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Effect of Al₂O₃ on Crystallization, Microstructure, and Properties of Glass Ceramics Based on Lead Fuming Furnace-Slag

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Abstract: In the paper, glass ceramics used as architectural materials were prepared based on lead fuming furnace-slag (LFFS) by a synergistic sinter-crystallization method. The effects of Al₂O₃ addition on the crystallization phase, crystallization kinetics, and mechanical performance of glass ceramics were investigated. The results showed that the phases of the glass ceramics prepared were composed of gehlenite and wollastonite, and crystallization kinetics analysis showed that bulk crystallization dominated the overall crystallization process in the Al₂O₃ content range from 2% to 8%. The glass transition temperature and the crystallization peak temperature of the glass ceramics generally increased with the increase in the Al₂O₃ content. Additionally, the crystalline morphology gradually developed from sheet-like to spherical, while the number of pores increased and the bulk density gradually decreased. When the Al₂O₃ content was 2%, the bending strength of glass ceramics reached its maximum, 75.1 MPa, corresponding to a bulk density of 2.24 g·cm^{−3}. Owing to the high strength and relatively low bulk density, the sintered glass ceramics appear promising for potential applications in lightweight construction tiles.

Keywords: lead fuming furnace-slag; glass ceramics; Al₂O₃ content; crystallization kinetics; lightweight construction tiles



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1. Introduction

Lead fuming furnace-slag (LFFS) is a by-product of lead production, which contains SiO₂, CaO, Al₂O₃, and so on, and improper disposal can cause a serious waste of resources and environment problems [1]. Research on the disposal and recycling of LFFS has been reported. Zhang et al. [2] prepared the porous foamed ceramic with the main crystal phase of wollastonite based on LFFS, and no heavy metal ions were detected in the toxicity leaching experiments, indicating that the foamed ceramic product is environmentally friendly. The foamed ceramics prepared were suitable for insulation materials on building exterior walls. The utilization rate of LFFS was approximately 70%. Guo et al. [3] prepared the geopolymer based on LFFS by adding alkaline activators (NaOH and Na₂SiO₃). However, the negative environmental impacts of alkaline activators limit the popularization of geopolymers. Pan et al. [4] prepared the glass ceramics with hedenbergite as the main crystal phase based on LFFS. Under optimal conditions, the glass ceramics had good densification, high bending strength, and good corrosion resistance. However, the utilization rate of LFFS was only 50%. Therefore, efficient and high-value utilization is the key to the disposal and recycling of LFFS.

In addition, during the preparation of glass ceramics, the crystallization and microstructure of the glass ceramics are critical for performance [5]. Therefore, significant research is needed to adjust the formulation or crystallization process to improve product performance. Al₂O₃ as an intermediate of the network [6] exists either as [AlO₄] tetrahedrons, participates with [SiO₄] tetrahedron to form a uniformed glass network, or as [AlO₅]

[AlO₆], which locates in the cavities of the [SiO₄] network and varies with the amount of content. When it exists in the form of [AlO₄], Al³⁺ forms a uniformed network with [SiO₄] tetrahedron. A small amount of Al₂O₃ in silicate glass allows for the formation of Al₂O₃ tetrahedron with non-bridging oxygens, which integrates itself into the silica network, reconnects the broken network, and strengthens the glass structure [7]. When a higher amount of Al₂O₃ is added, partial Al³⁺ exists as [AlO₅] or [AlO₆] and as a positive ion outside the silica backbone, which increases the crystallinity, decreases the viscosity, and weakens the structural strength of the glass [8,9]. Many researchers have reported on the influence of Al₂O₃ on the structure and properties of glass ceramics based on solid waste [10–16], indicating that the addition of an amount of Al₂O₃ has a significant impact on the structure and properties of glass ceramics. However, little research about the crystallization behavior of glass ceramics prepared based on LFFS influenced by the addition of Al₂O₃ has been reported.

In summary, this paper focuses on the efficient and high-value utilization of LFFS and adopts “material separation” technology to prepare glass ceramics. The influence of Al₂O₃ content on the crystallization mechanism from a dynamic perspective was investigated. The relationship between the crystallization kinetics process, structure, and properties of glass ceramics was studied. The study provided theoretical guidance for the production and application of glass ceramics based on LFFS in the future.

2. Materials and Methods

2.1. Materials

The LFFS was supplied by a company in Henan Province, China. The X-ray fluorescence analysis of LFFS is shown in Table 1. LFFS was treated using the carbothermal reduction method [2], and the obtained residue was the main material used to prepare the glass ceramics. The main components of the residue are listed in Table 2. Analytical pure Al₂O₃ powder (>99.0%) was provided by a chemical reagent factory in Tianjin City, China.

Table 1. X-ray fluorescence analysis of LFFS (wt%).

Component	Content	Component	Content
Fe ₂ O ₃	46.48	SrO	0.22
SiO ₂	26.80	Na ₂ O	0.20
CaO	13.89	P ₂ O ₅	0.19
Al ₂ O ₃	5.79	Cr ₂ O ₃	0.13
K ₂ O	1.91	CuO	0.11
MgO	1.27	BaO	0.08
SO ₃	1.02	ZrO ₂	0.07
MnO	0.79	MoO ₃	0.05
ZnO	0.62	As ₂ O ₃	0.01
TiO ₂	0.33	Cl	0.01

Table 2. The main components of LFFS and residue (wt%).

Materials	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	Na ₂ O	K ₂ O	TiO ₂	Cr ₂ O ₃	CuO	BaO	Others
LFFS	25.65	12.60	5.55	1.90	44.80	2.09	1.74	0.32	0.12	0.10	0.07	5.14
Residue	45.72	25.94	13.49	3.57	0.19	2.87	2.05	0.47	-	-	0.25	5.45

2.2. Preparation of Glass Ceramics

In general, the main compositions of glass ceramic are as follows: 45–65% SiO₂, 15–30% CaO, 5–15% Al₂O₃, 1–3% Na₂O, and 1–4% K₂O. The component of the residue is similar to that of basic glass according to the phase diagram of the CaO–Al₂O₃–SiO₂ ternary system [17]. The residue was crushed and sieved through 200 mesh. The quality of the corresponding pure reagent (Al₂O₃) was added into the residue, and the residue (100 g) and the corresponding pure reagent (Al₂O₃) were weighed, as illustrated in Table 3. The

compositions of the samples with different Al_2O_3 contents are listed in Table 4. Each group of powder mixture was mixed thoroughly in a mixer and sintered at 1450°C for 3 h in an electrical furnace with a heating rate of $10^\circ\text{C}/\text{min}$. Then, the molten mixture was rapidly poured into a container with cold water, and a granular glassy material was then formed. After drying and grinding, the glassy material was sieved with 200 mesh to obtain the basic glass with Al_2O_3 dosages of 0%, 2%, 4%, 6%, and 8%, labeled as BG0, BG1, BG2, BG3, and BG4, respectively. Approximately 20 mg of each group of basic glass powders was used by differential scanning calorimetry (DSC) measurement to analyze their crystallization kinetics. Afterwards, the basic glass powder was mixed with 10 wt% H_2O and then compacted and pressed into cylinders at a pressure of 8–9 ton in a PIKE IR hydraulic press (Crush Technologies). Then, the cylinders had a heat treatment at nucleation temperature for 1 h and crystallization temperature for 1 h, respectively, as the DSC results. Finally, the glass ceramics obtained were polished and stored for subsequent testing.

Table 3. Mass (g) of raw materials employed in the fabrication of glass ceramics.

