

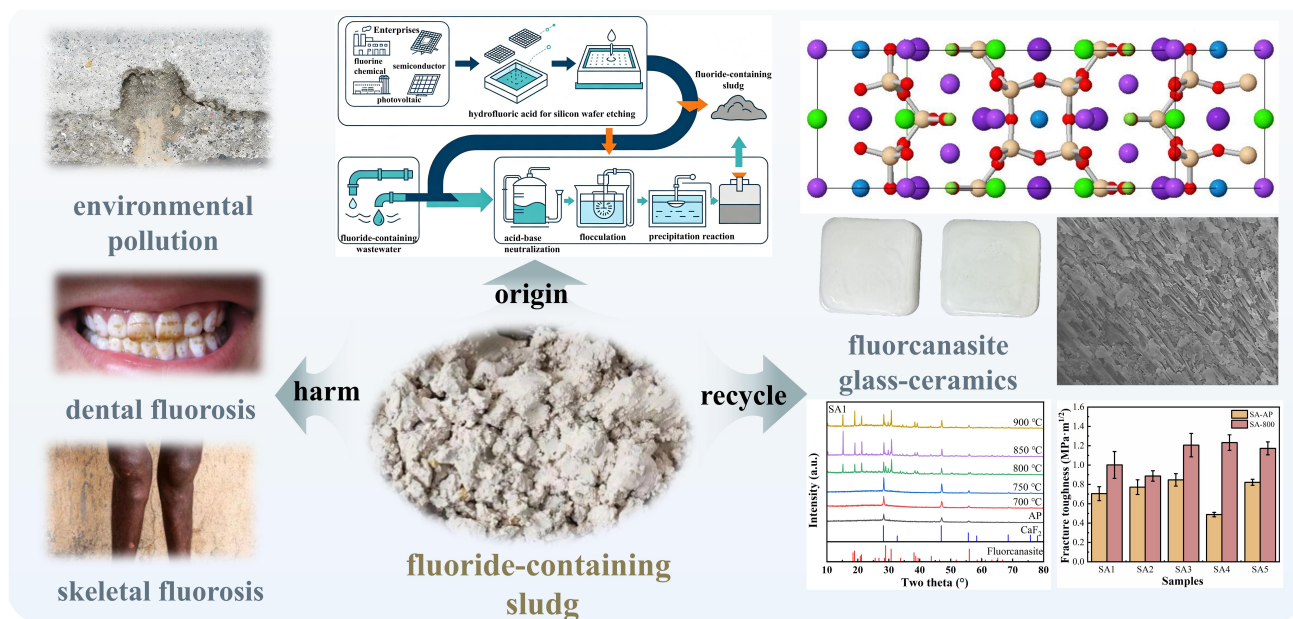
Original Research Report

Effect of Al_2O_3 substitution for SiO_2 on fluorosilicate glass-ceramics fabricated from fluoride-containing sludge

Cairu Peng¹, Jinmiao Chen¹, Zheng Liu¹, Zhiyong Zhao^{1, 2, 3, *}, Feng He^{1, 2, 3}, Yingliang Tian^{1, 2, 3, *}¹ School of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China² College of Carbon Neutrality Future Technology, Beijing University of Technology, Beijing 100124, China³ National Engineering Research Center of FPD Glass Technology, Xianyang 71200, China

* Corresponding Authors: Z. Zhao (zhaozhiyong@bjut.edu.cn), Y. Tian (tianyl@bjut.edu.cn)

Graphical abstract



Citation: C. Peng, J. Chen, Z. Liu, Z. Zhao, F. He, Y. Tian. Effect of Al_2O_3 substitution for SiO_2 on fluorosilicate glass-ceramics fabricated from fluoride-containing sludge. *Materials Reports: Solidwaste and Ecomaterials*, 2026, 2: 9520038. <https://doi.org/10.26599/MRSE.2026.9520038>.

Received 22 July 2026; Received in revised form 11 September 2026; Accepted 23 September 2026

Abstract: The safe disposal and resource utilization of industrial fluoride-containing sludge represent a critical environmental challenge. In this study, high-performance fluorcanasite glass-ceramics were successfully synthesized from industrial sludge via a melt-quenching followed by heat treatment method. The effects of equimolar substitution of Al_2O_3 for SiO_2 on the phase composition on the glass network structure, crystallization behavior, mechanical properties, and fluoride leaching were systematically investigated. Structural analyses revealed that lower Al_2O_3 content (1-1.5 mol%) favored the formation of layered Q^3 units, promoting the precipitation of an interlocking lath-like fluorcanasite main phase at 800 °C. Conversely, higher Al_2O_3 substitution (>2 mol%) induced the precipitation of xonotlite. The optimized fluorcanasite glass-ceramic (1 mol% Al_2O_3) exhibited exceptional mechanical performance, achieving a maximum flexural strength of 296.71 ± 22.18 MPa, an elastic modulus of 75.33 ± 0.03 GPa, and a fracture toughness of 1.00 ± 0.14 $\text{MPa}\cdot\text{m}^{1/2}$. Furthermore, the fluorcanasite crystalline phase effectively immobilizes F^- ions, and its layered structure enhances chemical durability. This work provides a promising method for the resource utilization of fluoride-containing sludge.

Key words: glass-ceramics; fluoride-containing sludge; glass solidification; fluorcanasite; $\text{Al}_2\text{O}_3/\text{SiO}_2$

1. Introduction

In recent years, the rapid development of new energy and information technology sectors has led to an increasing number of fluorine chemical, semiconductor, and photovoltaic enterprises. These enterprises commonly use hydrofluoric acid for silicon wafer etching, generating large amounts of fluoride-containing wastewater. After conventional acid-base neutralization and flocculation, the wastewater forms fluoride-containing sludge, primarily composed of CaF_2 , SiO_2 , CaCO_3 and CaSO_4 [1, 2]. If not properly disposed, fluoride ions (F^-) from the sludge can contaminate water resources and soil through rainwater leaching and surface runoff. Excessive fluoride accumulation in the human body can lead to health problems such as dental fluorosis and skeletal fluorosis [3]. Therefore, the proper disposal of fluoride-containing sludge is crucial for protecting the ecological environment and human health.

Common disposal methods for fluoride-containing sludge include landfilling, stockpiling, and utilization as building materials. Landfilling and stockpiling carry the risk of F^- ions leaching, therefore are unsuitable for large-scale sludge disposal. For building material utilization, cement solidification suffers from limited solidification capacity, low efficiency, and poor chemical stability, which restrict its practical application [4]. Hence, it is urgent to develop a treatment approach that can efficiently immobilize F^- ions, reduce solid waste volume, and minimize environmental pollution. Vitrification is a high-temperature solid waste treatment technique that converts waste into a stable vitreous matrix through melting followed by rapid cooling. This method offers advantages such as high immobilization

efficiency, high sludge utilization rate, and significant volume reduction [5]. Fan et al. [6] used waste glass and fluoride-containing sludge from the TFT-LCD industry as raw materials to prepare porous glass-ceramics with anorthite, diopside, and cordierite as the main crystalline phases, verifying the feasibility of fabricating porous glass-ceramics from fluoride-containing sludge and waste glass. Zhao et al. [7] prepared diopside-based glass-ceramics via a one-step method using municipal solid waste incineration (MSWI) fly ash, sludge, and waste glass; the resulting material exhibited a Vickers hardness of 13.11 GPa, a flexural strength of 135.84 MPa, and acid and alkali resistance of 98.65% and 99.88%, respectively, meeting industrial requirements.

