

Effects of Co_2O_3 on Crystallization and Colorization of Lithium Aluminosilicate Glass Ceramics

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ABSTRACT

The effects of Co_2O_3 on the crystallization and colorization of lithium aluminosilicate glass ceramic were investigated by using differential thermal analysis (DTA), X-ray diffractometry (XRD) and scanning electron microscope (SEM). The results showed that the introduction of Co_2O_3 not only changed the color of lithium aluminosilicate glass but also affected its crystallization by increasing the crystallizing maximum peak temperature (T_p) and weakening the crystallization ability. In addition, the color of LAS glass ceramics could be achieved by controlling the suitable Co_2O_3 and appropriate crystallization temperature.

Keywords: Glass Ceramic; Crystal Size; Crystallization; Microstructure

1. Introduction

The lithium aluminosilicate ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, LAS) system glass ceramic has been widely studied because of its low expansion, high heat resistance, outstanding chemical durability and excellent mechanical properties [1-5]. The colorization of LAS glass ceramics has become a hotspot in this field. The coloring process of glass ceramic is not only related to the system of glass ceramics, but also depends on the composition of coloring agent and heat treatment process. There are not too many studies to investigate the effects of single Co_2O_3 on crystallization, structure and performances of lithium aluminosilicate glass ceramics.

Based on our previous studies on the nucleation and crystallization of LAS glass [6-9], this paper aims to investigate the effect of single Co_2O_3 on the crystallization and colorization of LAS glass ceramics by employing DTA, XRD and SEM.

2. Experimental

2.1. Glass preparation

Acid washed quartz sands, Li_2CO_3 , Al_2O_3 , MgO , ZnO , TiO_2 and other compositions were used to produce the glass batch, whose proportions were listed in **Table 1**. The different ratios of Co_2O_3 were added into the glass

batch and employed as a coloring agent. The raw materials all together were melted for 4 - 6 h at 1673 - 1723 K and moulded in a pre-heated die. The glass samples were then annealed at 773 K for 1 h to eliminate internal stress [4-6].

2.2. Nucleation and Crystallization

The heat-treatment of the annealed glass samples was carried out at 873 K, 893 K, 993 K, 1093 K and 1193 K for 1 h with a heating rate of $20 \text{ K}\cdot\text{min}^{-1}$, respectively. Subsequently, the samples were fast-cooled, ground and sieved through a 200-mesh screen to obtain the glass powder.

Differential thermal analysis (DTA) of the annealed glass samples was carried out on a differential thermal

Table 1. Main compositions of the glass batches (wt%).

Compositions	G-0	G-1	G-2	G-3
SiO_2	62	62	62	62
Li_2O	10	10	10	10
Al_2O_3	18	18	18	18
$\text{MgO} + \text{ZnO} + \text{BaO} + \text{B}_2\text{O}_3$	2.0	2.0	2.0	2.0
TiO_2	4	4	4	4
$\text{K}_2\text{O} + \text{Na}_2\text{O}$	3.0	3.0	3.0	3.0
Sb_2O_3	1	1	1	1
Co_2O_3	0	0.001	0.01	0.1

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analyzer (NETZSCH STA 409 PC Luxx, Germany) with alumina as the reference and the samples were heated at $5\text{-}20\text{ K}\cdot\text{min}^{-1}$ from 293 K to 1573 K . The crystalline phases of the samples were analyzed by the X-ray diffraction (XRD) method on a XJ 10-60 X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation in the range of $2\theta = 10^\circ - 80^\circ$ with a scanning speed of $2^\circ/\text{min}$. The surface of the samples was polished and eroded by HF (2 wt%) for 30 - 40 s for the further morphology observation on the scanning electron microscopy (FEI SIRION).

3. Results and Discussions

3.1. Crystallization

Figure 1 shows the DTA curves obtained from as-cast LAS glass and **Table 2** shows the crystallizing peak maximum temperatures (T_p) from DTA curves at different heating rates. According to curves, it is shown that

crystallizing maximum peak temperature (T_p) increases with the increase of heating rates and Co_2O_3 contents, respectively.