Sample	Residue	Al_2O_3
A0	100.00	0.00
A1	100.00	2.37
A2	100.00	4.85
A3	100.00	7.45
A4	100.00	10.19

Table 4. The chemical composition of the samples with different Al_2O_3 contents (wt%).

Content	SiO_2	CaO	Al_2O_3	MgO	FeO	Na_2O	K_2O	Others
A0	45.72	25.94	13.49	3.57	0.19	2.87	2.05	6.17
A1	44.66	25.34	15.49	3.49	0.19	2.80	2.00	6.03
A2	43.61	24.74	17.49	3.40	0.18	2.74	1.96	5.88
A3	42.55	24.14	19.49	3.32	0.18	2.67	1.91	5.74
A4	41.49	23.54	21.49	3.24	0.17	2.60	1.86	5.61

2.3. Characterization

The chemical compositions of the materials were determined using X-ray fluorescence (XRF) spectrometry (PANalytical Axios, FRRB International Co., Ltd. in Holland.). The non-isothermal crystallization kinetics of glass ceramics were quantitatively analyzed by differential thermal analysis (Netzsch Instrument Manufacturing Co., Ltd. Selbi, Germany) with $\alpha\text{-Al}_2\text{O}_3$ powder as the reference material at different heating rates of $5\text{--}25^\circ\text{C}/\text{min}$ in Ar flow. The based glass and glass ceramics were dried and ground to less than 200 mesh. The phases were examined using an X-ray diffractometer (Bruker, D8 ADVANCE, Saarbrücken, Germany) with Cu K_α radiation over the 2θ range of $10\text{--}90^\circ$ at a scanning speed of $6^\circ/\text{min}$. The microstructural observation and elemental analysis of glass ceramics were performed using a scanning electron microscopy system equipped with an energy dispersive X-ray spectroscopy (SEM/EDS, Hitachi S-4800, Tokyo, Japan) analyzer. The sample surfaces were polished and then chemically etched by immersion in an aqueous HF solution (5 vol%) for 20 s. Finally, the samples were ultrasonically washed with distilled water and dried in a vacuum.

Bulk density (ρ_1) characterizes the mass per unit volume of glass ceramics. The bulk density (ρ_1) was calculated as

$$\rho_1 = \frac{M}{V} \quad (1)$$

where M and V are the mass and volume of the glass ceramics, respectively.

The glass ceramics were processed to $3 \times 4 \times 20$ mm, and their bending strengths were determined according to GB/T5486—2008 [18] using a controlled electronic universal

testing machine (Guanteng Automation Technology Co., Ltd., Jilin, China). All rectangular bars were carefully polished. Each data point represents the average value of at least three individual tests.

3. Results and Discussion

3.1. Crystalline Phase and Kinetics Analyses

Figure 1 shows the DSC curves of the BG0–BG4(A0–A4) samples at a heating rate of 10 °C/min. As the Al_2O_3 content increased, the glass transition temperature (T_g) increased, the first crystallization peak (T_{p1}) values increased first and then decreased, and the second crystallization peak (T_{p2}) values generally increased. It could be explained that Al^{3+} in the glass can connect the glass network with four coordinated $[\text{AlO}_4]$, increasing the degree of polymerization of the glass network. On the other hand, Al^{3+} can also exist with six coordinated $[\text{AlO}_6]$, which plays a role in disrupting the glass network and reducing the degree of polymerization of the network [19]. For BG0–BG3 samples, Al^{3+} connected to a glass network in the form of $[\text{AlO}_4]$ and the degree of polymerization of the glass network increased, which is not conducive to the diffusion of ions during the crystallization process, leading to an increase in the glass transition temperature and first crystallization peak temperature. Due to the precipitation of crystalline phases on the surface of glass powder, the viscosity of the glass increases, hindering the further diffusion of ions and hindering crystallization, resulting in an increase in the second crystallization temperature [20,21]. Notably, the first crystallization peak of the BG4 sample abnormally decreased, and that is because Al^{3+} exists with six coordinated $[\text{AlO}_6]$, which reduces the degree of network polymerization, facilitates ion diffusion during crystallization, and is more conducive to the reduction in crystallization temperature.

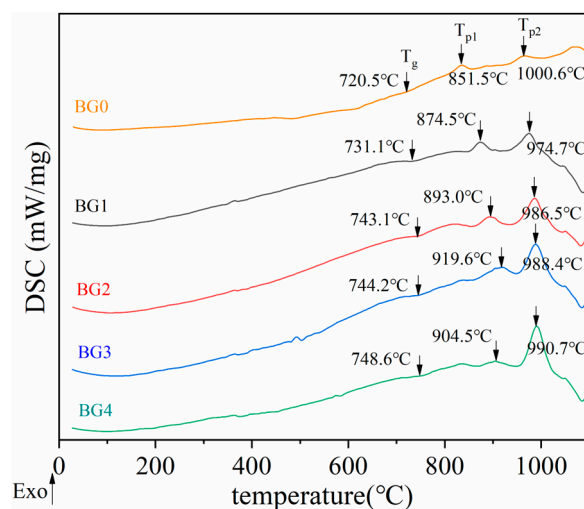


Figure 1. DSC curves of the BG0–BG4 samples (heating rate:10 °C/min).

The heat treatment of the samples included two main stages: nucleation and crystallization [13]. The nucleation temperature (T_N) is usually 50–100 °C higher than the glass transition temperature [22] ($T_N = T_g + 50$ °C in this study). The BG0–BG4 samples were heat treated at T_{p1} and T_{p2} , respectively. The glass ceramics (GC0–GC9) were obtained according to the heat treatment conditions, as shown in Table 5.

Figure 2 shows the XRD patterns of the BG0–BG4 samples. It can be observed that there was almost no diffraction peak, except just an amorphous hump around 30°. This result indicates that there were no crystals precipitated in basic glass without heat treatment. Figure 3 shows the XRD patterns of the GC0–GC9 samples. All samples obtained have the same crystal phase composition, consisting of two crystal phases: gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$ PDF#35-0755) and wollastonite (CaSiO_3 PDF#27-0088). Simultaneously, the diffraction peak intensity of gehlenite is strong, while the diffraction peak intensity of wollastonite is

relatively weak, indicating that gehlenite is the main crystalline phase, while wollastonite is the secondary crystalline phase. With the increase in the Al_2O_3 content, the diffraction peak intensity of wollastonite phase gradually weakened, while the diffraction peak intensity of gehlenite phase gradually strengthened.

Table 5. Heat treatment parameters of the BG0–BG4 samples.

Samples	T_N (°C)	Time (min)	T_p (°C)	Time (min)	Glass Ceramics
BG0	771	60	852	60	GC0
	771	60	1001	60	GC1
BG1	781	60	875	60	GC2
	781	60	975	60	GC3
BG2	793	60	893	60	GC4
	793	60	987	60	GC5
BG3	794	60	920	60	GC6
	794	60	988	60	GC7
BG4	799	60	905	60	GC8
	799	60	991	60	GC9

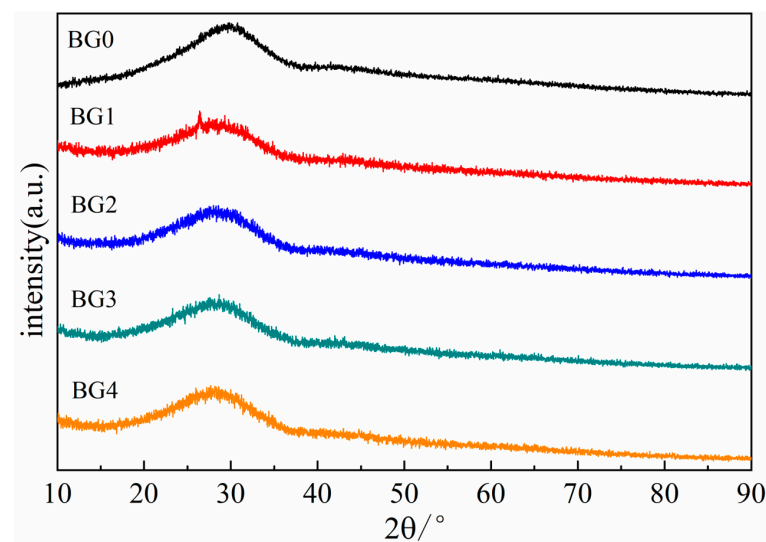


Figure 2. XRD patterns of the BG0–BG4 samples.

