Review

Effects of Li replacement on the nucleation, crystallization and microstructure of Li$_2$O–Al$_2$O$_3$–SiO$_2$ glass

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1. Introduction

Glass ceramics obtained by controlling the crystallization of glass is a kind of multi-phase materials [1–4]. Lithium aluminum silicate (Li$_2$O–Al$_2$O$_3$–SiO$_2$, LAS) glass ceramic is one of the most valuable and widely used glass ceramic systems because of its low expansion, high heat resistance and excellent mechanical properties [5–8]. The glass ceramic plate product (such as induction cooker plate) is one of the important applications of glass ceramic and is developing quickly. At present, the cost of raw materials for LAS glass ceramic, especially Li$_2$O, increases for the production of LAS glass ceramic, which restricts its application in cookers, architecture and so on. Therefore, how to solve these problems has become very critical. On the basis of previous studies of LAS glass ceramic [4–8] referred in this paper, the Li replacement was introduced, in which the Li$_2$O was partly replaced by other oxides, and the expensive chemical material Li$_2$CO$_3$ was partly replaced by cheap spodumene mineral. The effects of Li$_2$O content and spodumene proportion on the nucleation, crystallization mechanism and microstructure of LAS glass were studied.

2. Experimental

Acid washed quartz sand and high purity Li$_2$CO$_3$, Al$_2$O$_3$, MgO, ZnO, ZrO$_2$, TiO$_2$, P$_2$O$_5$, F$^-$ and other minor additives were used to produce glass batches (Table 1), in which ZrO$_2$, TiO$_2$, P$_2$O$_5$ and F$^-$ were employed as a complex nucleating agent. The contents of Li$_2$O were 4.5% (L4.5), 4.0% (L4.0) and 3.5% (L3.5) respectively, i.e., the Li$_2$O was replaced by Na$_2$O, K$_2$O and other melting aids. The Li$_2$O came from expensive chemical Li$_2$CO$_3$, and the replacement proportions in weight of Li$_2$CO$_3$ by spodumene (Table 2) were 25% (K25), 50% (K50) and 75% (K75) respectively. The raw materials of each glass batch were melted at 1600–1650°C and moulded in a pre-heated die. The glass was then annealed at 580°C for 1 h to eliminate internal stress.

Differential thermal analysis (DTA) of the annealed glass samples was carried out on a differential thermal analyzer (NETZSCH STA 409 PC Luxx, Germany) with alumina as the reference and the sample was heated at 5-20°C min$^{-1}$ from 20°C to 1100°C. The crystalline phases of the samples were analyzed by the X-ray diffraction (XRD) method on a XJ10-60 X-ray diffractometer using nickel filtered CuKa radiation in the range of 2θ = 10–80° with a scanning speed of 2° min$^{-1}$. The surface of the samples was polished and eroded by HF (2 wt%) for 30–40 s for the morphology observation on the SEM (scanning electron microscopy, FEI SIRION).

3. Results

3.1. DTA of annealed LAS glass

Fig. 1 shows the DTA results obtained from annealed glass powders. It is noted that the prominent exothermic peaks of L4.5, L4.0 and L3.5 samples at 871.4°C, 877.1°C and 964.7°C may be...
attributed to the formation of main crystallization phase (LiAl-Si$_2$O$_6$) shown below, and 862.5 °C, 853.9 °C and 853.9 °C for K25, K50 and K75 samples respectively. It is obvious that the crystallization maximum temperature ($T_p$) increases with the decrease of Li$_2$O contents and appreciably decreases with the increase of spodumene proportion. It indicates that the Li$_2$O replacement by other oxides restricts the crystallization of LAS glass and the Li$_2$CO$_3$ replacement by spodumene promotes it.

3.2. Nucleation of LAS glass

Due to many nuclei with a nanometer size forming in the pre-nucleating stage, the glass will absorb much thermal energy during continuous heat treatment and it is shown that the crystallization maximum temperature ($T_p$) shifts to a lower temperature in DTA curve. Therefore, the shift of crystallization temperature may be used to study the nucleation process of LAS glass [4].