The crystallization kinetic characteristics of lithium aluminosilicate glass can be decided as follows by Arrhenius [11], Kissinger [12] and Augis-Bennett [13], which are respectively expressed as

$$k = v \exp\left(-\frac{E}{RT}\right) \quad (1)$$

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

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

where in E is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R the gas constant, v the frequency factor, a the DTA heating rate

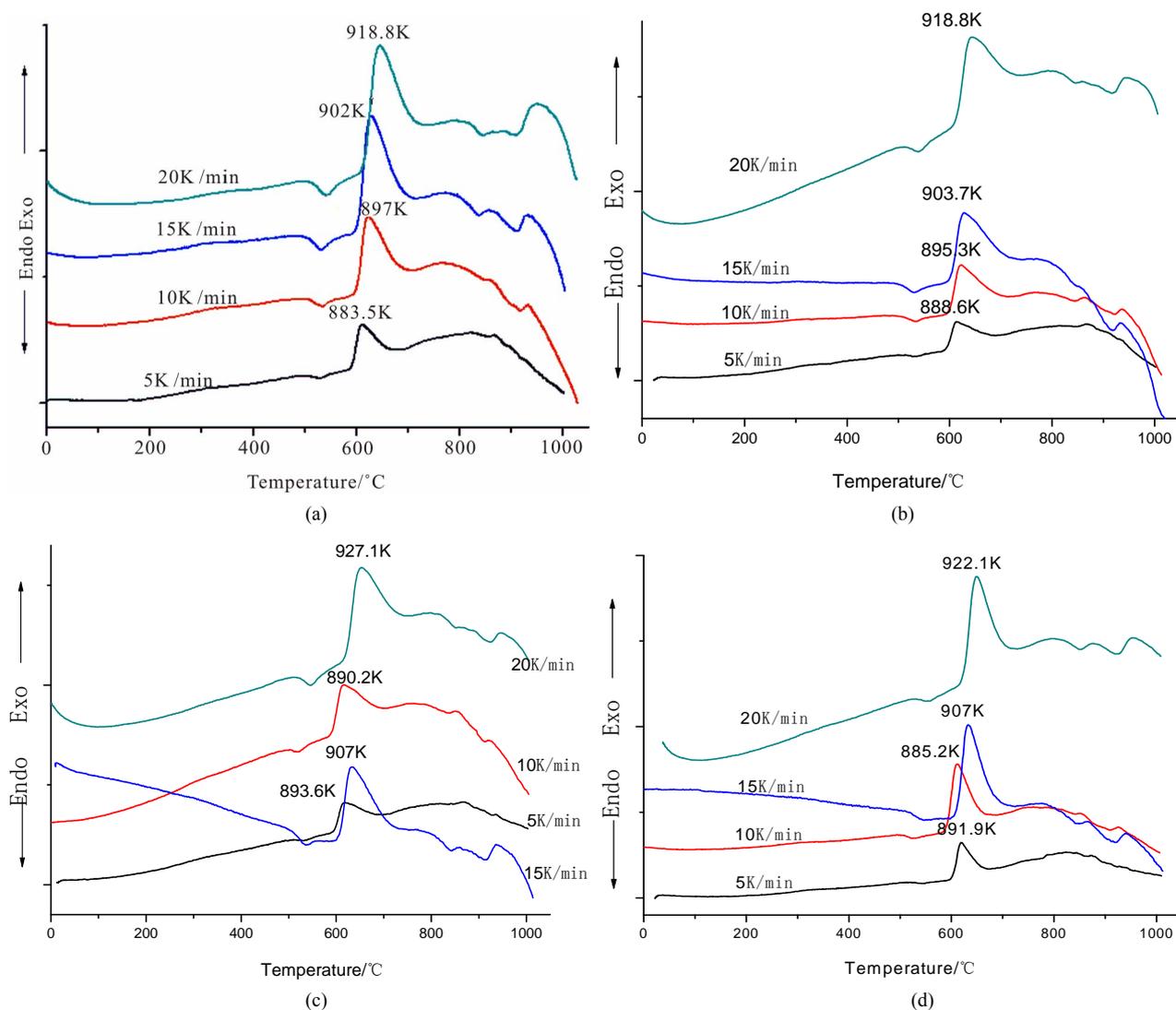
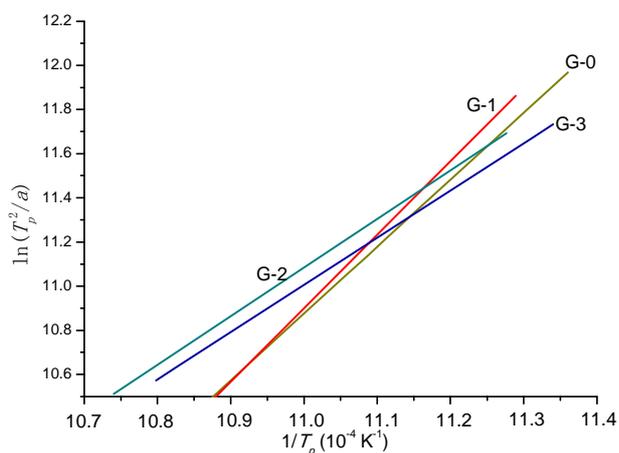