The fluorcanasite glass-ceramics (compositionally based on $(\text{K,Na})_6\text{Ca}_5\text{Si}_{12}\text{O}_{30}(\text{OH,F})_4$) offer distinct advantages for fluorine immobilization. Theoretically, this unique crystal structure can stably capture F^- ions through strong chemical bonding and direct incorporation into the crystal lattice, thereby fundamentally inhibiting fluoride leaching [8-12]. The crystals display a lath-like morphology and are interlocked within the glass matrix, which effectively disperses stress, reduces stress concentration, and increases the energy required for crack propagation, resulting in a flexural strength of up to 300 MPa and a fracture toughness of $5.0 \text{ MPa}\cdot\text{m}^{1/2}$ [13-17]. This combination of chemical stability and mechanical strength makes fluorcanasite glass-ceramics an ideal candidate for the high-value recycling of fluoride sludge. However, most existing studies on fluorcanasite glass ceramics have employed chemically pure raw materials and focused primarily on biomedical materials (e.g., dental and orthopedic restorative materials), whereas investigations using industrial fluoride-containing sludge with complex compositions as a raw material have been rarely reported.

In silicate glass systems, SiO_2 acts as the main network former, while Al_2O_3 can enter the network as $[\text{AlO}_4]$ tetrahedra substituting for Si^{4+} or exist in octahedral coordination, thereby altering network connectivity and charge balance [18,19]. For fluorcanasite crystallization, the partial substitution of Si^{4+} by Al^{3+} is expected to directly modify the coordination environment of F^- ions and the nucleation and growth behavior of fluorcanasite crystals. This provides a critical entry point for optimizing the performance of fluorcanasite glass ceramics derived from fluoride-containing sludge. However, this $\text{Al}_2\text{O}_3/\text{SiO}_2$ substitution strategy has not been systematically investigated in such systems.

In this work, fluorcanasite glass ceramics were prepared by a conventional melt-quenching method followed by heat treatment. The effects of Al_2O_3 substitution for SiO_2 on the crystallization, microstructure, physicochemical properties and fluoride leaching performance were investigated. This study provides a theoretical basis and a practical strategy for the compositional design and high-value environmental application of sludge-derived fluorcanasite glass-ceramics.

2. Materials and methods

2.1. Specimen preparation

The chemical composition of the glass is presented in Table 1. A series of specimens were prepared by the conventional melt-quenching method. To investigate the effect of partially substituting Al_2O_3 for SiO_2 on the crystallization, microstructure, and physicochemical properties of fluorcanasite glass ceramics, the SiO_2 content in the batch was gradually reduced from 59 mol% to 57 mol%, while the Al_2O_3 content was increased from 1 mol% to 3 mol%. The corresponding specimens were designated as SA1 to SA5. The fluoride-containing sludge was obtained from a glass thinning enterprise and subjected to drying, grinding, and mixing pretreatment before its chemical composition was analyzed, the results are given in Table 2. In addition, all CaF_2 sourced from fluoride-containing sludge, SiO_2 and Na_2O were introduced from silica sand and soda ash, Al_2O_3 and K_2O from potash feldspar, and CaO from limestone. The actual weighed masses of each raw material when the total batch mass was 70 g in Table S1.

Table 1. Chemical composition of glass (mol%).

Specimen	Chemical composition					
	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	CaF_2
SA1	59	1	10	5	10	15
SA2	58.5	1.5	10	5	10	15
SA3	58	2	10	5	10	15
SA4	57.5	2.5	10	5	10	15
SA5	57	3	10	5	10	15

Table 2. Chemical composition of fluorine-containing sludge.

Chemical composition	mass fraction/wt%
CaF_2	49.27
CaCO_3	28.75
SiO_2	10.06
Al_2O_3	4.25
CaSO_4	3.52
MgO	1.64
BaO	0.63
CeO_2	0.44
Na_2O	0.28
B_2O_3	0.25
SrO	0.21
La_2O_3	0.20
P_2O_5	0.19
Fe_2O_3	0.10
K_2O	0.02
Others	0.19
Total	100

Powder raw materials with a total mass of 70 g were weighed and mixed by ball milling for 10 h. To suppress fluorine volatilization at high temperatures, the mixture was placed in an alumina crucible, covered with a lid, and melted at 1250 °C in air for 1 h. The homogeneous glass melt was poured into a graphite mold to obtain the as-prepared specimen (SA-AP), which was then immediately transferred to an annealing furnace and held at 500 °C for 3 h to relieve internal stresses. XRF analysis was performed on the SA-AP specimens, and the results are presented in Table S2. The fluorine volatilization rate was calculated to be in the range of 31.03%-40.44 wt%. Based on the differential scanning calorimetry (DSC) results of the SA-AP specimens, a crystallization heat treatment schedule was established: to eliminate internal stress from quenching and avoid premature nucleation, the samples were heated to 500 °C at a rate of 10 °C/min. Then, to ensure uniform sample temperature and prevent excessive grain coarsening, the samples were heated to 700-950 °C at 5 °C/min and held for 1 h. After natural cooling to room temperature, the prepared glass ceramics were cut and polished for subsequent tests.

2.2. Characterization

The thermal properties of the specimens were analyzed using a differential scanning calorimeter (DSC, STA 449 F5 Jupiter, NETZSCH, Germany). X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (XRD, SmartLab 3, Rigaku, Japan). The microstructure was examined by a field-emission scanning electron microscope (FE-STEM, SU9000, Hitachi, Japan); specimens for SEM characterization were polished and subsequently etched with 10 wt% HF for 20-40 s. Raman spectra were acquired in the range of 50-1600 cm⁻¹ using a Raman spectrometer (RMS 1000, Edinburgh Instruments, UK).

