In addition to these applications, β-spodumene glass ceramics have a potential to be used as the material suitable for packaging of large-scale integrated circuits due to its low dielectric constant and low thermal expansion [3,4].

Conventionally, lithium aluminosilicate glass–ceramics have been fabricated mainly by melt-quenching and crystallization processes. But there arises a problem that it is very difficult to obtain homogeneous and fine β-spodumene without proper nucleating agent [5,6]. However, the incorporation of nucleation aids can result in large thermal expansion coefficient [7]. The other problem is the exorbitant high temperature of melting glass. Some oxides, such as ZnO, CaO, Na_2O and K_2O, were added in order to lower the melting temperature [8–10]. The addition of these oxides can cause the formation of mostly β-spodumene and phases consisting of quartz, Zn_2SiO_4, quartz solid solution, diopside, corundum and combination thereof. The formation of these phases can exert undesirable influence on the thermal expansion and mechanical properties. Another problem is that little information is available for thermal and mechanical properties of β-spodumene with pure $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ composition. Ostertag et al. [11] studied thermal expansion behavior of β-spodumene using high-temperature X-ray diffraction techniques. The results indicated that β-spodumene glass ceramics had a pronounced anisotropy of thermal expansion and average CTE in a bulk specimen was $0.19 \times 10^{-6}\,K^{-1}$. Ogiwara et al. [12] prepared high purity β-spodumene via solid-state reaction route. The average CTE was $0.2 \times 10^{-6}\,K^{-1}$. However, there are still no reports on the detailed thermal expansion behavior of β-spodumene glass ceramics over all the measurement range.

This study aims to prepare β-spodumene glass ceramics monolith with pure $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ composition via sol gel process followed by hot pressing method, using lithium nitrate, boehmite sol and silica sol as raw materials. The effect of hot pressing temperature on the mechanical properties and thermal expansion behavior was investigated.

2. Material and methods

Precursor powders with molar ratio of Li:Al:Si keeping at 1:1:2 corresponding to β-spodumene phase were prepared by

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mixing boehmite sol, silica sol and lithium salt. For the preparation of lithium–aluminum sol, calculated quantity of $LiNO_3$ was then added to the boehmite sol under stirring until obtained lithium–aluminum sol. After that, calculated quantity of silica sol was added to the lithium–aluminum sol under active stirring and then obtained lithium–aluminum–silicon sol. The resultant sol was heated at 60 °C for 2–3 h to obtain mass like gel. The precursor powders were prepared by drying the gel at 100 °C for a week. This process of preparation was discussed in detail in our previous work [13]. The precursor powders were ground and sieved to pass through 200 mesh B.S. The monolithic lithium glass–ceramics were prepared by hot pressing the precursor powders at 1200–1350 °C for 30 min under a pressure of 10 MPa in vacuum. The X-ray diffraction (XRD, Rigaku D/max) studies for all the specimens sintered at different temperatures were carried out using Cu Kα radiation and Ni filter and scanning from 10° to 90° at the scanning speed of 4° $\min^{-1}$.

Apparent porosities of the samples were measured with deionized water as immersion medium according to the Archimedes principle. The morphology of the crystalline phases developed after hot-pressing sintering was investigated using scanning electron microscopy (SEM, Tescan Vega II). Polished specimens were etched with approximately 5 vol.% HF solution for 60 s. The morphology of crystalline phase was exposed because the glass phases dissolved in HF solution. Vicker's hardness tests were carried out using a HMV 2000 (Shimadzu, Kyoto, Japan) machine with a load of 40 N and a holding time of 10 s. The specimens for flexural strength were machined into bars with dimension of 36 mm × 4 mm × 3 mm before a three-point bending test was conducted at a cross-head speed of 0.5 mm $\min^{-1}$ and a span of 30 mm on a universal testing machine. Six bars were tested for each measurement. Specimens 4 mm × 2 mm × 20 mm with 2 mm open depth were used to measure the fracture toughness K_{IC} at a crosshead speed of 0.05 mm $\min^{-1}$ by single-edge notched-beam (SENB) testing. Thermal expansion was tested using Shimadzu dilatometry (TMA60) at a heating rate of 10 °C $\min^{-1}$ in ambient atmosphere. The linear thermal strain was calculated by following formula:

$$\varepsilon = \frac{L - L_0}{L_0} \tag{1}$$

The CTE (α) is calculated by the following equation:

$$\alpha(T) = \frac{\varepsilon}{T - T_0} \tag{2}$$

where T_0 is the room temperature, T the tested temperature, l_0 the specimen length at room temperature, and l the specimen length at the tested temperature.

3. Results and discussions

XRD patterns in Fig. 1 demonstrate that β-spodumene (JCPDS 35-0797) and β-eucryptite (JCPDS 75-2329) precipitate in the lithium aluminosilicate glass ceramics hot pressed at 1200, 1300 and 1350 °C. For the specimen hot pressed at 1350 °C, in addition to β-spodumene and β-eucryptite, Al_2O_3 (JCPDS 43-1484) is also detected.