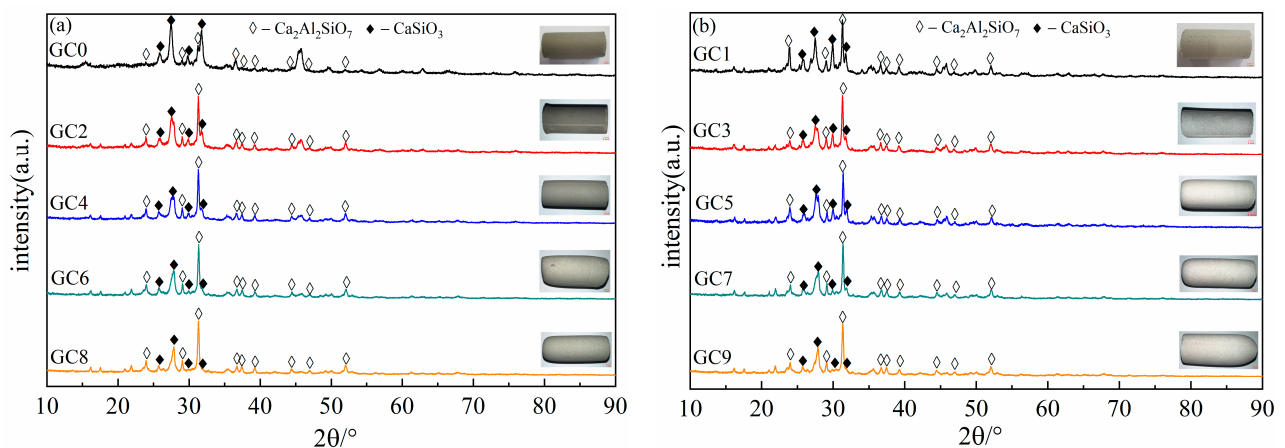


Figure 3. XRD patterns of the GC0–GC9 samples (a) T_{p1} (b) T_{p2} .

It can be explained that Al^{3+} directly participates in the formation of gehlenite, so an increase in Al_2O_3 content is beneficial for the precipitation of gehlenite. On the other hand, as a network intermediate, Al_2O_3 can replace Si^{4+} with $[\text{AlO}_4]$ to participate in the composition of glass networks and crystal phases and can also damage the network structure of glass in the form of $[\text{AlO}_6]$ [6,19]. With the increase in the Al_2O_3 content, Si^{4+} in the glass network structure decreased, and the increased $[\text{AlO}_6]$ damaged the glass network, reduced the degree of network polymerization, and is conducive to the precipitation of gehlenite with a lower anionic polymerization degree. On the other hand, the increase in Al_2O_3 content leads to more Al^{3+} replacing Si^{4+} in the network, which is also conducive to the formation of $[\text{Al}_2\text{SiO}_7]$ anion groups, thereby promoting the precipitation of gehlenite. Due to the large precipitation of gehlenite phase in glass ceramics, the silicon–oxygen content in the glass decreases, and the anionic groups forming the secondary crystalline phase decrease, resulting in a decrease in the wollastonite phase content. The results of XRD showed that the precipitation of gehlenite and wollastonite phase is in a competitive relationship, and the addition of alumina promotes the precipitation of gehlenite phase and hinders the precipitation of wollastonite phase. The chemical reaction equations for this process are as follows:



The effects of Al_2O_3 on the crystallization kinetics of glass ceramics were analyzed by the non-isothermal DSC method at different heating rates. The DSC curves of the BG0–BG4 samples at different heating rates are shown in Figure 4. The crystallization temperatures of the BG0–BG4 samples at different heating rates are listed in Table 6. It is clear that the T_{p1} and T_{p2} values increased with the increase in the heating rate, which is due to the later heating and melting for the glass system at a high heating rate, resulting in an increase in the temperature peak.

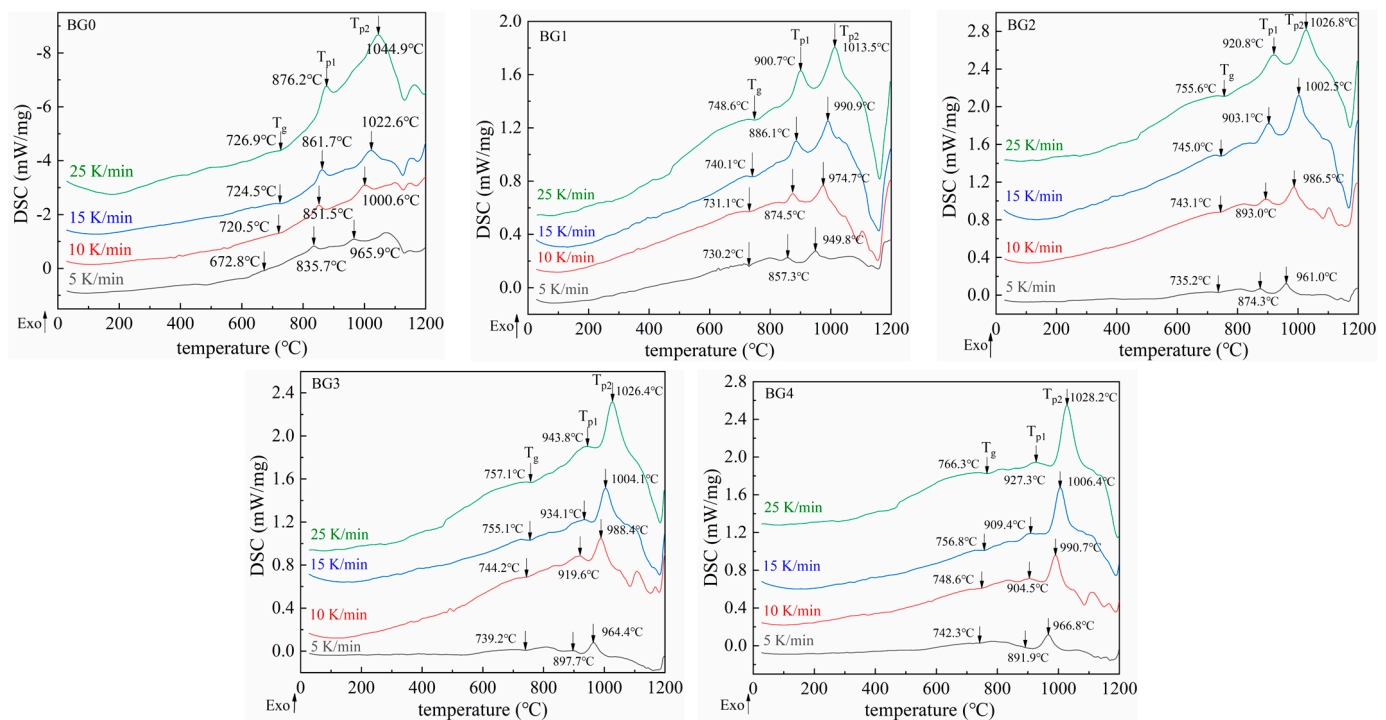


Figure 4. DSC curves of the BG0–BG4 samples at different heating rates.