The range of the nucleating temperature is from $T_n$ to $T_g$ [9]. According to the result of DTA (Fig. 1), the pre-nucleating temperatures are supposed to be in the range of 600–840 °C (every 20 °C) and the pre-nucleating time is supposed to be in the range 0.5–2 h (every 0.5 h) at the suitable nucleation temperature. Fig. 2 shows the relationship between crystallization maximum peak temperatures ($T_p$) and pre-nucleating temperatures of L4.5, L4.0 and L3.5 samples, in which crystallization maximum peak temperatures ($T_p$) and pre-nucleating temperatures of L4.5, L4.0 and L3.5 samples are 770 °C, 790 °C and 810 °C, respectively, which increases with the decrease of Li$_2$O content. Above the suitable nucleation temperature, the nuclei merge and the amount of nuclei reduce, resulting in the $T_p$ shifting to higher values. That is to say, the suitable nucleation temperature of LAS glass is the pre-nucleation temperature when the $T_p$ is at the lowest point. Li$_2$O can accelerate phase separation of glass, which improves the nucleation and crystallization. Therefore, the decrease of Li$_2$O content in glass will restrict the above mechanism and leads to an increase of the suitable nucleation temperature of LAS glass.

Using the same method, the effect of spodumene proportions on the nucleation of LAS glass was also studied. The suitable nucleation temperature of K25, K50 and K75 samples is 790 °C in all cases, indicating that the Li$_2$CO$_3$ replacement by spodumene does not basically affect the nucleation of LAS glass.

The nucleation time of LAS glass ceramic determines the amount and growth of nuclei in nucleation stage, and it affects the crystallization in the subsequent heat treatment and the microstructure and properties of glass ceramic. By changing pre-nucleation time (0.5–2 h, every 0.5 h) at the suitable nucleation temperature, the crystallization maximum peak temperatures of L4.5, L4.0 and L3.5 samples was further studied using DTA analysis. Fig. 3 shows the relationship between the crystallization maximum peak temperatures ($T_p$) and pre-nucleation time at the suitable nucleation temperature. The $T_p$ of LAS glass decreases with the increase of pre-nucleation time, becomes the lowest at 1 h, and then increases rapidly again, which indicates that for LAS glass

### Table 1

Main compositions of the glass batches, wt%  

<table>
<thead>
<tr>
<th>Composition</th>
<th>L4.5</th>
<th>L4.0</th>
<th>L3.5</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.5</td>
<td>18.5</td>
<td>18.5</td>
<td>Basic glass composites</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>68.5</td>
<td>68.5</td>
<td>68.5</td>
<td></td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>4.5</td>
<td>4.0</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ + ZrO$_2$ + P$_2$O$_5$ + F$^-$</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>Complex nucleating agent</td>
</tr>
<tr>
<td>ZnO + MgO + BaO</td>
<td>1.2</td>
<td>1.4</td>
<td>1.6</td>
<td>Melting aid</td>
</tr>
<tr>
<td>K$_2$O + Na$_2$O</td>
<td>2.0</td>
<td>2.3</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>As$_2$O$_3$ + Sb$_2$O$_3$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>Clarifying agent</td>
</tr>
</tbody>
</table>

### Table 2

Compositions of spodumene mineral, wt%  

<table>
<thead>
<tr>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Li$_2$O</th>
<th>CaO</th>
<th>P$_2$O$_5$</th>
<th>MnO</th>
<th>TiO$_2$</th>
<th>K$_2$O + Na$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>19.41</td>
<td>74.35</td>
<td>5.0</td>
<td>0.11</td>
<td>0.11</td>
<td>0.04</td>
<td>0.02</td>
<td>0.52</td>
<td>&lt;0.13</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. DTA traces obtained from LAS glass powders.

Fig. 2. Relationship between crystallization maximum peak temperatures ($T_p$) and pre-nucleating temperatures.
The suitable nucleation time is 1 h, without being affected by the Li$_2$O content.

The XRD patterns of L4.5, L4.0 and L3.5 glasses after heat treatment for 1 h at different nucleation temperature are shown in Fig. 4. It can be seen that L4.5 glass heat treated at 750 °C and blew this temperature is amorphous, the L4.0 glass keeps amorphous until 790 °C and L3.5 glass nucleated at 810 °C or at a lower temperature is amorphous. The formation of crystalline phase of hexagonal LiAl(SiO$_3$)$_2$ (31-0706) is found in L4.5 sample nucleated at 770 °C, and two coexisting phases (tetragonal LiAlSi$_2$O$_6$ (76-0921) and hexagonal LiAl(SiO$_3$)$_2$) are observed in the same samples heat treated at 790 °C and at 830 °C for L3.5 glass. The nucleation of glass usually aims at the highest nuclear density, rather than nucleation phase. According to the XRD results, the suitable nucleation temperatures should be considered below 770 °C for L4.5 glass (790 °C for L4.0 glass and 810 °C for L3.5 glass). It shows that the Li$_2$O replacement increases the crystallization temperature of LAS glass, which is in agreement with the results by DTA.

