Effect of Neodymium on the Crystallization, Microstructure and Colorization of Li$_2$O-Al$_2$O$_3$-SiO$_2$ Glass Ceramics

Xingzhong Guo, Wenyan Li, Hui Yang, Jiajie Zhao, Wenda Zhao

Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China.
Email: msewj01@zju.edu.cn

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ABSTRACT

The effect of single coloring agent Nd(NO$_3$)$_3$ on the crystallization, microstructure and colorization of Li$_2$O-Al$_2$O$_3$-SiO$_2$ (LAS) glass ceramics were investigated by differential thermal analysis (DTA), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The introduction of little neodymium has no effect on the crystallization manner and the formation of main crystallization phase, but more neodymium will weaken the crystallization of LAS glass. Little neodymium can increase the glossiness of LAS glass ceramic, while more neodymium can color LAS glass with light purple or red purple. The colorability of neodymium for LAS glass ceramic decreases with the increase of crystallization temperature.

Keywords: Glass Ceramic; Crystallization; Colorization; Neodymium

1. Introduction

Lithium aluminosilicate (Li$_2$O-Al$_2$O$_3$-SiO$_2$, LAS) is well-known as one of the most valuable glass ceramic systems, and has been extensively used in many fields because of its high heat resistance, low expansion, excellent mechanical properties and outstanding chemical durability [1-9]. Many studies on the LAS glass ceramics have mainly focused on crystallization mechanism, microstructure and properties of glass ceramics. At present the colorization of LAS glass ceramics has been becoming a research hotspot in this field. Macalik [10] studied the effects of Fe, Co and Mn on crystallization and structure of lithium aluminosilicate glass ceramic. ZHANG Zhi-Yong [11] investigated the effects of Cr$_2$O$_3$, CoO, NiO, MnO$_2$ and heating process on colorization of LAS glass ceramics. Li Yao-Hui [12] analyzed the effects of V$_2$O$_5$ and Nd$_2$O$_3$ on the crystallization and coloration of transparent LAS glass ceramics. We have also studied the effects of Fe, Co and Ni on colorization and microstructure of LAS glass ceramics [13,14].

The coloration mechanism of ions in the glass ceramic is greatly different from glass, resulting from lots of crystals existing in glass ceramics, and the colors of two materials are quite distinct from each other. The coloring agent can affect not only the color of glass ceramics, but also the melting, crystallization and microstructure of glass ceramic. There are not many studies to investigate the effects of single neodymium on crystallization, structure and performances of LAS glass ceramics. Based on our previous studies on the nucleation and crystallization mechanism of LAS glass [15-19], this paper aims to investigate the effect of single neodymium on the crystallization, structure and colorization of LAS glass ceramics.

2. Experimental

2.1. Glass Preparation

The raw materials of glass batch include acid washed quartz sands and chemical reagents of high purity Li$_2$CO$_3$, Al$_2$O$_3$, MgO, ZnO, TiO$_2$ and other compositions, and their compositions were listed in Table 1. The different compositions of the batches (wt%).

<table>
<thead>
<tr>
<th>Compositions</th>
<th>G-0</th>
<th>G-1</th>
<th>G-2</th>
<th>G-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>62</td>
<td>62</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>MgO + ZnO + BaO + B$_2$O$_3$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>K$_2$O + Na$_2$O</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sb$_2$O$_3$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ratio of Nd(NO$_3$)$_3$</td>
<td>0</td>
<td>0.1</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
ratios of Nd(NO₃)₃ were added into the glass batch and employed as a coloring agents. The raw materials were mixed for 6 h at ball milling, melted for 4 - 6 h at 1673 - 1723 K and moulded to obtain glass in a pre-heated die. The glass samples were then annealed at 773 K for 1 h to eliminate internal stress.

2.2. Crystallization and Characterization

The annealed glass samples were heat-treated at 873 K, 893 K, 993 K, 1093 K and 1193 K for 1 h with a heating rate of 20 K·min⁻¹. Subsequently, the heat-treated glass samples were fast-cooled, ground and sieved through a 200-mesh screen.