Figure 1. DTA traces obtained from: (a) G-0; (b) G-1, (c) G-2 and (d) G-3 LAS glass powders.

Table 2. T_p (K) values from DTA curve of LAS glass samples at different heating rates.

Heating rates (K/min)	G-0	G-1	G-2	G-3
5	883.5	888.6	893.6	891.9
10	897	895.3	890.2	885.2
15	902	903.7	907	907
20	918.8	918.8	927.1	922.1

**Figure 2.** Relationship between $\ln(T_p^2/a)$ and $1/T_p$: G-0, G-1, G-2, G-3.

(K/min), k the reaction rate constant, which is related to the E and ν , n the crystallization index, *i.e.* Avrami ex-

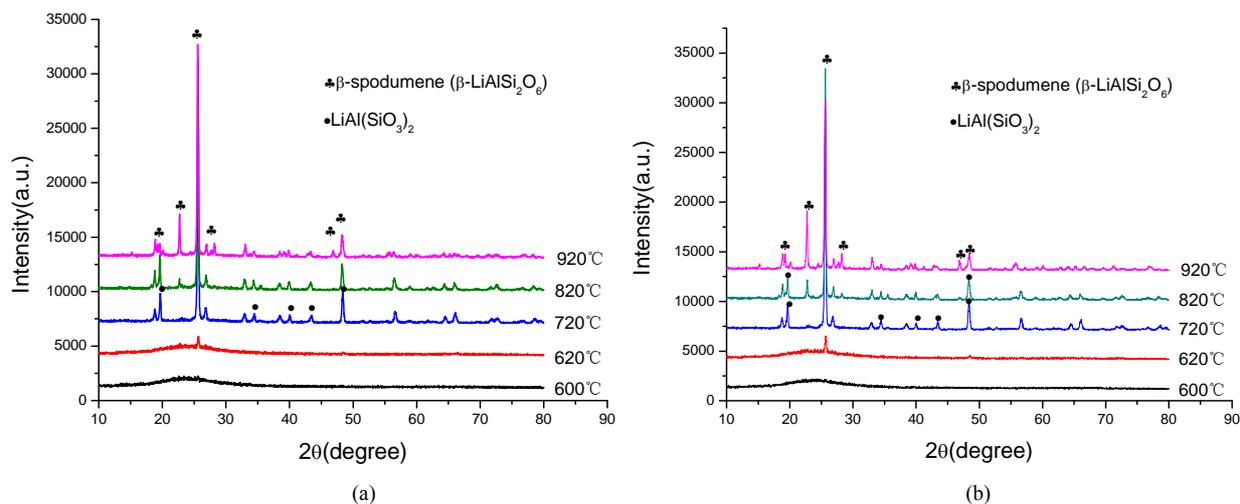
ponent, depending upon the morphology or directionality of crystal growth and ΔT is the half-height temperature wideness of the maximum exothermic peak of DTA. According to Equations (1)-(3), low E value and high ν lead to high k , indicating high crystallization rate and crystallinity. Crystallization index n is related to crystallization manner, $n \approx 1$, surface crystallization, $n \approx 2$ two-dimension growth crystallization and $n \approx 3$, volumetric crystallization [8].

