# Crystallization and thermal expansion behavior of lithium zinc silicate sealing glass

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## A R T I C L E   I N F O

## A B S T R A C T

Effect of heat treatment schedule on the crystallization and thermal expansion behavior of a lithium zinc silicate glass system was investigated by differential scanning calorimeter (DSC), X-ray diffraction, and linear thermal expansion test. Two well-defined crystallization exothermic peaks were observed from the DSC trace. According to the apparent activation energies and avrami parameter values calculated from the two crystallization exothermal peaks, the first crystallization exothermal peak was attributed to a combining surface and internal crystallization behavior, while the second one was found to be internal crystallization. Additionally, the phase evolution and the thermal expansion behavior with increasing heat treatment temperature were found to be closely related. Interestingly, it was found in comparison with previous reports that addition of CaO varies the phase composition of the resulting glass–ceramic in an opposite way to $K_2O$ and the deep rooted reason has been discussed which may cast light on the modulation of properties of glass–ceramic involved crystalline phase of quartz or cristobalite. At last, average thermal expansion coefficient of $7.99–15.38 \times 10^{-6}\,K^{-1}$ in the temperature range of 25–400 °C has been obtained with different heat treatment schedules.

## 1. Introduction

Glass-to-metal-sealing or glass-ceramic-to-metal-sealing technology is widely used in electrical and electronic devices. Generally speaking, tight hermeticity, high electrical insulation and good chemical durability are needed for reliable sealing components. Comparing with other candidates, materials from lithium zinc silicate (LZS) glass system, pioneered by McMillan [1], do offer a number of distinct advantages including excellent glass-forming ability over a wide composition range, moderate sealing temperatures ( $< 1000$ °C) coupled with high fluidity and excellent wetting characteristics and high electrical resistivity. In particular, thermal expansion behavior of the LZS based glass ceramics can be modulated in a wide range of thermal expansion coefficient (TEC) (from $5 \times 10^{-6}$ to $20 \times 10^{-6}\,K^{-1}$), indicating their extensive applicability to seal a variety of metals.

Thermal expansion behavior of the LZS based glass ceramics primarily depends on the constituents and the heat treatment schedules of original glass. $P_2O_5$ as nucleating agent [2–13], transition metal oxide including $TiO_2$, $ZrO_2$, $HfO_2$, $V_2O_5$, $Nb_2O_5$, $Ta_2O_5$, $Cr_2O_3$, $MoO_3$, $WO_3$, NiO and CuO as nucleating additives [3,4,14],

$Na_2O$ and $B_2O_3$ as fluxing agents [3–5,7,9–12], $Al_2O_3$ as net modifier or net former [4–6,8,14], $Sb_2O_3$ as a refining agent [7,8], alkali metal oxide $K_2O$ [2,4,13] and alkaline earth metal oxide such as MgO [5,7–9], BaO [10] have been added into the LZS based glass systems. Variation of species and contents of additives has been found to significantly affect the crystalline phase compositions and the thermal expansion behavior of the resultant glass ceramics. Moreover, even for specific compositions of the original glasses, the final crystalline phase and the thermal expansion behavior of resultant glass ceramics were largely influenced by heat treatment schedule. Typically, Goswami et al. [12] found that the final crystalline phase composition and the TEC of resultant glass have enormous differences between cooling schedule and heating schedule for both LZS with low ZnO and high ZnO contents. Although CaO additive has also been used in some low ZnO content LZS systems [13], detailed studies on the crystallization and thermal expansion behavior in high ZnO content LZS glass systems are limited. Thus, it would be quite desirable to prepare a high ZnO content LZS glass with CaO additive, to investigate the effect of heat treatment schedule on the crystallization and thermal expansion characteristics and to determine how their correlation occurs.

In this paper, a glass system with the composition of $18.1Li_2O–20.1ZnO–55.8SiO_2–3.3CaO–1.4P_2O_5–1.3K_2O$ (mol%) has been prepared via a melt-annealing technique, the phase evolution

with various heat treatment temperatures has been investigated by X-ray diffraction (XRD) measurements. And the activation energies for different crystalline phases have also been derived from the DSC data. Moreover, the role of CaO additive on the production of resulting phase composition has been discussed in comparison with previous studies. At last, the influence of heat treatment schedule on the thermal expansion behavior of the LZS glass ceramics was studied in combination with the crystallization process. The aim of the study was to understand the relation between crystallization and thermal expansion behavior of the LZS glass-ceramics so that suitable heat-treatment schedules could be chosen for producing glass-ceramics with desired properties for sealing to different kind of metals.

## 2. Experimental procedure

Parent glass samples used in this study with the composition of $18.1Li_2O–20.1ZnO–55.8SiO_2–3.3CaO–1.4P_2O_5–1.3K_2O$ (mol%) were prepared by a melt-annealing technique. The powder containing appropriate amounts of $SiO_2$ ($\geq 99.0\%$), ZnO ($\geq 99.0\%$), $Li_2CO_3$ ($\geq 97.0\%$), $CaCO_3$ ($\geq 99.8\%$) and $P_2O_5$ ($\geq 99.0\%$) was well-mixed and melted in a platinum crucible at 1550 °C for 3 h and cast into a preheated graphite mold with an inner cavity of 30 mm diameter and 20 mm height. Then the casted glass was immediately annealed at 550 °C for 5 h to relieve residual stresses followed by slow cooling to room temperature. At last, transparent and bubble-free glasses were obtained.