Table 6. Crystallization temperatures of the BG0–BG4 samples at different heating rates.

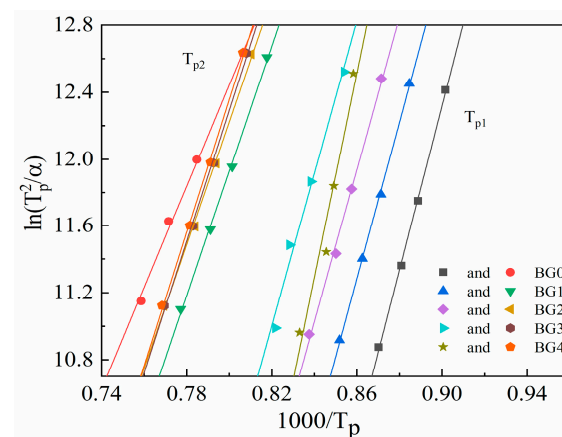
Samples	α (K/min)	T_{p1} (°C)	T_{p2} (°C)	Samples	α (K/min)	T_{p1} (°C)	T_{p2} (°C)
BG0	5	835.7	965.9	BG3	5	897.7	964.4
	10	851.5	1000.6		10	919.6	988.4
	15	861.7	1022.6		15	934.1	1004.1
	25	876.2	1044.9		25	943.8	1026.4
BG1	5	857.3	949.8	BG4	5	891.9	966.8
	10	874.5	974.7		10	904.5	990.7
	15	886.1	990.9		15	909.4	1006.4
	25	900.7	1013.5		25	927.3	1028.2
BG2	5	874.3	961.0	-	-	-	-
	10	893.0	986.5		-	-	-
	15	903.1	1002.5		-	-	-
	25	920.8	1026.8		-	-	-

The Kissinger equation [23] was applied to determine the crystallization activation energy and relevant parameters:

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{E_c}{RT_p} + \ln\left(\frac{E_c}{R\nu}\right) \quad (4)$$

where α is the heating rate, T_p is the crystallization peak temperature, R is the gas constant, ν is the frequency factor, and E_c represents the activation energy.

E_c can be obtained from the plot of $\ln(T_p^2/\alpha)$ vs. T_p^{-1} for glass ceramics crystallization, respectively, shown in Figure 5. The relevant parameters of the crystallization kinetic of the BG0–BG4 samples crystallized at T_{p1} and T_{p2} are listed in Table 6, respectively.

**Figure 5.** Plot of $\ln(T_p^2/\alpha)$ vs. T_p^{-1} for the BG0–BG4 samples.

In Table 7, the correction coefficients (r^2) of the fitting curves to calculate E_{c2} are close to 1, indicating good fitting linearity and reflecting the reliability of the calculated E_{c2} data. However, the r^2 values to calculate E_{c1} have a certain difference from 1, indicating a slightly poor fitting linearity. It is very likely that the calculation process of the Kissinger equation only involves the peak temperature of the crystallization exothermic peak and heating rate, and the angular coefficient, linear coefficient, and frequency factor of the curve were not considered. In Figure 3, the crystallization exothermic peak shape of T_{p1} is wide and not sharp, the angular relationship between peak shapes is unclear, and the linear relationship is poor, which indicates that the reliability of the calculated crystal activation energy is slightly poor.

Table 7. Crystallization kinetic parameters (E_c , r^2) of the GC0–GC9 samples.

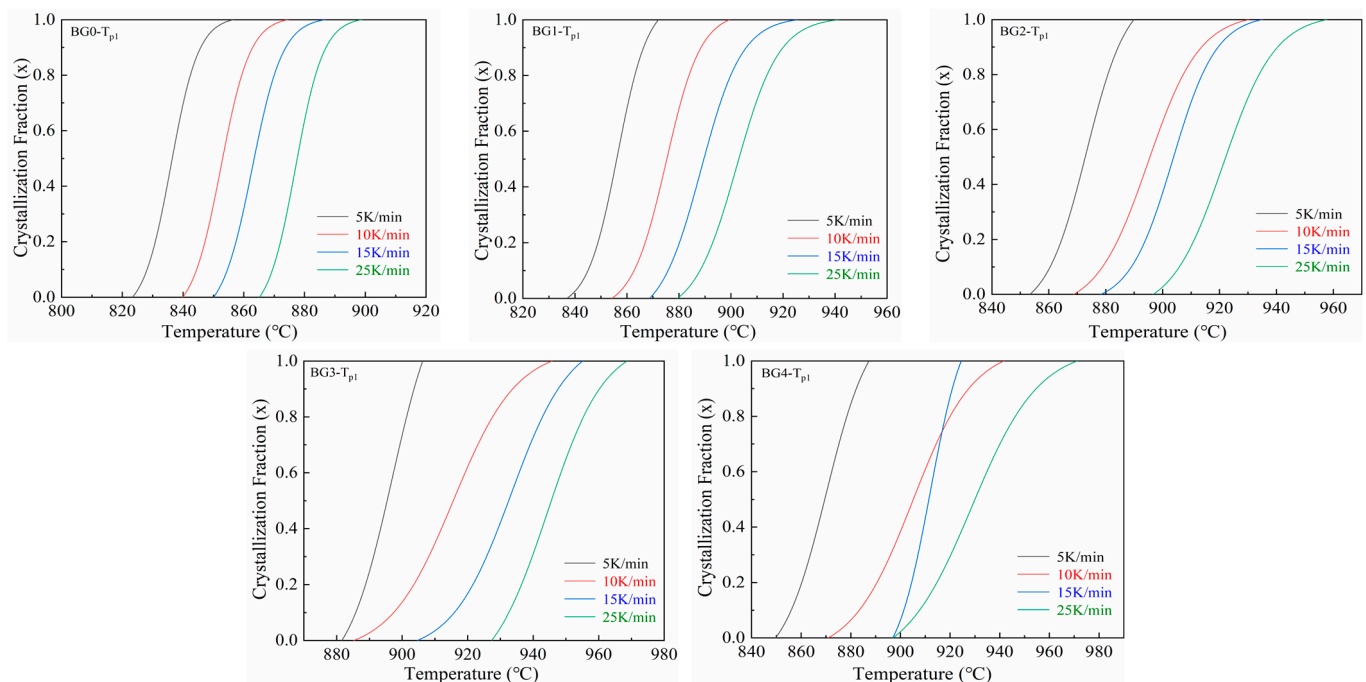
Samples	Slope	E_{c1} (kJ/mol)	r^2	Samples	Slope	E_{c2} (kJ/mol)	r^2
GC0	49.13	408	0.9983	GC1	30.30	252	0.9944
GC2	46.79	389	0.9987	GC3	37.29	310	0.9977
GC4	45.49	378	0.9941	GC5	36.85	306	0.9958
GC6	45.52	378	0.9753	GC7	39.27	326	0.9968
GC8	61.15	508	0.9341	GC9	39.79	331	0.9974

The Ozawa equation [24] can be also used to calculate the crystallization activation energy as follows:

$$\ln \alpha = \ln \left(\frac{K_0 E_c}{f(x)} \right) - 1.0516 \frac{E_c}{RT} - C_2 \quad \left(20 \leq \frac{E_c}{RT} \leq 60 \right) \quad (5)$$

where E_c is the crystallization activation energy, K_0 is the frequency factor, α is the heating rate, C_2 is a constant, T is the corresponding crystallization temperature when the crystallinity is x , and $f(x)$ is a function of crystallinity. When the crystallinity (x) is a constant, $f(x)$ is a constant.