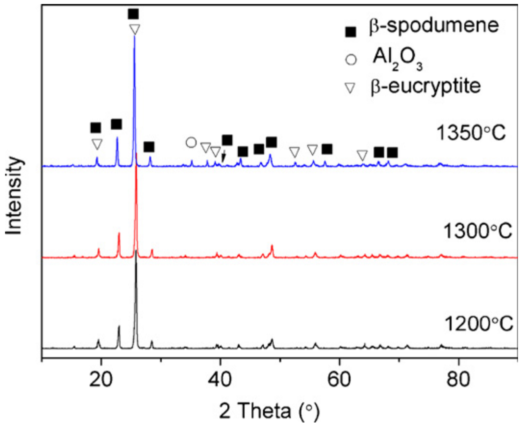

Fig. 1. X-ray diffraction patterns of lithium aluminosilicate glass–ceramics hot pressed at different temperatures.

Fig. 2 shows the morphology of the etched surface of the glass–ceramics hot pressed at different temperatures. The specimens sintered at different temperatures show distinct bulk crystallization characteristics. The size of the crystals increases slightly with sintering temperature increasing from 1200 to 1300 °C, where the morphology of crystals demonstrates polygonal shape (Fig. 2a and b). In contrast, the crystals in the specimen sintered at 1350 °C show flake-like microstructure (Fig. 2c and d).

The apparent porosity, mechanical properties and microhardness of hot pressed lithium aluminosilicate glass–ceramics are summarized in Table 1 and Fig. 3. These results indicate that the porosity and microstructure have a significant effect on the mechanical properties. Porosity decreases with sintering temperature increasing from 1200 to 1300 °C, and the flexural strength inevitably increases. The maximum flexural strength and fracture toughness are 115 ± 8 MPa and 1.99 ± 0.05 MPa $m^{1/2}$, respectively. However, the flexural strength, toughness and microhardness decrease suddenly for the specimens sintered at 1350 °C. The decrease of mechanical properties can attribute to the increase of crystal size and existence of microcracks.

Fig. 4 presents thermal expansion of the samples in the measurement range of 30–800 °C. The sample hot pressed at 1200 °C shrinks slightly from RT to 800 °C and CTE ranges from $-0.03 \times 10^{-7}\ K^{-1}$ to $-0.97 \times 10^{-7}\ K^{-1}$. Sample hot pressed at 1300 °C has a bit positive CTE, ranging from 0.76 to $1.82 \times 10^{-7}\ K^{-1}$. The samples hot pressed at 1200 and 1300 °C exhibit nearly zero CTE, indicating superior dimension stability of the lithium aluminosilicate glass

Table 1
Apparent porosity, crystallinity and microhardness of β-spodumene glass–ceramics sintered at different temperatures.

Sintering temperature (°C)	Apparent porosity (%)	Crystallinity (%)	Microhardness (MPa)
1200	4.43	60	650.3 ± 23.2
1300	3.22	63	431.4 ± 13.6
1350	1.56	79	398.3 ± 15.2