In order to predict the crystallization procedure, the glass was crushed and sieved through a 120 mesh to produce glass powder suitable for DSC measurement in a DSC/TGA thermal analysis system (SDT Q600, USA) at various heating rates $\beta$. The samples subjected to controlled crystallization were fired in air at temperatures from 640 to 850 °C for 1 h, with a heating rate of 5° C/min. X-ray diffraction (Model-D8 Advance, Bruker AXS, Karlsruhe, Germany) analysis were applied on the parent glass and the glass ceramic specimens to investigate the phase evolution.

The measurements of the linear thermal expansion behavior were carried out using a automatic recording multiplier dilatometer (Linseis L76/1250, Germany) with $\alpha$-$Al_2O_3$ as a reference material in the temperature range of 25–520 °C for the glass specimens and 25–800 °C for the glass-ceramics, respectively, and the heating rate is 5 °C/min. The average linear TECs ($\overline{\alpha}$) of the glass-ceramics were calculated based on the measurement of constant slopes of each curve within a specified temperature range according to the following equation:

$$\overline{\alpha} = \Delta L / (L_0 \Delta T) \qquad (1)$$

where $\Delta L$, $L_0$, and $\Delta T$ are the linear expansion, the sample initial length, and the specified temperature interval, respectively. In this study, the value of $\overline{\alpha}$ was calculated in the temperature range of 25–400 °C.

## 3. Results and discussion

### 3.1. Crystallization process analysis

Heat treatment protocols for the as-annealed glass were guided by DSC analysis (Fig. 1). As it can be seen from Fig. 1, the glass transition point ($T_g$) of the glass has been found to be around 620 °C, and two well-defined exothermic peaks around 693 °C and 814 °C have been observed. These exothermic peaks are caused by the crystallization of different phases from glass matrix. Evolution and growth of phases during heat treatment were tracked by XRD
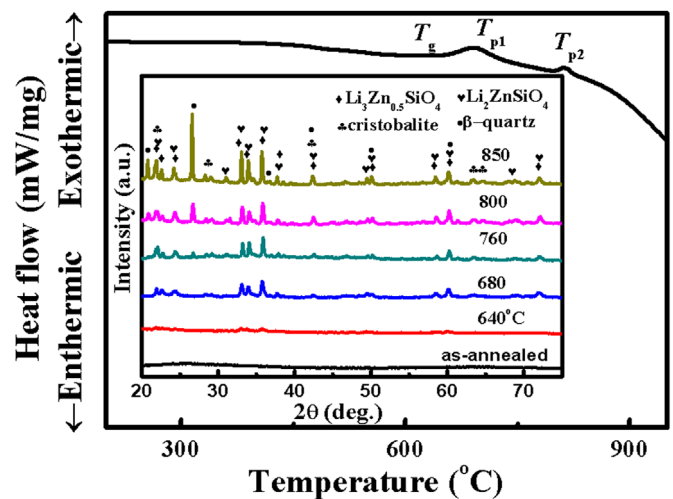


**Fig. 1.** DSC trace of the as-annealed LZS glass at the heating rate of 5 °C/min. Inset is the X-ray diffraction patterns of the as-annealed LZS glass and the LZS glass ceramic samples crystallized by one-stage heat treatment at different temperatures for 1 h.

analysis (inset Fig. 1). The as-annealed glass showed broad peaks when exposed to X-rays, which was indicative of the amorphous nature. The patterns for the first crystalline phase of $\gamma_{II}$ polymorph phase [15] was observed for specimen heat treated at 640 °C and significantly enhanced for specimen heat treated at 680 °C, which may corresponds to the first crystallized process in DSC trace. Patterns for new phases of $\beta$–quartz, cristobalite and $\gamma_0$ with the composition of $Li_2ZnSiO_4$ [15] appeared when the heat treatment temperature was increased above 760 °C and the intensity of the patterns increased with increasing temperature, which may corresponds to the second crystallized process in DSC trace.

The emerging of the first crystalline phase $Li_3Zn_{0.5}SiO_4$ indicates that the high temperature structure of the glass melt, which transform preferably to $\gamma_{II}$, could be retained at ambient temperature by quenching the material from high temperature. When the heat treatment temperature increased above 760 °C, on the one hand, the high temperature polymorph $\gamma_{II}$ transforms to the stable phase $\gamma_0$ by means of increasing the Zn to Li ratio due to the diffusion of zinc ions from the glass phase into the crystalline solid solution, on the other hand, β-quartz phase combining a minor amount of cristobalite formed from the lithium- and zinc-depleted residual glass phase. Since the inversion of solid solutions takes place gradually, no thermal effect can be found by DSC.

One interesting point is that the addition of CaO seems to play an opposite role in the formation of the final crystalline phase in comparison with $K_2O$. The addition of $K_2O$ is found to be helpful for the formation of cristobalite [2]. However, close inspection of XRD patterns reveals that there is more amount of β-quartz phase than cristobalite. This result demonstrates that the addition of CaO contribute to the formation of β-quartz over cristobalite. Similar result has been observed in a $BaO$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ glass system [19], in which the authors found that CaO addition can effectively suppressed the formation of cristobalite but promoted the formation of quartz. Since higher ionic potential will be more helpful to decrease the proportion of the non-bridge oxygen and $Ca^{2+}$ has higher ionic potential (1.89) than $K^+$ (0.75), $Li^+$ (1.28) and $Ba^{2+}$ (1.40), it should be reasonable to conclude that quartz is more easier to form than cristobalite in glass with relatively less non-bridge oxygen.

### 3.2. Crystallization mechanism analysis

The crystallization mechanism was analyzed via non-isothermal DSC measurements. As it can be seen from Fig. 2, with