The relationship between $\ln(T_p^2/a)$ and $1/T_p$ is constructed (**Figure 2**) to calculate the effective activation energy, frequency factor and crystallization index, as shown in **Table 3**. The G-1 specimen has the highest E and ν than other specimens. The G-2 and G-3 have lower E and ν than G-0. It is suggested that the G-1 (containing Co₂O₃ 0.001% content) can increase the activation energy and frequency factor, but the k value becomes lower than G-0 in the end. However, the G-2 and G-3 can lower the activation energy and frequency factor, their k values become lower too. In other words, comparing to G-0, the ability of crystallizations would be weakened with the increase of Co₂O₃ content.

The n values, which are calculated by using Equation (3), are given in the **Table 3**. The fact n value is near 1 indicates that crystallization manner of LAS glass is surface crystallization, while n value near 2 suggests two-dimensional growth crystallization. From **Table 3**, it can be seen that Co₂O₃ can change the crystallization manner of glass.

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

Crystallization parameter	G-0	G-1	G-2	G-3
E (kJ·mol ⁻¹)	252.06	276.784	183.173	177.804
ν (min ⁻¹)	1.74×10^{14}	4.90×10^{15}	1.13×10^{10}	5.83×10^9
n	1.3	1.11	1.84	2.29
k (when $a = 10$ K·min ⁻¹)	0.3678	0.3517	0.2031	0.189

**Figure 3.** XRD patterns of: (a) G-0 and (b) G-3 LAS glass heat treated at different crystallization temperatures.

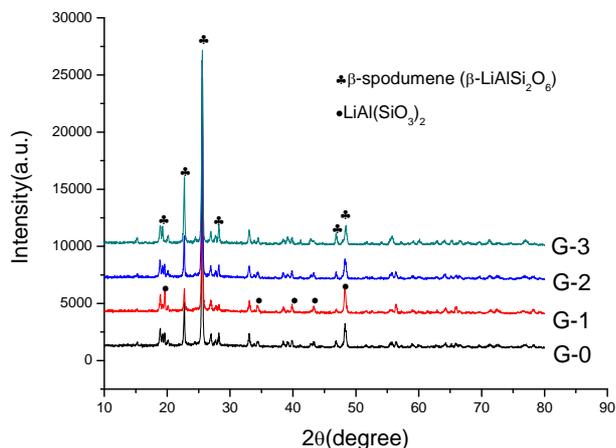


Figure 4. XRD patterns of G-0, G-1, G-2 and G-3 LAS glass heat treated at 1093 K.

The crystallization peaks on the DTA curves imply that crystal phase forms and transforms during the heat treatment. **Figure 3** shows the diffraction patterns of G-0 and G-3 samples. Both of G-0 and G-3 glass samples are amorphous phase below 893 K. There is only hexagonal $\text{LiAl}(\text{SiO}_3)_2$ crystal phase (JCPDS-PDF 31-0706) in the temperature range of 993 K to 1093 K, which is similar to α -spodumene. The β -spodumene (JCPDS-PDF 35-0797) was main crystallization phase in both samples at 1093 K. In addition, the specimen became opaque due to the crystallinity. It is also confirmed that, above 1093 K, the transformation of α -spodumene into β -spodumene finished.