To obtain the relationship between crystallinity (x) and temperature (T), it is necessary to deduct the substrate of the crystallization exothermic peak of T_{p1} and integrate for the crystallization exothermic peaks at different heating rates. As shown in Figure 6 and the Ozawa equation, the crystallinity temperatures were determined when the crystallinity was x ($x = 0.2, 0.3, \dots, 0.8$), and then linear fitting was operated for $\ln \alpha - 1000/T_i$, as shown in Figure 7. According to the slopes of the fitted straight lines in Figure 7, E_{c1} can be calculated, and the results are listed in Table 8.

**Figure 6.** Relationship between crystallinity and temperature of the BG0–BG4 samples at T_{p1} .

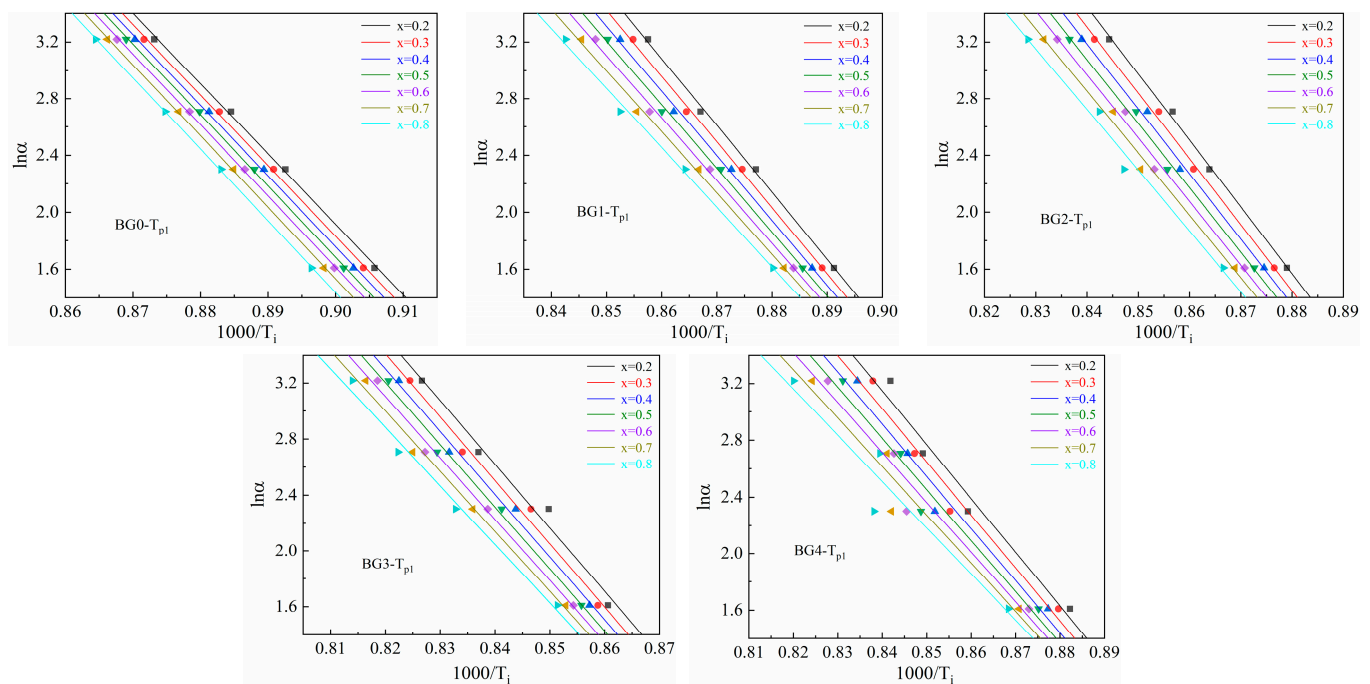


Figure 7. Plot of $\ln\alpha$ vs. $1000/T_i$ for the BG0–BG4 samples at T_{p1} .

Table 8. E_{c1} (kJ/mol) calculated by Ozawa method for BG0–BG4 samples.

$x (T_{p1})$	BG0		BG1		BG2		BG3		BG4	
	E_{c1}	$E_{c1}/(RT)$	E_{c1}	$E_{c1}/(RT)$	E_{c1}	$E_{c1}/(RT)$	E_{c1}	$E_{c1}/(RT)$	E_{c1}	$E_{c1}/(RT)$
0.2	392	40.98	426	45.66	431	45.52	426	44.15	448	47.61
0.3	393	41.13	420	44.93	427	45.03	426	43.99	445	47.05
0.4	394	41.21	414	44.21	423	44.50	423	43.58	440	46.46
0.5	396	41.43	409	43.54	419	43.95	419	43.18	435	45.73
0.6	396	41.44	402	42.78	415	43.42	433	44.54	427	44.88
0.7	397	41.57	394	41.85	407	42.56	407	41.80	418	43.84
0.8	398	41.67	385	40.75	399	41.62	398	40.73	406	42.38
Average	395		407		417		419		431	

As shown in Table 8, $E_{c1}/(RT)$ satisfies the condition of $20 \leq E_{c1}/(RT) \leq 60$, ensuring the reliability of data calculation using the Ozawa equation. Finally, the E_{c1} of the BG0–BG4 samples is 395, 407, 417, 419, and 431 kJ/mol, respectively, and the E_{c2} of the BG0–BG4 samples is 252, 310, 306, 326, and 331 kJ/mol, respectively. The results showed that as the Al_2O_3 content increased, E_{c1} increased, indicating that the addition of Al_2O_3 reduces the formation barrier of gehlenite and promotes its crystallization and increases the formation barrier of wollastonite and inhibits its crystallization (consistent with the analysis results in Figure 3a). However, during the crystallization process, the activation energy is positively correlated with the viscosity of the glassy phase, and the addition of Al_2O_3 increases the viscosity of the glassy phase, showing an increase in crystallization activation energy. Due to the precipitation of crystalline phases, the viscosity of the glass increased, hindering the further diffusion of ions and crystallization, resulting in the inhibition of the subsequent crystallization process, manifested as an increase in the E_{c2} values.

After obtaining E_{c1} and E_{c2} values, the crystallization index (n) could be calculated by applying the Augis–Bennett equation [25].

$$n = \frac{2.5RT_p^2}{\Delta T E_c} \quad (6)$$

where ΔT is the full width at half maximum of the exothermic peak, E_c is the crystallization activation energy, R is the gas constant, and T_p is the corresponding crystallization temperature.

If the n value is close to 1, this indicates the surface crystalline mechanism and one-dimensional growth in the crystallization process. If the n value is close to 2, that denotes the bulk crystalline mechanism and one-dimensional growth. If the n value is close to 3, that denotes the bulk crystalline mechanism and two-dimensional growth. If the n value is close to 4, that denotes the bulk crystalline mechanism and three-dimensional growth [26,27]. The Avrami parameters (n) for the crystal growth of the GC0–GC9 samples under various heating rates are shown in Table 9, respectively.