The Vickers hardness of the specimens was measured with a digital Vickers hardness tester (DHV-1000Z, China), and the average of 15 measurements was taken. The elastic modulus was determined by a three-point bending method using an electronic universal testing machine (CMT5105, China) on specimens with dimensions of 40 mm × 4 mm × 3 mm, in accordance with GB/T 22315-2008, and the average of 3 measurements was taken. Fracture toughness was evaluated according to GB/T 37900-2019 by creating indentations that generated microcracks using a micro-Vickers hardness tester (DHV-1000Z, China), and the average of 10 measurements was taken. The indentation fracture toughness (IFR) of the specimens was calculated using Equation:

$$IFR=0.026[E \cdot \frac{F}{(2c_1+2c_2)/4}]^{\frac{1}{2}} \cdot \frac{d_1+d_2}{2c_1+2c_2}$$

where IFR is the indentation fracture toughness (MPa·m^{1/2}), F is the applied test load (N), E is the elastic modulus of the specimen (GPa), d₁ and d₂ are the lengths of the two diagonals of the indentation (mm), and 2c₁ and 2c₂ are the total crack lengths extending along the directions of the indentation diagonals (mm).

Flexural strength was measured by a four-point bending method on specimens of 3 mm × 4 mm × 40 mm using an electronic universal testing machine (QJ211S–10kN, China), in accordance with GB/T 6569-2006, and the average of 8 measurements was taken.

The chemical durability of the specimens was tested according to GB/T 32644-2016 by immersing them in 5 wt% HCl solution at 95 °C for 24 h and in 5 wt% NaOH solution at 95 °C for 6 h, respectively. The specimens were polished to dimensions of 50 mm × 25 mm × 1 mm and tested using a thermostatic water bath oscillator (SHA-C, China).

According to the Chinese standard HJ 557-2010, fluoride ions leaching analysis were performed. Specimens were broken into particles and passed through a 3 mm sieve, and then oscillated for 8 h at room temperature with a water bath oscillator (SHA-C, China) at 110 times/min. The leachate was analyzed using an ion chromatography (ICS-5000+, Thermo Fisher Scientific Aqueous on RFIC).

3. Results and discussion

3.1. DSC analysis

Fig.1 shows the DSC curves of the SA-AP specimen. As the Al₂O₃ content increases from 1 mol% to 3 mol%, both the glass transition temperature (T_g) and the first crystallization peak temperature (T_{p1}) initially decrease and then increase, whereas T_{p2} exhibits an overall upward trend. At low Al₂O₃ contents, Al³⁺ usually enters the glass network as [AlO₄] tetrahedra [20,21]. Because the Al-O bond energy is lower than that of Si-O, the thermal stability of the network is inferred to decrease, leading to a reduction in T_g . The corresponding local structural loosening may lower nucleation energy barrier, causing T_{p1} to shift to lower temperatures. With a further increase in Al₂O₃ content, the increasing concentration of [AlO₄] units in the structure rises, accompanied by the precipitation of a large amount of CaF₂, around which a high-viscosity, SiO₂-rich diffusion barrier layer formed. This may increase the resistance to nucleation and crystal growth and consequently shifts T_g and T_{p1} to higher temperatures [22, 23]. It should be noted that the above interpretation of the variations in T_g and T_{p1} is a reasonable inference based on the Raman results and literatures, rather than a direct experimental confirmation. The continuous increase in T_{p2} is related to a change in the primary crystalline phase. As revealed by XRD patterns, a high-melting-point xonotlite phase gradually precipitates, causing the second crystallization peak to shift to higher temperatures.

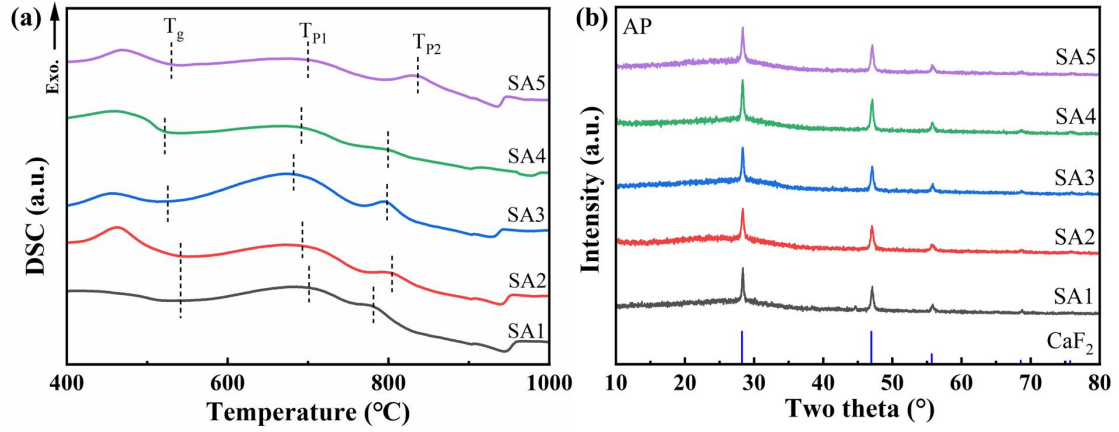


Fig. 1. (a) DSC curves and (b) XRD patterns of the SA-AP specimens.

3.2. Phase and microstructure

Fig. 2 presents the XRD patterns of the SA series specimens before and after heat treatment. The all SA-AP specimens precipitated CaF_2 (JCPDS No.87-0971). Based on the Scherrer formula, the average crystallite sizes of CaF_2 were calculated to be 31.5 nm, 20.0 nm, 28.9 nm, 26.8 nm, and 24.2 nm for SA1-AP to SA5-AP, respectively. After heat treatment at 800 °C, the crystallinity of SA1-SA5 specimens was 37.08%, 38.64%, 15.65%, 25.50%, and 14.88%, respectively. The main crystalline phase in specimens SA1 and SA2 was fluorcanasite (JCPDS No.45-1398), with CaF_2 as a minor phase. In specimens SA3 to SA5, the characteristic diffraction peak of fluorcanasite ($2\theta \approx 31^\circ$) disappeared and was replaced by the xonotlite phase (JCPDS No.72-2396) as the main crystalline phase.