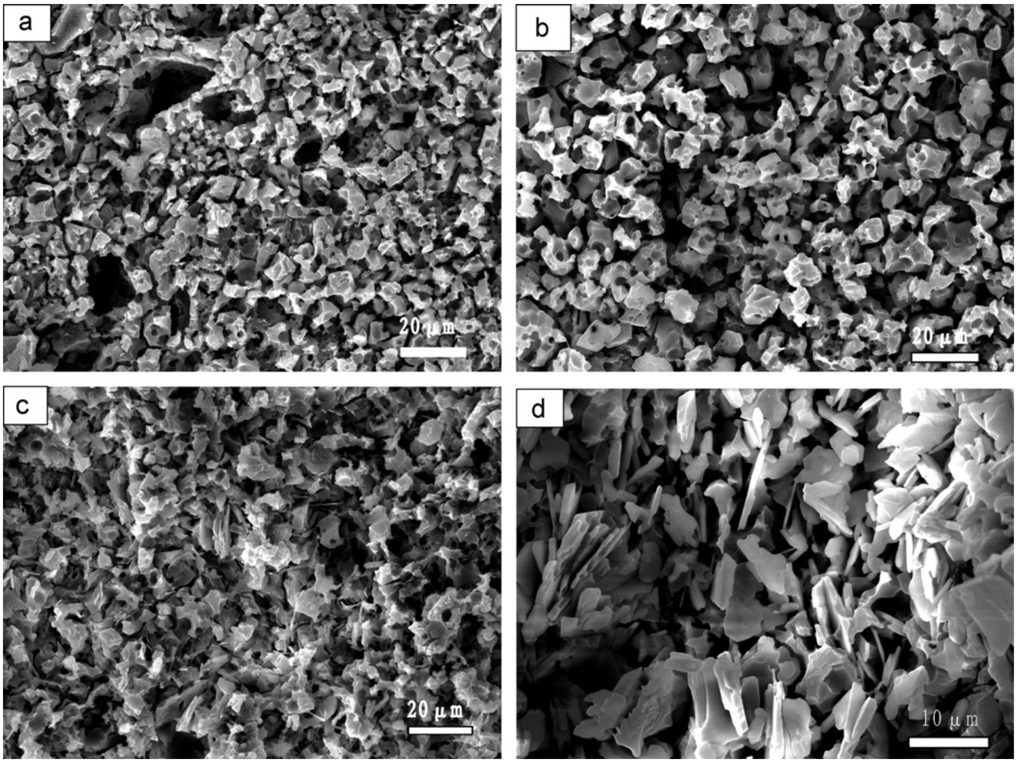

Fig. 2. SEM images of the etched surfaces of lithium aluminosilicate glass–ceramics pressed at different temperatures for 30 min: (a) 1200 °C, (b) 1300 °C, (c) 1350 °C, and (d) high-resolution micrographs of (c) photograph.

ceramics. However, the sample hot pressed at 1350 °C shows different thermal expansion behavior and its CTE decreases initially followed by rapid increase in the temperature range of 600–800 °C.

The thermal properties are dependent on amorphous phase, crystalline phases and the degree of crystallization [14]. Theoretically, average CTE of β-spodumene without crystal orientation should be $1.9 \times 10^{-7}\ \mathrm{K}^{-1}$. The CTE of samples hot pressed at 1200 and 1300 °C are lower than theoretical value, resulting from the existence of β-eucryptite in the glass ceramics. β-Eucryptite exhibits an extremely anisotropic thermal expansion behavior which has negative bulk CTE of around -0.40×10^{-6}/°C [15,16].

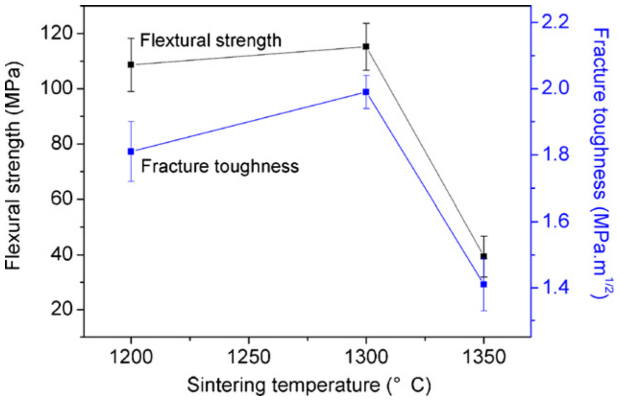

Fig. 3. Mechanical properties of lithium aluminosilicate glass–ceramics as a function of hot pressing temperatures.

The abrupt decrease in values of mechanical properties for the sample sintered at 1350 °C is closely related to the decrease in CTE. The negative thermal expansion can result from the existence of microcracks [17]. The residual stresses in glass–ceramics are unavoidable due to the mismatch between the thermal and elastic properties of the crystalline and amorphous phases [18–20]. This value is sufficiently high to evolve microcracks [21,22]. Accordingly, the β-eucryptite crystal can shrink freely with the temperature increase after cooling, contributing to the large negative CTE and low mechanical properties in the sample containing microcracks.

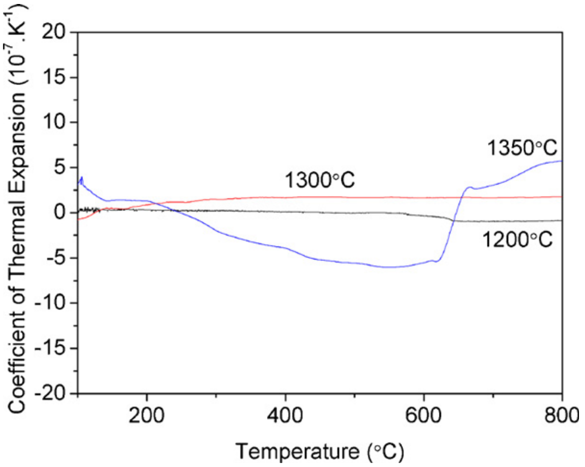

Fig. 4. CTE curves of lithium aluminosilicate glass–ceramics pressed at different temperatures.

Amorphous phase in the glass ceramics also play an important role to determine the thermal expansion behavior. Generally, CTE of glasses is dependent on the asymmetry of the amplitude of thermal vibrations, which decreases with increase of rigidity of the glass network [23]. For the sample sintered at 1350 °C, the precipitation of Al_2O_3 from lithium aluminosilicate glass can introduce non-bridging ions into glass, leading to the decrease of rigidity of glass. As a result, the CTE of sample sintered at 1350 °C increases at high measurement temperature.

4. Conclusions

Lithium aluminosilicate glass–ceramics were fabricated by sol–gel process followed by hot pressing technique. β-Spodumene was the only phase that was detected by XRD in the samples hot pressed at 1200 and 1300 °C. The mechanical properties increased with increasing sintering temperature from 1200 to 1300 °C, and decreased at 1350 °C. The maximum flexural strength was 115 ± 8 MPa. CTE, affected by amount and type of crystalline phases, were nearly zero from room temperature to 800 °C for the specimens hot pressed at 1200 and 1300 °C.

Acknowledgments

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