![Fig. 3. Relationship between crystallization peak temperatures (T$_p$) and pre-nucleation times.](image)

![Fig. 4. XRD patterns of LAS glass nucleated at different temperatures for 1 h.](image)

![Fig. 5. XRD patterns of L4.5, L4.0, L3.5 LAS glass ceramics crystallized at 830–1030 °C for 2 h.](image)
The decrease of Li$_2$O content does not affect the formation of this crystallization phases at 830–1030 °C and 970 °C are tetragonal LiAlSi$_2$O$_6$ (880 °C for 2 h, as shown in Figs. 7 and 8. The crystal size of the samples crystallized at 830 °C belongs to nanometer grade and is 30–150 nm. It decrease with the decrease of Li$_2$O content and increases with the increase of spodumene proportion. The crystallinity of L3.5 sample is the lowest and that of K50 sample is the highest. The crystal size and crystallinity of all samples increase with the increase of heat-treatment temperature. The over-growth of crystal at a high heat-treatment temperature will worsen the mechanical properties of glass ceramic. Therefore, the crystallization temperature of 880 °C, 930 °C and 970 °C are suitable for L4.5, K4.0 and K3.5 samples, respectively, and 930 °C, 880 °C and 880 °C for the K25, K50 and K75 samples, which is in agreement with the results by DTA and XRD analysis.

### 4. Discussions

The effects of Li$_2$O replacement by other oxides and Li$_2$CO$_3$ replacement by spodumene on the heat treatment of LAS glass were analyzed by two approaches: activation energy of crystal growth and structure of silicate.

The crystallization kinetic characteristics of LAS glass were measured by a non-isothermal DTA method using the Arrhenius [9], Kissinger [10–11] and Augis–Bennett [12] equation as follows:

$$k = v \exp \left( \frac{-E}{RT} \right)$$

$$\ln \left( \frac{T_p}{\alpha} \right) = \frac{E}{RT_p} + \ln \frac{E}{R} - \ln v$$

$$n = \frac{2.5}{\Delta T} \times \frac{R T_p^2}{E},$$

wherein, $E$ is the activation energy, kJ/mol; $R$ is the gas constant; $v$ is the frequency factor; $\alpha$ is the DTA heating rate, °C/min; $K$ is the reaction rate constant, which is related to the $E$ and $v$; $n$ is known as the crystallization index, i.e., Avrami exponent depending upon the actual nucleation and growth mechanism, $\Delta T$ is the half-height width of the crystallization exothermical peak. Crystallization index $n$ is related to crystallization manner, $n \approx 1$, surface crystallization and $n \approx 3$, volumetric crystallization.

Table 3 shows the crystallization maximum peak temperatures ($T_p$) from DTA curves at different heating rates. The relationship between $\ln(T_p^2/\alpha)$ and $1/T_p$ is constructed (Fig. 9) to calculate the effective activation energy and crystallization index, as shown in Table 4. With the decrease of Li$_2$O content, the activation energy $E$ of LAS glass increases. The $E$ decreases with the increase of spodumene proportion, which becomes the lowest at 50% of spodumene proportion and increases again above the 50% of spodumene proportion. This indicates that the decrease of Li$_2$O content restrain the crystallization of LAS glass but the Li$_2$CO$_3$ replacement by spodumene improve it.

The n values, which are calculated by using Eq. (3), are given in Table 4. The fact that n value is near 3 indicates that crystallization of LAS glass is volumetric crystallization. The n value of LAS glass decreases with the decrease of Li$_2$O content and increases with the increase of spodumene proportions, suggesting that the decrease of Li$_2$O slows crystal growth rate while increasing spodumene proportions accelerates the crystal growth rate.

![Fig. 6. XRD patterns of K25, K50, K75 LAS glass ceramics crystallized at 830–970 °C for 2 h.](image-url)
Fig. 7. SEM graphs of L4.5, L4.0 and L3.5 glass ceramics crystallized at 830–930 °C for 2 h.