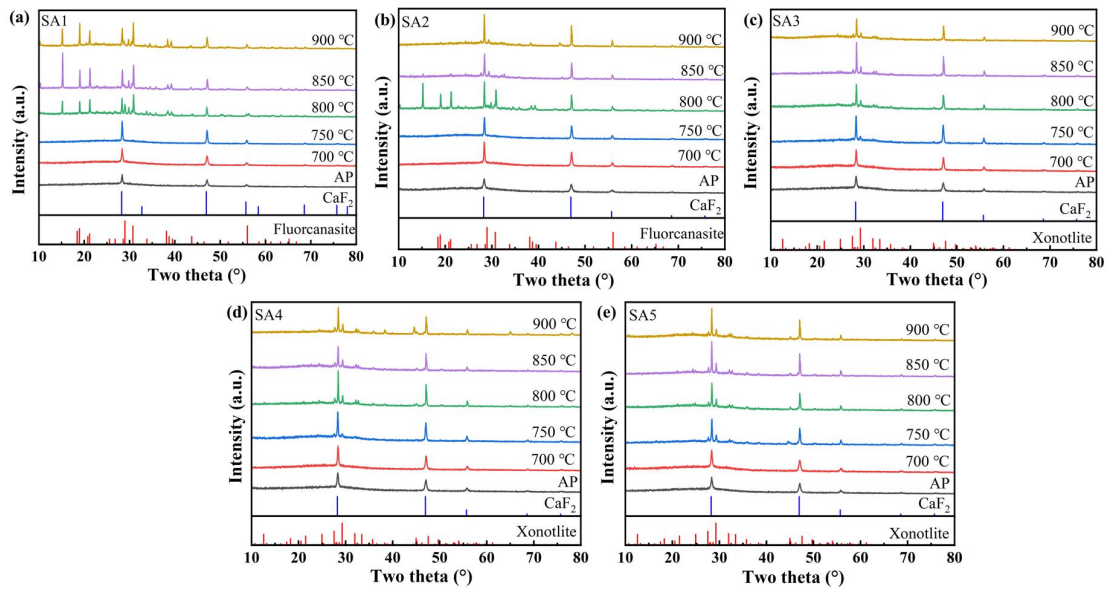


Fig. 2. XRD patterns of SA specimens before and after heat treatment.

Fig. 3 displays the Raman spectra of the SA-AP specimens. The characteristic peak in the range of 320-350 cm^{-1} can be attributed to the Ca-F bonds ^[24]. The region from 500 to 850 cm^{-1} corresponds to symmetric stretching vibrations of Si-O-Si or Si-O-Al bonds, along with stretching vibrations of Al-O bonds in $[\text{AlO}_4]$ tetrahedral units. The band at 850-1250 cm^{-1} is assigned to the antisymmetric stretching vibrations of Si-O bonds in $[\text{SiO}_4]$ tetrahedra ^[25,26]. The high-frequency region was deconvoluted by Gaussian fitting (Fig.3c), where Q^1 represents symmetric stretching of $[\text{Si}_2\text{O}_7]^{6-}$, Q^2 symmetric stretching of $[\text{Si}_2\text{O}_6]^{4-}$, Q^3 primarily symmetric stretching of $[\text{Si}_2\text{O}_5]^{2-}$, and Q^4 antisymmetric stretching of SiO_2 ^[17]. The distribution of Q^n structural units is presented in Fig.3b. The network polymerization of the AP specimens is dominated by Q^2 and Q^3 units, indicating that the glass network is mainly composed of chain or ring metasilicate structural units (Q^2) and layered disilicate structural units (Q^3). With increasing Al_2O_3 content, the Q^2 fraction shows an overall upward trend, whereas the Q^3 fraction declines. This reflects changes in vibrational coupling caused by the incorporation of $[\text{AlO}_4]$ units ^[27]. The formation of $[\text{AlO}_4]$ requires charge compensation by alkali metal ions, which induces a redistribution of the network structure and consequently promotes the partial conversion of Q^3 to Q^2 . Fluorcanasite is a layered silicate. Specimens SA1 and SA2 possess the highest proportion of Q^3 units, which facilitated the precipitation of fluorcanasite as the main crystalline phase during heat treatment at 800 °C. With a further increase in Al_2O_3 content, the layered Q^3 units continuously diminish, and the abundant chain-like Q^2 units together with short-range Ca-F bonding make the precipitation of chain-structured xonotlite more favorable.

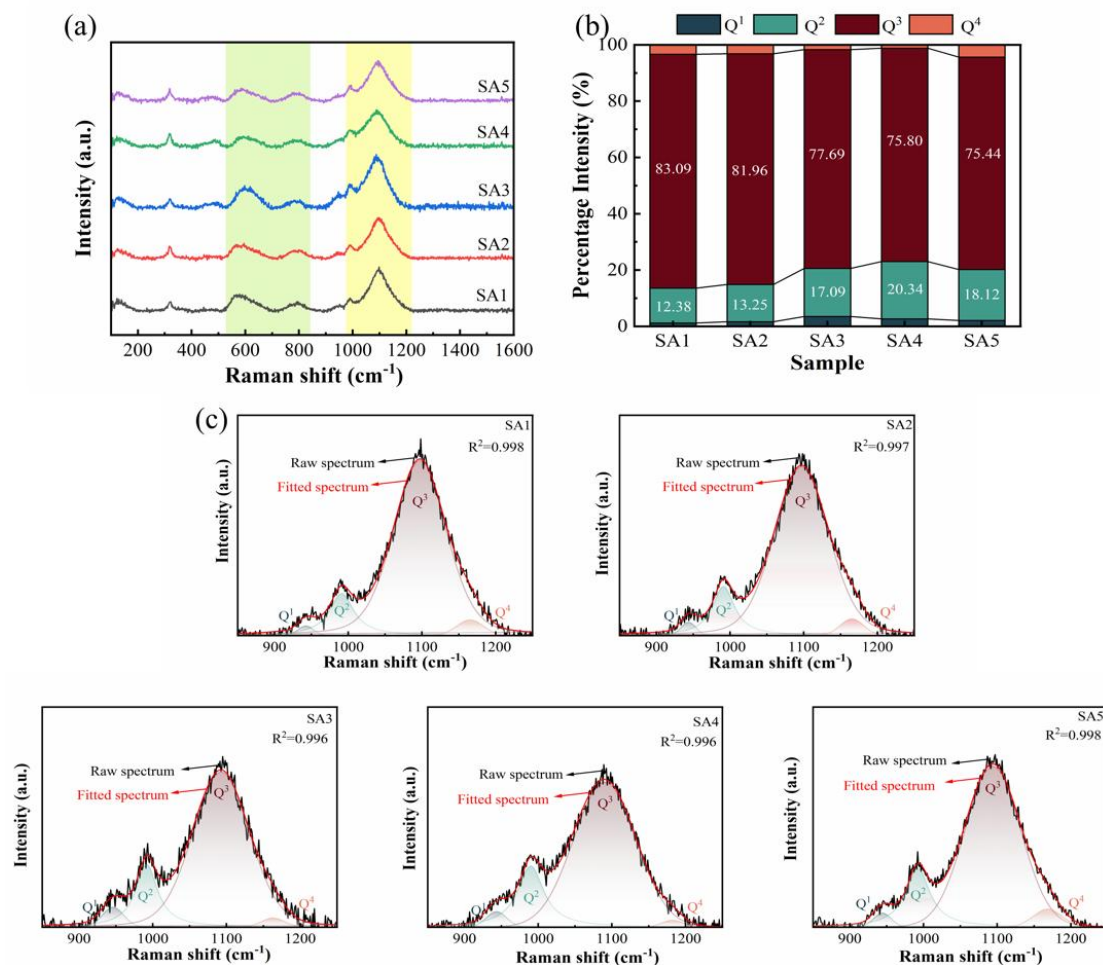


Fig. 3. (a) Raman spectra, (b) Proportion of Q^n structural units, and (c) peak division in the range of 850-1250 cm^{-1} .