According to the XRD patterns of G-0, G-1, G-2 and G-3 LAS glass samples heat treated at 1093 K (**Figure 4**), G-0, G-2 and G-3 have the formation of main crystallization phase of β - $\text{LiAlSi}_2\text{O}_6$, but we can find only $\text{LiAl}(\text{SiO}_3)_2$ in the G-1. It indicates that the content of 0.001% Co_2O_3 can restrain the main phase transformation of α -spodumene into β -spodumene at 1093 K.

Figure 5 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 grain size of both G-0 and G-3 samples increases with the crystallization temperatures, and the grain size of G-0 specimen is similar to that of the G-3 specimen. The G-3 crystal grain becomes from sphere-shape to needle. And both of specimen still exist amorphous phase below 993 K, crystal phase grain is about 20 - 30 nm. According to **Figure 5 (c)-(j)**, it is found that Co can slow crystal growth rates, which indicates that the addition of Co has no significant effect on the grain size, but it can control crystal growth rate of LAS glass ceramics. This was certificated by analyzing **Table 3**.

Figure 6 shows the microstructures of G-0, G-1, G-2 and G-3 samples heat treated for 1 h at 1093 K. The G-0, G-1 and G-2 specimens have similar complete structures;

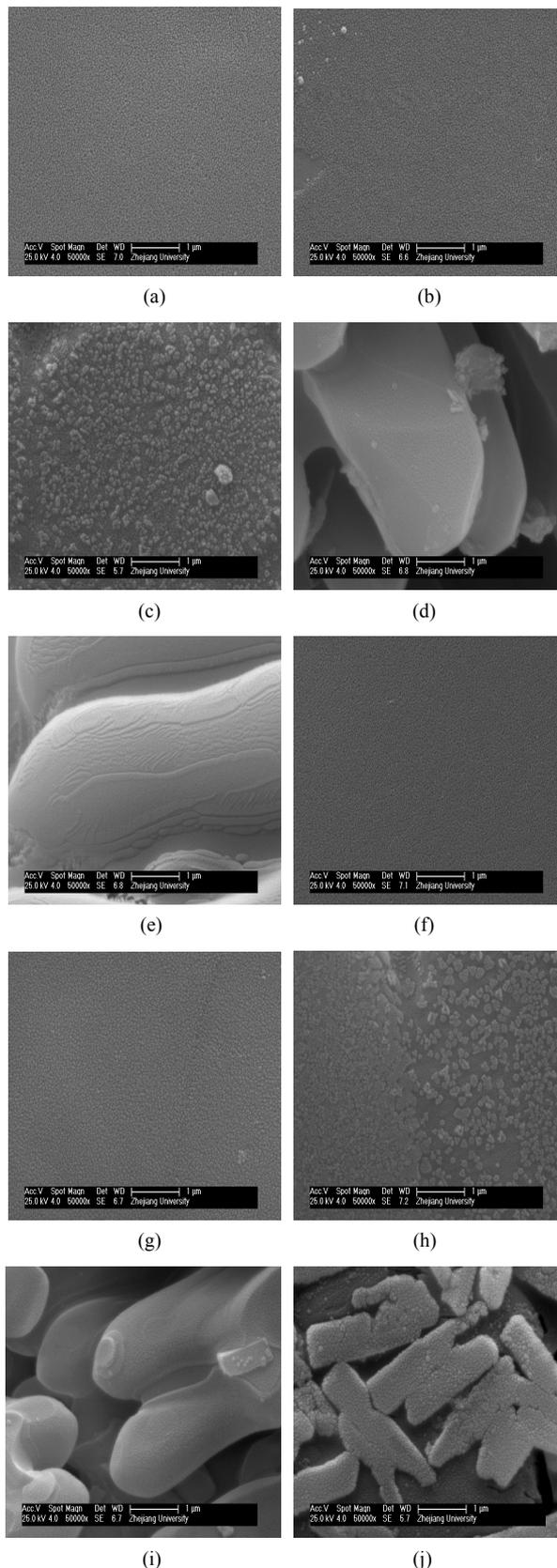


Figure 5. SEM images of G-0 and G-3 glass samples heat treated for 1 h at different crystallization temperatures.