Table 9. Avrami parameters (n) for crystal growth of the GC0–GC9 samples under various heating rates, respectively.

Samples (T_{p1})	Method	Heating Rates ($^{\circ}\text{C}/\text{min}$)				Average
		5	10	15	25	
GC0	Ozawa	3.17	3.48	3.96	3.63	3.56 (≈ 4)
GC2	Ozawa	3.08	2.71	2.91	2.38	2.77 (≈ 3)
GC4	Ozawa	2.62	2.04	2.27	2.06	2.25 (≈ 2)
GC6	Ozawa	1.82	1.98	2.24	2.31	2.09 (≈ 2)
GC8	Ozawa	2.94	1.64	2.87	1.47	2.23 (≈ 2)
Samples (T_{p2})	Method	Heating rates ($^{\circ}\text{C}/\text{min}$)				Average
		5	10	15	25	
GC1	Kissinger	5.18	5.44	4.05	2.69	4.34 (≈ 4)
GC3	Kissinger	4.73	3.41	4.18	2.90	3.80 (≈ 4)
GC5	Kissinger	3.48	3.12	3.56	2.36	3.13 (≈ 3)
GC7	Kissinger	3.23	3.13	3.03	2.49	2.97 (≈ 3)
GC9	Kissinger	2.84	3.26	3.02	2.48	2.90 (≈ 3)

As shown in Table 9, the Al_2O_3 content has a significant impact on the crystallization process of glass ceramics. Among all the samples, the n values at T_{p1} are between 2 and 4, indicating that the crystalline growth mechanism is bulk nucleation, shifting from three-dimensional to one-dimensional and then to two-dimensional growth. Meanwhile, the n values at T_{p2} are between 3 and 4, indicating that the crystal growth mechanism is bulk nucleation, shifting from three-dimensional to two-dimensional growth.

3.2. Microstructure of Glass Ceramics

Figures 8 and 9 show the SEM images of the sintered glass ceramics at T_{p1} and T_{p2} , respectively. With the Al_2O_3 content increasing, the glass ceramics sintered at T_{p1} and T_{p2} have similar morphological changes. There are pores in the glass structure attributed to the transformation process of $[\text{AlO}_4]$ and $[\text{AlO}_6]$, making the glass structure loose, forming pores. The porosity of glass ceramics substantially increased, and the pores altered the sheet-like and spherical shape morphology, showing an irregularly interconnected network [28]. Spherical crystallites could be observed, while sheet-like crystallites were identified below 6% Al_2O_3 content. With the increase in the Al_2O_3 content, the number of sheet-like crystallites gradually decreased, while the number of spherical crystallites gradually increased. According to the phase analysis results for Figure 3, the sheet-like crystallites are assigned to the wollastonite phase, and the spherical crystallites are assigned to the gehlenite phase. The elemental compositions of the selected spots are listed in Table 10. For the sheet-like and spherical crystallites, with the Al_2O_3 content increasing, the

atomic ratio of Ca^{2+} to Al^{3+} gradually both decreased, indicating that the phase content of wollastonite decreased, while the phase content of gehlenite increased.

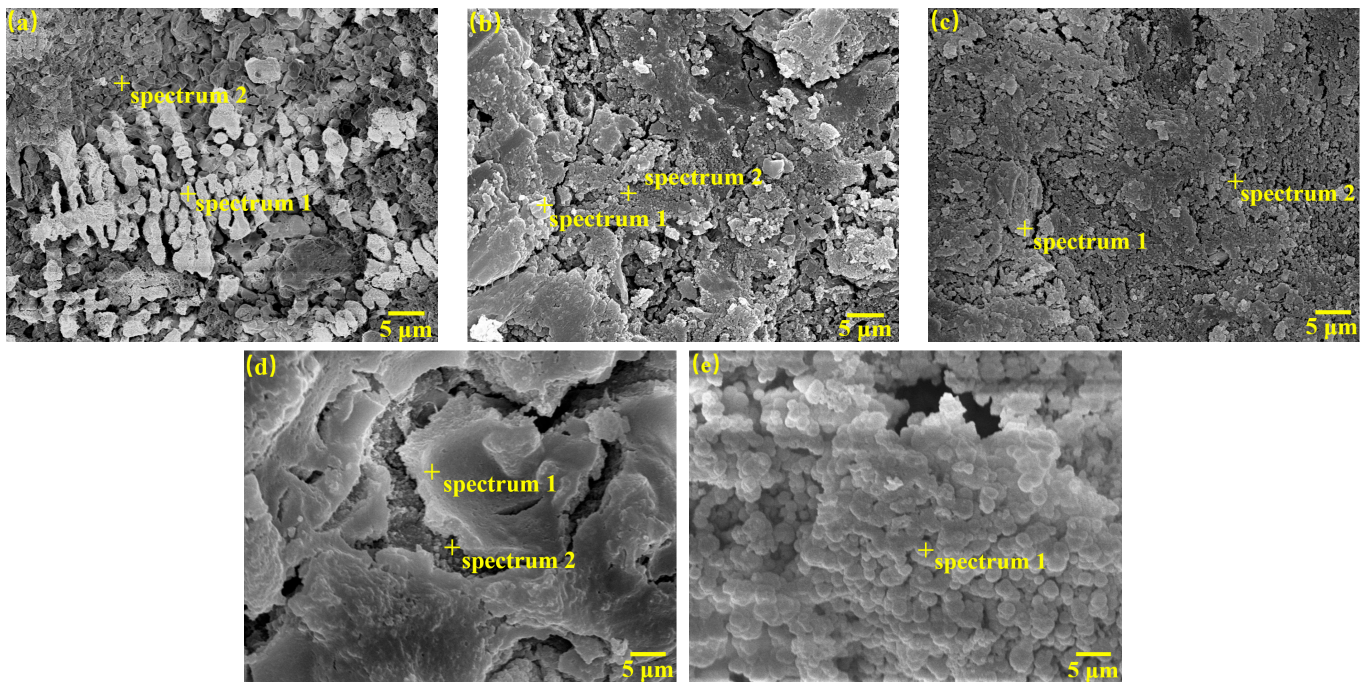


Figure 8. SEM images of glass ceramics at T_{p1} : (a) GC0; (b) GC2; (c) GC4; (d) GC6; (e) GC8.