The SEM images are shown in Fig. 4. Spherical particles formed in the SA-AP specimens, and the size exhibited a trend of first decreasing and then increasing with increasing Al_2O_3 content. Particle size distribution analysis was performed on 50 randomly selected spherical particles in the SEM images (Fig. S1). The average diameters of the spherical particles in specimens SA1-AP to SA5-AP were determined to be 181 ± 5 nm, 133 ± 2 nm, 67 ± 2 nm, 485 ± 9 nm, and 246 ± 48 nm, respectively. These values are far larger than the crystallite sizes calculated from XRD results. The TEM results (Fig. S2) show the presence of spherical agglomerated regions in the sample. Fig. S3 indicates that these regions are significantly enriched in Ca and F, whereas the contents of Si, Al, and O are relatively low and are mainly present in the residual glass phase. In the high-resolution TEM image (Fig. R3(e)), lattice fringes of nanocrystals can be clearly observed, and the calculated interplanar spacing is 0.236 nm, corresponding to the (220) plane of calcium fluoride (CaF_2) (JCPDS card no. 77-2093), which is consistent with the XRD results. These results confirm that the opacification of glass is caused by the generation of phase separation droplets which rich in calcium and fluorine, and the CaF_2 nanocrystals are precipitated inside the separated phases. Our previous research has also

confirmed this conclusion [28]. After heat treatment at 800 °C, specimens SA1-800 and SA2-800 exhibited an interlocking lath-like morphology, which is characteristic of fluorcanasite. In specimens SA3-800 to SA5-800, needle-like crystals appeared, corresponding to the xonotlite phase, which is a chain silicate that grows one-dimensionally along the chain direction.

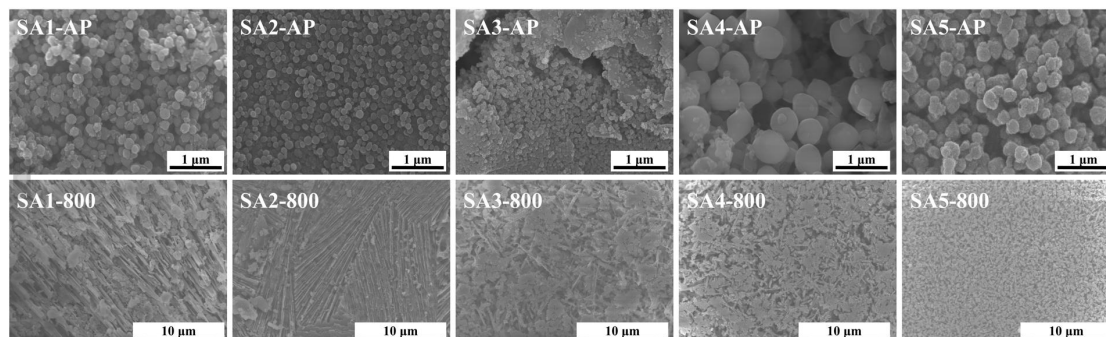


Fig. 4. SEM images of SA specimens before and after heat treatment at 800 °C.

3.3. Mechanical properties

The Vickers hardness of all specimens is presented in Fig. 5. The SA-AP specimens exhibited higher hardness than the crystallized specimens. Based on XRD results, after heat treatment at 700 °C, a substantial amount of the low-hardness CaF_2 (Vickers hardness ~160-180 HV) precipitated, exerting a pronounced dilution effect on the matrix and thereby reducing the hardness. After treatment at 800 °C, the main crystalline phase in specimens SA1 and SA2 was fluorcanasite, which possesses a layered structure. Under the indenter stress field, the crystals tended to undergo directional cleavage slip along the weak interlayer planes, leading to a decrease in hardness. In specimens SA3-SA5, the chain like xonotlite phase had not yet formed a continuous rigid skeleton, which contributing to the observed decrease in hardness.

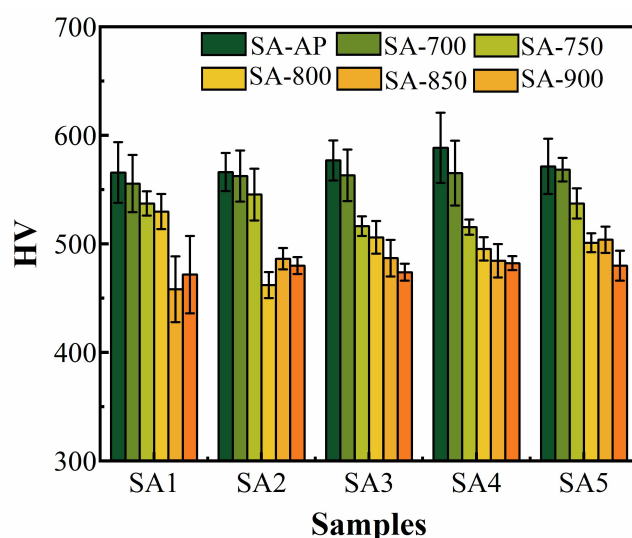


Fig. 5. Vickers Hardness Diagram of SA Series Specimens.

Fig. 6 presents the elastic modulus results for the SA-AP specimens and the specimens heat-treated at 800 °C. The elastic modulus of SA-AP specimens exhibited an initial increase followed by a decrease with Al₂O₃ substitution for SiO₂, and the SA3 specimen reached a maximum value of 78.09 ± 0.05 GPa. Within the low Al content range, Al³⁺ entered the glass network as [AlO₄] tetrahedra, enhancing the network compactness. When the Al₂O₃ content exceeded 2 mol%, the excess demand for charge compensation induced structural distortion and increased local inhomogeneity, together with a pronounced decrease in Q³ units and a tendency toward chain-like network structures, leading to a decline in elastic modulus. After heat treatment at 800 °C, the elastic modulus was primarily governed by the crystalline phase composition. Fluorcanasite exhibits an interlocking lath-like morphology that can effectively bear elastic loads, and the elastic moduli of samples SA1 and SA2 reach 75.33 ± 0.03 GPa and 73.915 ± 0.01 GPa, respectively. Xonotlite possesses a relatively high intrinsic modulus, and therefore specimens SA4 and SA5 exhibited higher elastic modulus values.

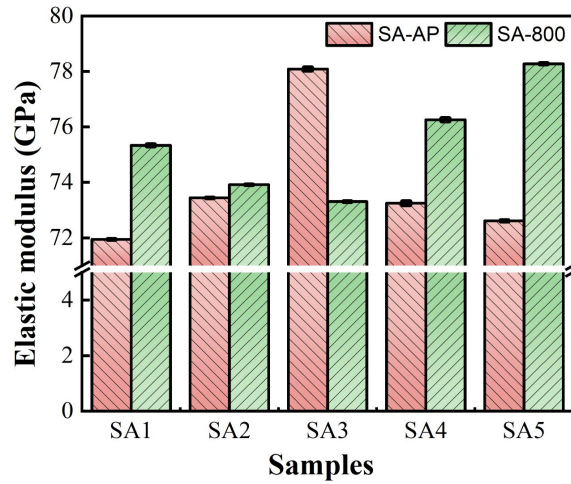


Fig. 6. Elastic modulus of Series SA specimens before and after heat treatment at 800 °C.