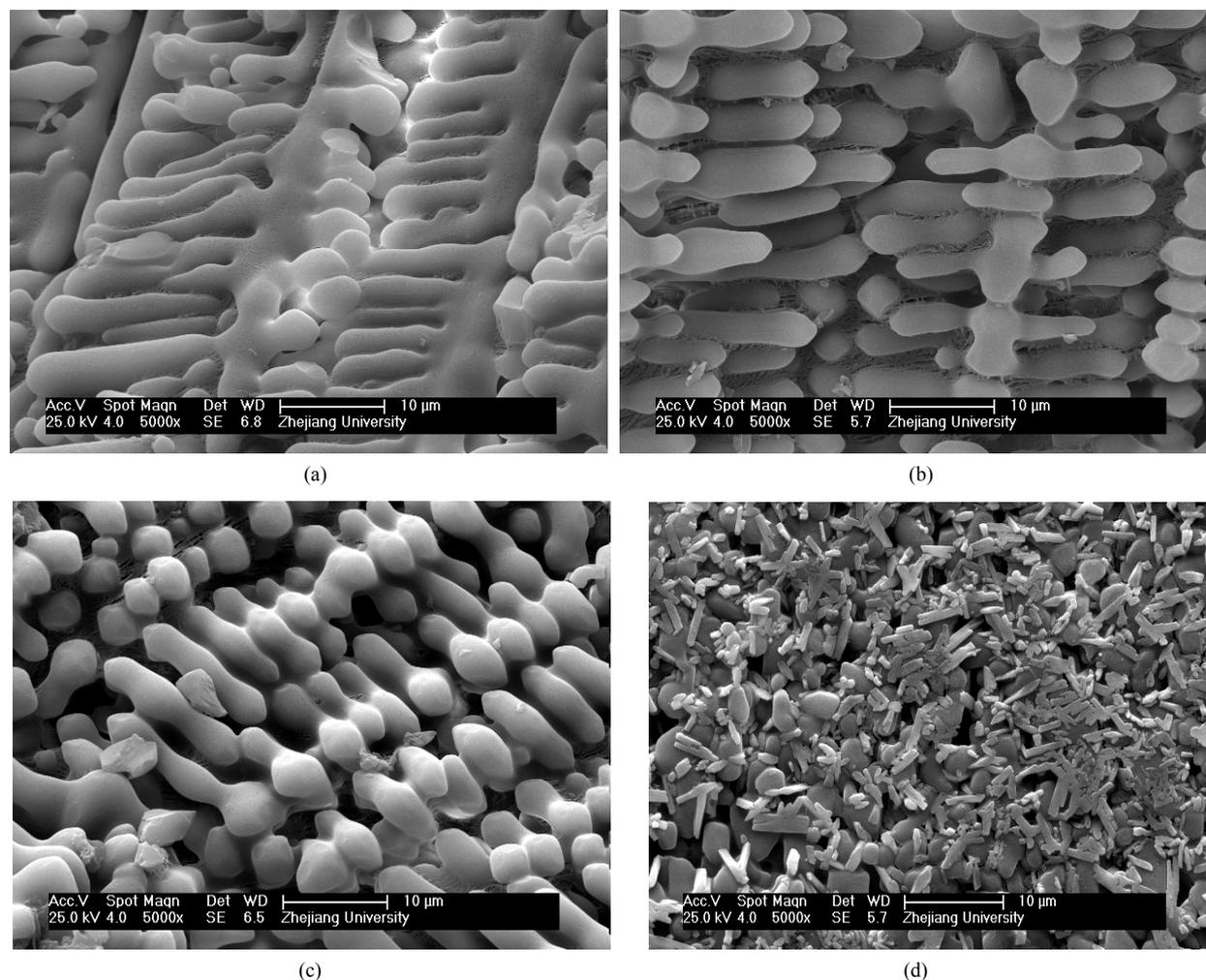


Figure 6. SEM images of G-0, G-1, G-2 and G-3 glass samples heat treated for 1 h at 1193 K.