Fig. 8. SEM graphs of K25, K50, K75 glass ceramics crystallized at 830–930 °C for 2 h.
The effect of oxides on the crystallization depends on the radius and electric charge of metal positive ions, and it is well-known that metal positive ions with small radius and high field energy are easier to be encircled by regular oxygen ions than that with large radius and low field energy, indicating that small metal positive ions are beneficial to the formation of complete crystal structure [9].

The radius \( r \) and field energy \( z/r \) of \( \text{Li}^+ \) is 6 nm and 2.78, that of \( \text{Na}^+ \) is 9.5 nm and 1.11, and that of \( K^+ \) is 3.5 nm and 0.57. It proves that compared with \( \text{Na}^+ \) or \( K^+ \), \( \text{Li}^+ \) is easier to be encircled by oxygen ions to form complete crystal phase. It is the reason why the decrease of \( \text{Li}_2\text{O} \) restrains the nucleation and crystallization of LAS glass. Furthermore, \( \text{Li}_2\text{O} \) is one of main compositions of crystalline phase for LAS glass ceramic, the decease of \( \text{Li}_2\text{O} \) content can restrict the formation of main crystalline phases. The spodumene mineral not only contains the compositions of nucleation agents, such as \( \text{P}_2\text{O}_5 \) and \( \text{TiO}_2 \), but also contains \( \text{ZnO} \) and \( \text{MgO} \), which accelerate phase separation of LAS glass. These compositions can improve the nucleation and crystallization of LAS glass by mixed alkali effect.

5. Conclusions

The objective of this study was to investigate the effect of Li replacement, including \( \text{Li}_2\text{O} \) replacement by other oxides and \( \text{Li}_2\text{CO}_3 \) replacement by spodumene mineral, on the nucleation, crystallization and microstructure of \( \text{Li}_2\text{O}–\text{Al}_2\text{O}_3–\text{SiO}_2 \) glass by employing DTA, XRD and SEM techniques. This study succeeded in obtaining the crystallization kinetic parameters, nucleation and crystallization characteristics of LAS system glass with Li replacement. As a result, with the \( \text{Li}_2\text{O} \) content decreasing from 4.5% to 3.5%, the crystallization activation energy of LAS glass increased from 335.05 kJ mol\(^{-1}\) to 369.97 kJ mol\(^{-1}\), and crystallization index decreased from 2.88 to 2.74, nucleation temperature increased from 770°C to 810°C and crystallization temperature increased from 880°C to 970°C. With the spodumene proportion increasing from 25% to 75%, the crystallization activation energy of LAS glass decreased, the crystallization index increased, and the crystallization temperature decreased but no charge in the nucleation. The \( \text{Li}_2\text{O} \) replacement restrained the nucleation and crystallization of LAS glass by restricting the formation of main crystalline phase and the \( \text{Li}_2\text{CO}_3 \) replacement promoted the nucleation and crystallization by adding some beneficial compositions with the mixed alkali effect.

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References


Table 3
Crystallization peak temperatures of LAS glass samples at different heating rates

<table>
<thead>
<tr>
<th>Heating rate/°C min(^{-1})</th>
<th>Crystallization peak temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>L4.5</td>
<td>L4.0</td>
</tr>
<tr>
<td>5</td>
<td>1202.4</td>
</tr>
<tr>
<td>10</td>
<td>1140.7</td>
</tr>
<tr>
<td>15</td>
<td>1154.4</td>
</tr>
<tr>
<td>20</td>
<td>1161.3</td>
</tr>
</tbody>
</table>

Table 4
Crystallization activation energy of LAS glass samples

<table>
<thead>
<tr>
<th>L4.5</th>
<th>L4.0</th>
<th>L3.5</th>
<th>K25</th>
<th>K50</th>
<th>K75</th>
</tr>
</thead>
<tbody>
<tr>
<td>E/kJ mol(^{-1})</td>
<td>335.05</td>
<td>363.32</td>
<td>369.97</td>
<td>322.58</td>
<td>297.64</td>
</tr>
<tr>
<td>n</td>
<td>2.88</td>
<td>2.76</td>
<td>2.74</td>
<td>2.75</td>
<td>2.79</td>
</tr>
</tbody>
</table>

![Fig. 9. Relationship between ln(Tp/2) and 1/Tp ((a) Li2O replacement by other oxides; and (b) Li2CO3 replacement by spodumene).]