The fracture toughness results are shown in Fig. 7. The SA-AP specimens exhibited overall low fracture toughness, ranging from approximately 0.49 to 0.85 MPa·m^{1/2}. With Al₂O₃ substitution for SiO₂, the specimen SA4-AP showed a relatively low value, which can be attributed to the presence of the largest spherical droplets. These large phase-separated droplets introduced long-range, continuous weak interfaces in the glass matrix. Under the crack-tip stress field, these weak interfaces cracked preferentially. After heat treatment at 800 °C, the fracture toughness increased significantly, mainly due to the crystal toughening mechanism. The fracture toughness values of specimens SA1 and SA2 were 1.00 ± 0.14 MPa·m^{1/2} and 0.89 ± 0.05 MPa·m^{1/2}, respectively. The fluorcanasite crystals were distributed in an interlocking pattern within the glass matrix, effectively hindering straight crack propagation and causing crack deflection, thereby increasing the fracture energy and improving fracture toughness [29-31]. For specimens SA3 to SA5, toughening relied on the acicular morphology

of xonotlite and the plastic deformation of the residual glass, yielding a fracture toughness of up to $1.23 \pm 0.08 \text{ MPa}\cdot\text{m}^{1/2}$.

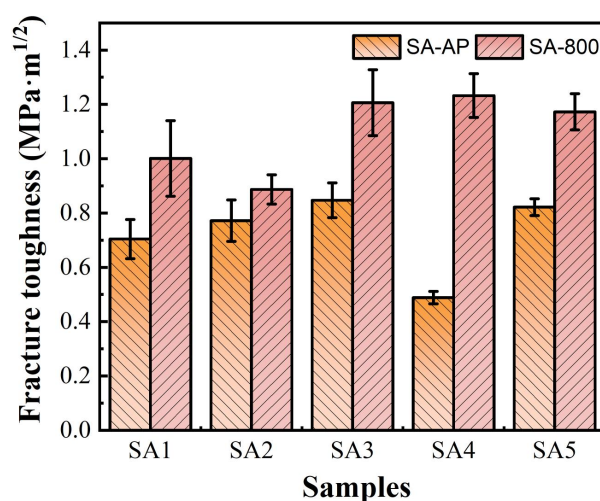


Fig. 7. Fracture toughness of the SA series specimens before and after heat treatment at 800 °C.

Fig. 8 presents the flexural strength results of the SA series specimens before and after heat treatment at 800 °C. For the SA-AP specimens, the flexural strength fluctuated with Al_2O_3 content, with SA1 exhibiting the highest value. Because a higher SiO_2 content leads to a more continuous and homogeneous glass network with smaller internal defects, thereby increasing the crack initiation strength. With increasing Al_2O_3 content, the charge compensation effect is enhanced, and local structural rearrangements may introduce micro-scale inhomogeneities, resulting in a decrease in flexural strength. After heat treatment at 800 °C, the flexural strength increased significantly overall, which is primarily attributed to crystal toughening mechanisms. SA1 achieved the highest strength, up to $296.71 \pm 22.18 \text{ MPa}$, owing to the integral interlocking framework of fluorcanasite laths. SA4 exhibited the second highest strength, relying on xonotlite fiber reinforcement.

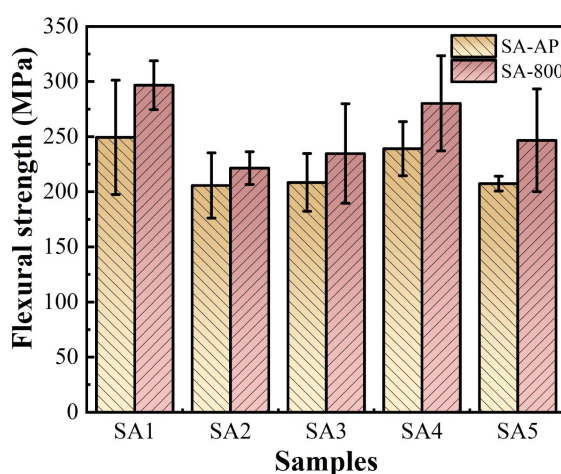


Fig. 8. Flexural strength of the SA series specimens before and after heat treatment at 800 °C.

3.4. Chemical stability

The chemical stability test results are shown in Fig. 9. The acid resistance of the SA-AP glasses (Fig. 9a) was superior to that of the heat-treated specimens. Because fluorcanasite and xonotlite are prone to decomposition in acidic environments [32], whereas the residual glass phase and CaF_2 crystalline phase exhibit relatively higher chemical stability in acidic media [16]. The corrosion of silicate glass by HCl proceeds primarily through ion exchange between H^+ and network modifier cations (Na^+ , K^+ , Ca^{2+}) in the glass, followed by hydrolysis of aluminosilicate networks. Si–O–Al linkages are generally more susceptible to electrophilic attack by H^+ than Si–O–Si bonds. The preferential leaching of network-forming Al^{3+} ions (dealumination) leads to localized disruption of the glass network, thereby accelerating acid corrosion. Fluorcanasite, as a layered silicate, has its silicon-oxygen tetrahedral layers connected by strong Si–O bonds. When exposed to acidic media, H^+ mainly attacks the interlayer Na^+/K^+ sites. Owing to the protection of the layered structure, the ion exchange rate is limited, and the intralayer Si–O framework remains intact, forming a protective silica-rich surface layer that hinders further corrosion. Xonotlite is a chain silicate, and the bonds between its Ca–O chains are susceptible to H^+ attack in acidic media. After Ca^{2+} leaching, the siloxane chain framework collapses, leading to decreased acid resistance. Fig. 9b presents the corrosion results of the SA series specimens in alkaline solution. Alkaline corrosion occurs primarily through OH^- attack on the Si–O–Si and Si–O–Al frameworks. In the aluminosilicate network, the stability is governed by the relative resistance of these bonds to nucleophilic OH^- attack. While Si–O–Si bonds are easily cleaved by hydroxyl ions to form soluble silicates, the presence of $[\text{AlO}_4]$ tetrahedra enhances the network connectivity and steric hindrance, rendering the Si–O–Al linkages relatively more robust against alkaline dissolution. Therefore, the overall alkali resistance is dictated by the structural balance and the proportion of these linkages. For the SA-AP glasses, the alkali resistance exhibited a trend of first decreasing and then increasing with increasing Al_2O_3 content. As revealed by the Raman results, with increasing Al_2O_3 content, the Q^2 structural units in the glass network first increased and then decreased, and the number of non-bridging oxygens followed the same trend, which is consistent with the variation in alkali resistance of the SA-AP specimens. For the SA-800 specimens, crystalline phases precipitated after heat treatment. The interfaces between the crystalline phases and the residual glass phase are more susceptible to attack in alkaline solution, thereby accelerating the dissolution process and increasing the mass loss of the samples. Overall, SA1 exhibited the best resistance in both HCl and NaOH, attributable to the chemical stability of the layered fluorcanasite structure.