however, the G-3 has obviously different shape. It shows if the content of Co (containing 0.1% Co_2O_3) is high, it will have remarkable effect on the crystal grain shapes in that Co can capture ion O^{2-} (non bridge oxygen) which results in incomplete glass structure.

3.2. Colorization

Figure 7 shows the color of glass ceramic samples at different crystallization temperatures. Compared G-0 with G-1, it is shown that little Co (lower than 0.001% Co_2O_3) have hardly effect on the color of glass. With the increase of the contents of Co, all glass samples' color become from transparent to blue or navy blue (even near to black) at below 893 K. The color of G-2 and G-3 become light with the increase of the crystallization temperature. According to Figures 3 and 5, crystal phases have formed above 993 K. So we can obtain different color glass-ceramics by controlling the suitable contents of Co and appropriate crystallization temperature.

Co^{3+} ion is known to absorb visible light wavelengths

and used to colorize glass. The colorization Co^{3+} ions in the structure of glass are surrounded by O^{2-} ions to form different coordination ligands and states, which play an essential part in the glass structure and spectrum characteristics. Co^{3+} ions can form four or six ligands and join the silicon oxygen tetrahedron together. With radii of 0.065 nm, Co^{3+} ion is strong in terms of electric field intensity, which results in the high capacity of joining the silicon oxygen tetrahedrons and reducing the crystallization ability of LAS glass.

4. Conclusions

The crystallization mechanism and microstructure of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system glass ceramic containing Co_2O_3 was investigated by employing DTA, XRD and SEM. The introduction of Co_2O_3 increased the crystallization temperature of LAS glass, decreased the crystallization kinetic parameters and obtained the crystalline phases of β -spodumene. The color of LAS glass ceramics could be obtained by controlling the suitable contents of Co_2O_3

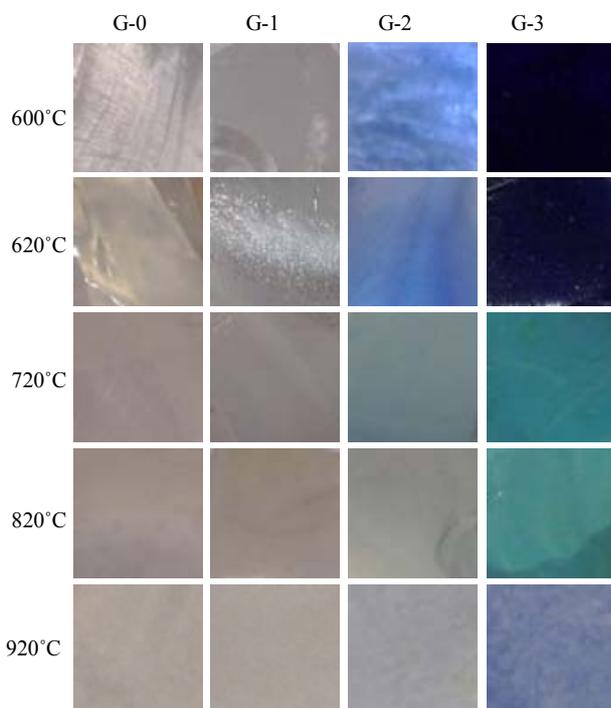


Figure 7. Color of glass ceramic samples at different crystallization temperatures.

and appropriate crystallization temperature. When the content of coloring agent Co_2O_3 was lower than 0.001%, it had no effect on crystal structure and colorization while it could restrain the main phase transformation of α -spodumene into β -spodumene at 1193 K.

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