Differential thermal analysis (DTA) of the annealed and heat-treated glass samples was measured on a differential thermal analyzer (NETZSCH STA 409 PC Luxx, Germany) with alumina as the reference and the samples were heated at 5 - 20 K·min⁻¹ from 293 K to 1573 K. The crystalline phases of the glass ceramic samples were analyzed by the X-ray diffraction (XRD) method on a XJ 10 - 60 X-ray diffractometer using nickel filtered Cu Kα radiation in the range of 2θ = 10° - 80° with a scanning speed of 2°/min. The morphology of the glass ceramic were observed on the SEM (scanning electron microscopy, FEI SIRION), and the surface of observed samples was polished and eroded by HF (2 wt%) for 30 - 40 s. The template is used to format your paper and style the text. All margins, column widths, line spaces, and text fonts are prescribed; please do not alter them. You may note peculiarities. For example, the head margin in this template measures proportionately more than is customary. This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations.

3. Results and Discussion

3.1. Crystallization Kinetics

Figure 1 shows the DTA curves of LAS glass containing different neodymium at different heating rates. Table 2 shows the crystallizing peak maximum temperatures ($T_p$) from DTA curves at different heating rates. It is noted that crystallizing peak maximum temperatures ($T_p$) of all glass samples increase with the increase of heating rates, and also increase with the ratios of Nd(NO₃)₃ at the same heating rate.

The crystallization kinetic characteristics of LAS glass can be deduced as follows by Arrhenius [1], Kissinger [20] and Augis-Bennett [21], which are respectively expressed as

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

$$ \ln \left( \frac{T_p^2}{\phi} \right) = \frac{E}{RT_p} + \ln \frac{E}{R} - \ln v $$

$$ n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} $$

where $E$ is the activation energy (kJ·mol⁻¹), $R$ is the gas constant, $v$ is the frequency factor (min⁻¹), $\phi$ is the DTA heating rate (K·min⁻¹), $k$ is the reaction rate constant, $n$ is the crystallization index and $\Delta T$ is the half-height temperature wideness of the maximum exothermic peak of DTA. Low $E$ value and high $v$ indicate high crystallization rate and crystallinity. Crystallization index $n$ is related to crystallization manner, $n \approx 1$, surface crystallization, $n \approx 2$ two-dimension growth crystallization, $n \approx 3$, volumetric crystallization, $n \approx 4$, homogeneous nucleation crystallization.

According to Table 2, the relationship between $\ln \left( T_p^2 / \phi \right)$ and $1/T_p$ is constructed (Figure 2) to calculate the effective activation energy, frequency factor and crystallization index. Table 3 is the $E$, $v$, and $n$ crystallization values of the LAS glass samples. It is shown

![Figure 1. DTA traces obtained from: (a) G-0; (b) G-1; (c) G-2; and (d) G-3 LAS glass powders.](image-url)
Effect of Neodymium on the Crystallization, Microstructure and Colorization of Li2O-Al2O3-SiO2 Glass Ceramics

Figure 2. Relationship between $\ln\left(\frac{T_2}{\phi}\right)$ and $1/T_\phi$ of G-0, G-1, G-2 and G-3 LAS glass samples.

Table 3. $E$, $v$, and $n$ crystallization values of the LAS glass samples.

<table>
<thead>
<tr>
<th>Crystallization parameter</th>
<th>G-0</th>
<th>G-1</th>
<th>G-2</th>
<th>G-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (kJ·mol$^{-1}$)</td>
<td>252.06</td>
<td>221.64</td>
<td>200.77</td>
<td>243.43</td>
</tr>
<tr>
<td>$v$ (min$^{-1}$)</td>
<td>$1.74 \times 10^{14}$</td>
<td>$2.24 \times 10^{12}$</td>
<td>$1.14 \times 10^{11}$</td>
<td>$1.99 \times 10^{12}$</td>
</tr>
<tr>
<td>$n$</td>
<td>1.3</td>
<td>1.42</td>
<td>1.43</td>
<td>3.45</td>
</tr>
</tbody>
</table>

that the G-0 specimen has higher $E$ and $v$ than other specimens. As the ratio of Nd(NO$_3$)$_3$ increases, the $E$ and $v$ of the samples become lower while both $E$ and $v$ increase again when the ratio reaches to 2 wt% (G-3). It is also suggested that the additions of more neodymium will weaken the ability of crystallizations of LAS glass. The fact $n$ values of G-0, G-1 and G-2 samples are near 1 indicates that crystallization manner of LAS glass is surface crystallization, while the $n$ value of G-3 sample is more than 3, suggesting volumetric crystallization. It indicates the addition of little Nd has no obvious effect on crystallization manner.