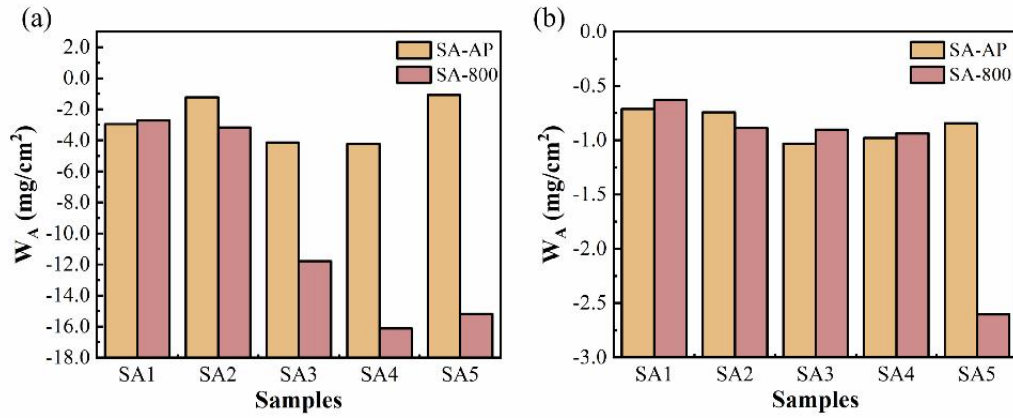


Fig. 9. Chemical durability of SA series specimens in (a) 5% HCl;(b)5% NaOH.

Fig. 10 presents the F^- ions leaching concentration results. In this experiment, the sludge accounted for approximately 30.93 wt% of the total batch mass (calculated for SA1), with all CaF_2 derived from the fluoride-containing sludge. The total content of trace elements such as Ba, Sr, Ce, La, and Fe in the sludge was below 2 wt%, and no independent crystalline phases containing these elements were detected by XRD, indicating that these elements were mainly dissolved in the residual glass phase or incorporated into the lattice of the main crystalline phases. After heat treatment at 800 °C, the fluoride leaching amounts of samples SA1 and SA2 were lower than those of the AP specimens, which is attributed to the effective immobilization of fluoride ions by the precipitated fluorcanasite phase. Moreover, the leaching values were below the limit of 100 mg/L specified in GB 5085.3-2007, meeting the regulatory requirements for building decoration applications. In contrast, the fluoride leaching amounts of samples SA3-SA5 were higher than those of the AP specimens, mainly because the crystalline phase precipitated after heat treatment was xonotlite rather than fluorcanasite, resulting in the enrichment of F^- ions in the residual glass phase or at grain boundaries, thus making them more susceptible to leaching.

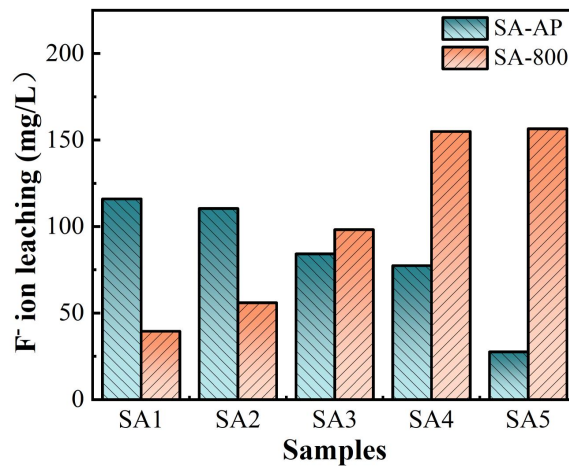


Fig. 10. Fluoride ion leaching concentration of SA series specimens.

4. Conclusions

In this paper, fluorcanasite glass ceramics were prepared using fluoride-containing sludge as a raw material. The effects of equimolar substitution of Al_2O_3 for SiO_2 on the phase composition, microstructure, and mechanical and chemical properties of the glass ceramics were systematically investigated. The main conclusions are as follows:

(1) When the Al_2O_3 content was ≤ 1.5 mol%, the main crystalline phase after heat treatment at 800 °C was fluorcanasite, exhibiting an interlocking lath-like microstructure. When the Al_2O_3 content was ≥ 2 mol%, the formation of fluorcanasite was suppressed, the xonotlite phase precipitated with a needle-like morphology, and CaF_2 became the main crystalline phase. The phase evolution is attributed to the transformation of Q^3 layered structural units into Q^2 chain structural units.

(2) Mechanical property results showed that the SA-AP glasses exhibited the highest Vickers hardness due to their homogeneous and dense network. After crystallization, the hardness of samples SA1 and SA2 decreased significantly because of the layered cleavage of fluorcanasite. And the interlocking lath structure imparted high fracture toughness ($1.00 \text{ MPa}\cdot\text{m}^{1/2}$) and high flexural strength (296.71 MPa). Samples SA3 to SA5 exhibited even higher fracture toughness (up to $1.25 \text{ MPa}\cdot\text{m}^{1/2}$) owing to xonotlite fiber toughening, but their flexural strength was slightly lower.

(3) Chemical durability and F^- immobilization results demonstrated that after crystallization at 800 °C, SA1 exhibited the optimal performance in both HCl and NaOH solutions, attributable to the layered fluorcanasite structure. Furthermore, the stable incorporation of F^- ions into the fluorcanasite crystal lattice in SA1 and SA2 achieved effective chemical immobilization, with fluoride leaching concentrations significantly below the regulatory threshold of 100 mg/L (GB 5085.3-2007).

In summary, fluorcanasite glass ceramics possess low hardness, high flexural strength, high fracture toughness, favorable acid and alkali resistance, and a certain fluoride immobilization capacity. They are capable of achieving the harmless disposal and high-value resource utilization of fluoride-containing sludge. This work provides a reliable theoretical basis and process support for the preparation of high-performance glass-ceramic materials from fluorine-containing solid waste.

Acknowledgments

This work was supported by Supported by the Opening Project of State Key Laboratory of Advanced Glass Materials (2025KF08).

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

Cairu Peng: Writing-original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Jinmiao Chen:** Writing-review & editing, Investigation, Formal analysis, Data curation. **Zheng Liu:** Methodology, Formal analysis, Supervision. **Zhiyong Zhao:** Writing-review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Feng He:** Conceptualization, Resources, Methodology. **Yingliang Tian:** Funding acquisition, Project administration, Resources, Supervision.

Use of AI statement

None.