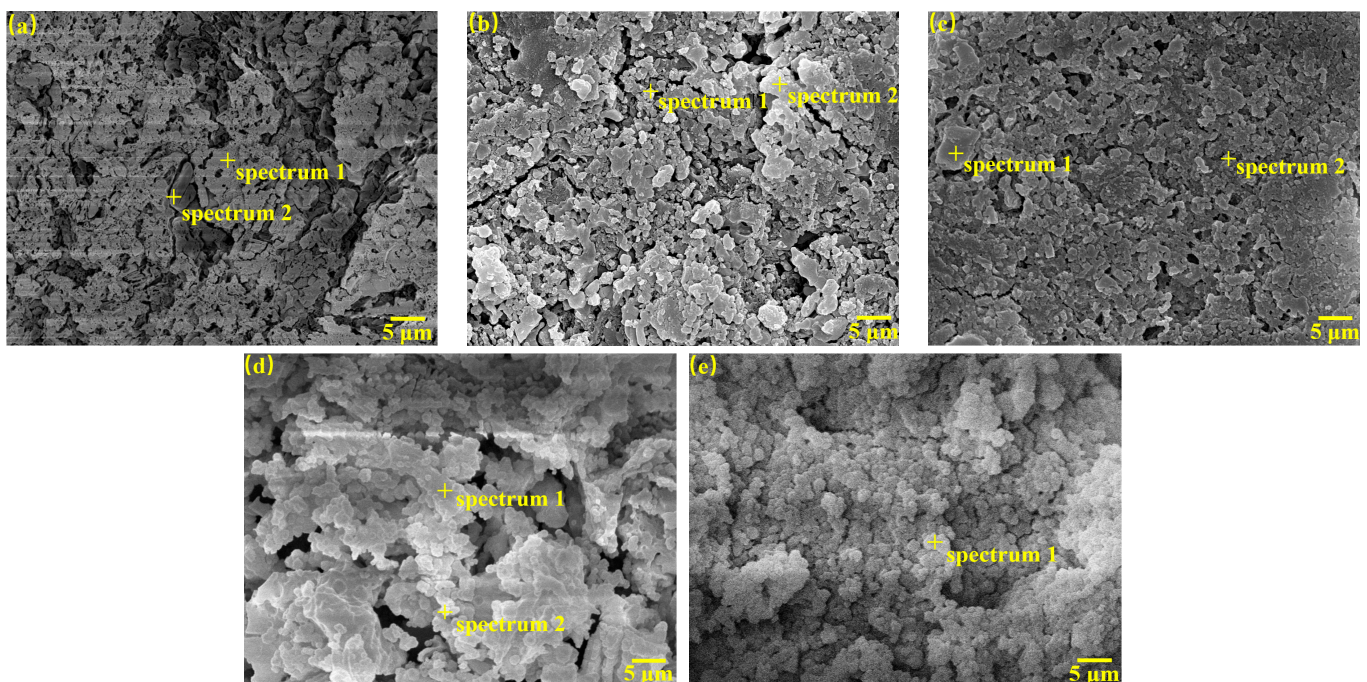
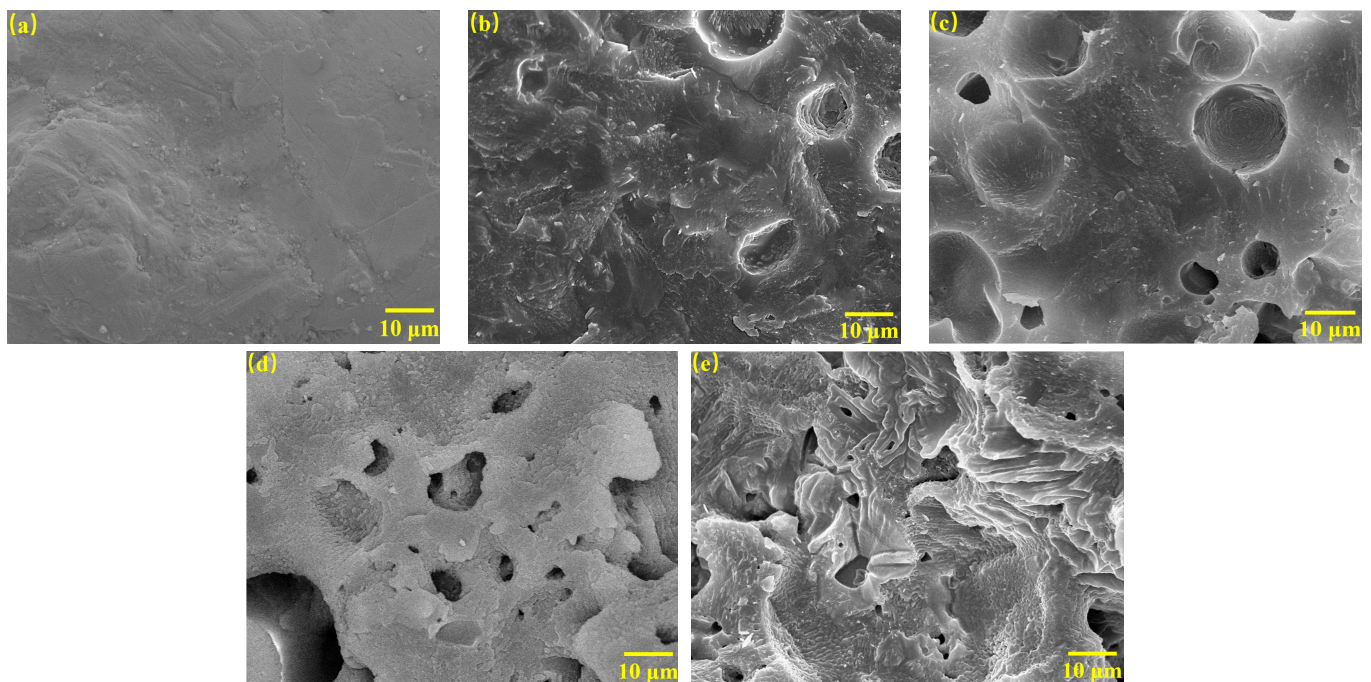


Figure 9. SEM images of glass ceramics at T_{p2} : (a) GC1; (b) GC3; (c) GC5; (d) GC7; (e) GC9.

Figures 10 and 11 show the SEM images of the cross-section of the GC0–GC9 samples. The wollastonite and gehlenite phase grew in an interwoven formation, and with the increase in the Al_2O_3 content, the wollastonite phase gradually decreased and even disappeared, while the gehlenite phase gradually increased. Moreover, the number of pores gradually increased, and the densification of the samples decreased.

Table 10. EDS results of elemental composition (at%) of different phases of the GC0-GC9 samples.

Sample	Spectrum	Phase Crystallite	O	Si	Ca	Al
GC0	1	sheet-like	15.80	1.64	58.81	23.76
	2	spherical	49.79	25.56	16.75	7.90
GC2	1	sheet-like	58.89	18.52	11.39	11.2
	2	spherical	57.00	20.66	12.06	10.28
GC4	1	sheet-like	57.87	19.25	10.94	11.94
	2	spherical	66.87	14.11	10.01	9.02
GC6	1	sheet-like	60.18	20.20	8.48	11.14
	2	spherical	58.09	15.05	13.03	13.82
GC8	1	sheet-like	-	-	-	-
	2	spherical	58.55	15.58	8.74	17.13
Sample	Spectrum	Phase	O	Si	Ca	Al
GC1	1	sheet-like	24.42	14.27	42.50	18.79
	2	spherical	38.83	24.25	20.88	16.08
GC3	1	sheet-like	54.65	21.01	13.49	10.86
	2	spherical	38.43	22.07	24.56	14.94
GC5	1	sheet-like	60.09	12.43	17.26	10.21
	2	spherical	47.12	12.28	23.49	17.11
GC7	1	sheet-like	66.80	31.85	11.04	23.70
	2	spherical	52.75	22.67	8.69	15.89
GC9	1	sheet-like	-	-	-	-
	2	spherical	52.17	18.01	12.64	17.19

**Figure 10.** SEM images of the cross-section of glass ceramics at T_{p1} : (a) GC0; (b) GC2; (c) GC4; (d) GC6; (e) GC8.