3.2. Crystalline Phases and Microstructure

Figure 3 shows the X-diffraction patterns of G-0 and G-3 samples, which were heat treated for 1 h at several temperatures above 873 K. Both of G-0 and G-3 glass samples are amorphous phase below 893 K. There are only hexagonal LiAl(SiO$_3$)$_2$ crystal phase (JCPDS-PDF 31-0706) at 993 K, which is similar to low-temperature stable phase $\alpha$-spodumene. The high-temperature stable phase $\beta$-spodumene (JCPDS-PDF 35-0797) was main crystallization phase in both samples at 1193 K. In addition, the specimen became opaque due to the crystallinity. It is also confirmed that the phase transformation of $\alpha$-spodumene into $\beta$-spodumene finished at 1193 K, and the additions of Nd have no effect on the formation of main crystallization phase.

The volume fraction, grain size and completion of crystallization phase, which determine the performances of glass ceramics, are influenced by glass composition and heat-treatment. Figure 4 shows the microstructures of G-0 and G-3 samples heat treated for 1 h at different crystallization temperatures. It can be seen that the crystal size of both samples increases with increase of the crystallization temperatures. The crystal shape of G-0 sample becomes needle while that of the G-3 sample is of block or particle, which coordinates with the results of crystallization manner.

3.3. Colorization of LAS Glass Ceramic

Figure 5 shows the color of different glass samples at different crystallization temperatures. It is seen that the color of glass before crystallization is greatly distinct from that after crystallization, and the phenomenon become more apparent at higher ratio of Nd(NO$_3$)$_3$. The color of glass ceramic samples crystallized below 993 K varies from light purple to red purple with the ratios of Nd(NO$_3$)$_3$, while those colors of glass ceramic samples crystallized above 993 K fades, and in the meantime the main crystal phases have formed above 993 K (according to Figures 3 and 4). It is also observed that the color of glass ceramic samples with lower ratio of Nd(NO$_3$)$_3$ become brighter than that of glass ceramic sample without Nd(NO$_3$)$_3$, in that the neodymium can decrease the faint yellow of LAS glass ceramics, which results from the addition of TiO$_2$. It improves that addition of single neodymium has a weak colorability to the coloration of LAS glass ceramic with higher crystal size, but little neodymium can improve the glossiness of glass ceramic.

4. Discussions

Neodymium exists as the state of Nd$^{3+}$ ion in glass, and
lies in low-symmetry lattice site outside the network [12]. Nd$^{3+}$ ion is known to absorb visible light wavelengths and used to colorize glass and has unusual two-color effect. The coloring of Nd$^{3+}$ ion is stable because its valence electrons are in the 4f track which is shielded by 5s$^2$5p$^6$ track, and it leads to f-f energy level transition.

(a)                                                            (b)

(c)                                                            (d)

(e)                                                            (f)
Nd³⁺ ions are surrounded by O²⁻ ions to form different coordination ligands and states, which play a vital part in the glass structure and spectrum characteristics. Nd³⁺ ions is strong in terms of electric field intensity with the ion radii of 0.1281 nm, and it can form ligands and join the silicon oxygen tetrahedron together, which is the reason why more Nd(NO₃)₃ can reduces the crystallization ability of LAS glass.

Nd³⁺ ions joins into the network of glass and participates the restructuring, correspondingly, the crystallization and crystal phases have an effect on the absorption spectrum of Nd³⁺ ions. The crystallinity and crystal size of LAS glass ceramic increase with the increase of crystallization temperature, which affects the absorption of Nd³⁺ ions in visible light wavelengths.

5. Conclusion

The crystallization mechanism, microstructure of Li₂O-Al₂O₃-SiO₂ system glass ceramics containing neodymium were investigated. The introduction of little neodymium has no effect on the crystallization manner and the formation of main crystallization phase, but more neodymium will reduces the crystallization ability of LAS glass and change the shape of crystals. Little neodymium can increase the glossiness of LAS glass ceramic, more neodymium can color LAS glass with light purple or red purple, but the colorability decreases for LAS glass ceramic with higher crystallization temperature.

REFERENCES


Figure 4. SEM images of G-0 and G-3 LAS glass samples heat treated for 1h at different crystallization temperatures. (a) G-0 873 K; (b) G-0 993 K; (c) G-0 1093 K; (d) G-0 1193 K; (e) G-3 873 K; (f) G-3 993 K; (g) G-3 1093 K; (h) G-3 1193 K.

Figure 5. Color of different samples at different crystallization temperatures.
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