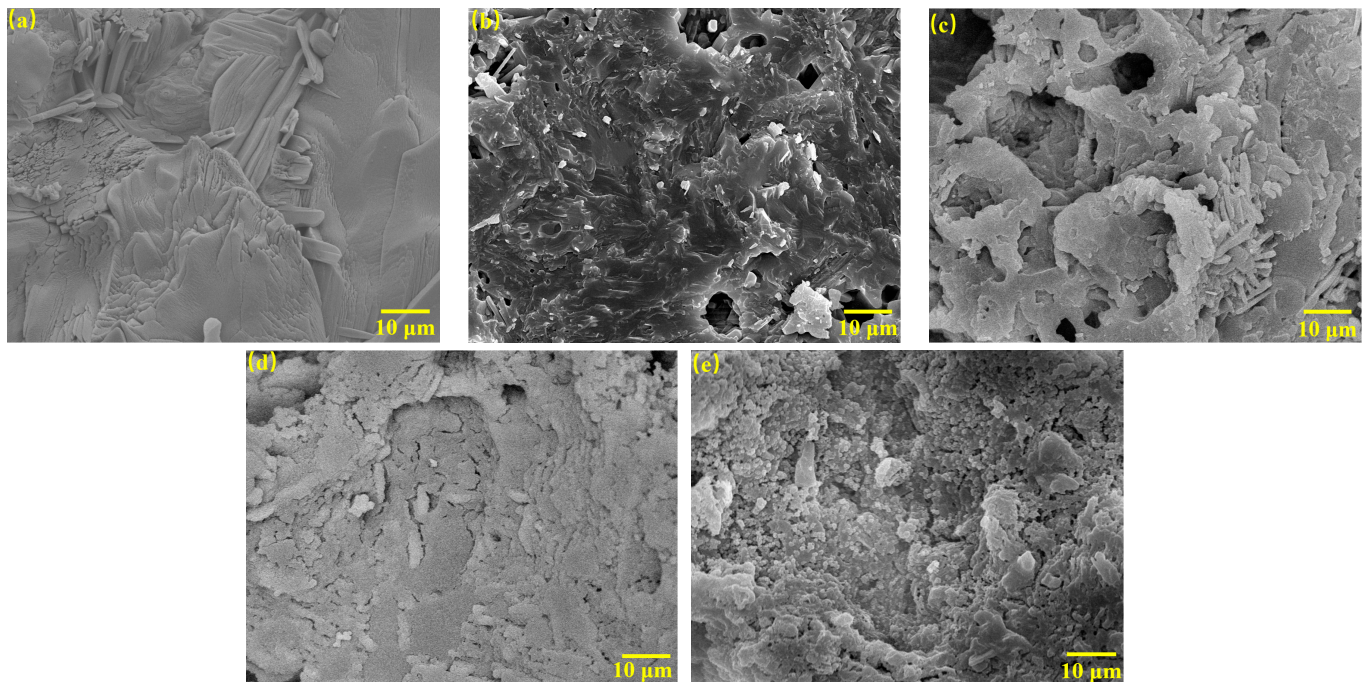


Figure 11. SEM images of the cross-section of glass ceramics at T_{p2} : (a) GC1; (b) GC3; (c) GC5; (d) GC7; (e) GC9.

3.3. Physical and Mechanical Properties of Glass Ceramics

As shown in Figure 12a, the bulk density of the GC0-GC9 samples took on a downward trend as the Al_2O_3 content increased. It can be explained that the pores were formed during the phase transition, resulting in a decrease in densification. Figure 12b shows the relationship between the bending strength of sintered glass ceramics and the Al_2O_3 content. The initial increase in the mechanical strength was followed by a severe decrease as the Al_2O_3 content increased. The maximum measured strength is 75.1 MPa, a value significantly higher than that of traditional porcelain [29]. The bending strength of glass ceramics is related to crystallinity. Generally speaking, the bending strength of the crystal is greater than that of the glass phase, so when subjected to external forces, microcracks will expand along the glass phase, ultimately leading to the destruction of the sample, and the increase in the degree of crystallinity will make the content of the glass phase decrease, so the higher the crystallinity of the crystal phase, the greater the bending strength of the microcrystalline glass; in addition, the bending strength of microcrystalline glass is also related to the microstructure (mainly pore), and the increase in the pore number will make the effective support sites inside the glass reduce, and the bending resistance becomes worse. From the XRD analyses reported above, during the sintering process, the formation of wollastonite and gehlenite crystals led to an increase in crystallinity. Consequently, the bending strength was enhanced, although the porosity slightly increased [23]. However, with the further increase in the Al_2O_3 content, the porosity increased to a larger extent, causing a strength reduction in the sintered glass ceramics.

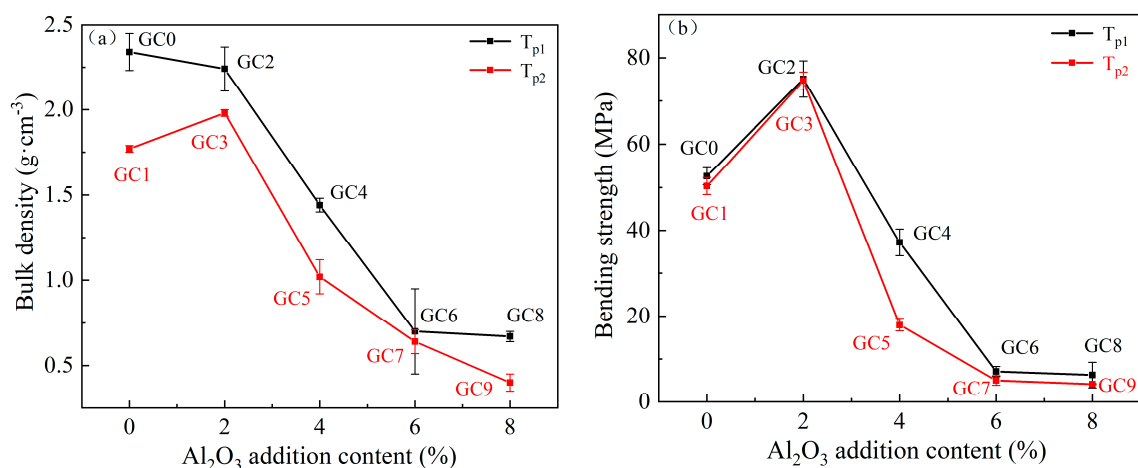


Figure 12. (a) Bulk density and (b) bending strength of the GC0–GC9 samples.

4. Conclusions

Glass ceramics were prepared based on lead fuming furnace-slag. The influence of Al_2O_3 content on the crystallization mechanism from a dynamic perspective was investigated. In addition, the relationship between the structure and properties of glass ceramics was studied. The main conclusions are summarized as follows:

The main crystalline phase of glass ceramics based on LFFS is gehlenite, and the secondary crystalline phase is wollastonite. Also, the amounts of the spherical gehlenite phase increased with the Al_2O_3 content, confirming the active role of Al_2O_3 during the formation of gehlenite crystallization.

The crystallization kinetic analyses showed that the crystallization activation energy increased with the Al_2O_3 content. The crystal growth mechanism is bulk nucleation, shifting from three-dimensional growth to two-dimensional growth.

The bulk density of the glass ceramics decreased with the increase in the Al_2O_3 content. The increase in crystallinity and the interwoven growth of wollastonite and gehlenite phase improved the bending strength. However, with the Al_2O_3 content increasing, mechanical weakness appeared owing to an increase in the number of pores.

When the addition of Al_2O_3 was 2%, the glass ceramics prepared under the conditions of nucleation at 781°C for 60 min and crystallization at 875°C for 60 min had the best overall performance, with a bulk density of $2.24\text{ g}\cdot\text{cm}^{-3}$ and a flexural strength of 75.06 MPa. The residue utilization rate was 97.7%. The glass ceramics prepared have high strength and low bulk density, holding promise for potential applications in lightweight construction tiles.

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