References

- [1] Yuan H., Huang Y., Wang R., et al. Disposal and utilization of calcium fluoride sludge. The Administration and Technique of Environmental Monitoring, 2014, 26(02): 12-16.
- [2] Jia J., Wang Q., Wu X. Research progress on re-utilization of fluorine-containing sludge. Modern Chemical Industry, 2023, 43(06): 103-106.
- [3] Zhu P., Xia B., Liu Q., et al. Research status of purification and resource utilization of calcium fluoride sludge. China Resources Comprehensive Utilization, 2022, 40(10): 104-111.
- [4] Tang W., Lin Z. Solidification treatment of fluorine-containing sludge by composite portland cement. Fine Chemicals, 2021, 38(8): 1705-1710.
- [5] Liu W., Li K. Application of reutilization technology to calcium fluoride sludge from semiconductor manufacturers. Journal of the Air & Waste Management Association, 2011, 61(1): 85-91.
- [6] Fan C., Li K. Production of insulating glass ceramics from thin film transistor-liquidcrystal display (TFT-LCD) waste glass and calcium fluoride sludge. Journal of Cleaner Production, 2013, 57: 335-341.
- [7] Zhao S., Liu B., Ding Y., et al. Study on glass-ceramics made from mswi fly ash, pickling sludge and waste glass by one-step process. Journal of Cleaner Production, 2020, 271: 122674.
- [8] Chen W., Deng Z., Ying T. Structure and properties of fluorosilicate glass ceramics. Bulletin of the Chinese Ceramic Society, 1998, (02): 39-42.
- [9] Barros R., Salata L., Sverzut C., et al. In vivo bone tissue response to a canasite glass-ceramic. Biomaterials. 2002, 23(14): 2895-2900.
- [10] Mallet V., Luiz J., Adalberto R., et al. Bone response to three different chemical compositions of

- fluorcanasite glass-ceramic. *Journal of Biomedical Materials Research. Part A*, 2007, 83(2): 480.
- [11] Kraipok A., Intawin P., Kamnony M., et al. Preparation and characterization of lithium disilicate-fluorcanasite glass-ceramics for dental applications. *Journal of the Mechanical Behavior of Biomedical Materials*, 2023, 137: 105548.
- [12] Bandyopadhyay-Ghosh S., Reaney M., Hurrell-Gillingham K., et al. Evaluation of modified fluorcanasite glass-ceramics for bone tissue augmentation. *Key Engineering Materials*, 2005, 511: 557-560.
- [13] Khomyakov A.P., Nechelyustov G.N., Krivokoneva G.K., et al. Fluorcanasite, $K_3Na_3Ca_5Si_{12}O_{30}(F,OH)_4 \cdot H_2O$, a new mineral species from the khibiny alkaline pluton, kola peninsula, russia, and new data on canasite. *Geology of Ore Deposits*, 2010, 51(8): 757-766.
- [14] Omar A., Hamzawy E., Farag M. Crystallization of fluorcanasite-fluorrichterite glasses. *Ceramics International*, 2009, 35: 301-307.
- [15] Abhijit V., Shankar V.K., Bandhu S.G., et al. Microstructural analysis and bioactive response of selectively engineered glass-ceramics in simulated body fluid. *Materials Technology*, 2021, 36(8):451-459.
- [16] Deng W., Cheng J.S., Tian P.J., et al. Chemical durability and weathering resistance of canasite based glass and glass-ceramics. *Journal of Non-Crystalline Solids*, 2012, 358(21): 2847-2854.
- [17] Fu Q., Beall G.H., Smith C.M. Nature-inspired design of strong, tough glass-ceramics. *Mrs Bulletin*, 2017, 42(03): 220-225.
- [18] Du W.F., Kuraoka K., Akal T., et al. Study of Al_2O_3 effect on structural change and phase separation in $Na_2O-B_2O_3-SiO_2$ glass by NMR. *Journal of Materials Science*, 2000, 35: 4865-4871.
- [19] Xie J., Xiao Z., Zheng W., et al. The effect of Al_2O_3/SiO_2 on the structure and properties of $Na_2O-CaO-Al_2O_3-SiO_2$ glasses. *Key Engineering Materials*, 2012, 509: 339-345.
- [20] Liu X., Gu Z., He O. The structural role of aluminum in $SiO_2-Al_2O_3$ glass. *Bulletin of the Chinese Ceramic Society*, 1989, (3):210-215.
- [21] Hou H., Gao Q. Coordination states of Fe^{3+} and Al^{3+} ions in non-typical vitreous phases. *Bulletin of the Chinese Ceramic Society*, 1991, 5: 17-21.
- [22] Martina S., Martin B., Christian B., et al. Microstructure and luminescence of erbium doped $Na_2O/K_2O/CaO/CaF_2/Al_2O_3/SiO_2$ nano glass-ceramics. *Journal of the European Ceramic Society*, 2018, 207: 36-43.
- [23] Rüssel C. Nanocrystallization of CaF_2 from $Na_2O/K_2O/CaO/CaF_2/Al_2O_3/SiO_2$ Glasses. *Chemistry of Materials*, 2005, 17(23): 5843-5847.
- [24] Cao X., Wang P., Wan R., et al. Structural insight of fluorophosphate glasses through F/O ratio: case study of raman and NMR spectra. *Journal of Non-Crystalline Solids*, 2024, 637: 123065.
- [25] Li Y., Liang K., Cao J., et al. Spectroscopy and structural state of V^{4+} ions in lithium aluminosilicate glass and glass-ceramics. *Journal of Non-Crystalline Solids*, 2010, 356: 502-508.
- [26] Ross S., Welsch A.M., Behrens H. Lithium conductivity in glasses of the $Li_2O-Al_2O_3-SiO_2$ system.

Physical Chemistry Chemical Physics, 2015, 17(1):465-474.

- [27] Jia X., Zhao R., Zhang J., et al. Effect of $\text{Al}_2\text{O}_3/\text{SiO}_2$ on crystallization behaviour and mechanical properties of $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ glass-ceramics. Bulletin of the Chinese Ceramic Society, 2026, 45(3):845-852.
- [28] Tian Y., Cheng W., He F., et al. Effect of fluorinated sludge content on the structure and properties of opal glass-ceramics. Ceramics International, 2025, 51: 56393-56399.
- [29] Song S., Cheng J., Zheng H., et al. Effect of mass fraction of Al_2O_3 on structure and crystallization of $\text{R}_2\text{O-CaO-SiO}_2\text{-F}$ glass-ceramics. Glass Enamel & Ophthalmic Optics, 2009, 37(04): 5-8.
- [30] Yan X., Huang Y. Wan L. Influence of Al_2O_3 on the crystallization and properties of $\text{R}_2\text{O-CaO-SiO}_2\text{-F}$ system glass-ceramics made from residual. Glass, 2018, 45(3): 1-5.
- [31] Zhang N, Anusavice K. Effect of alumina on the strength, fracture toughness, and crystal structure of fluorcanasite glass-ceramics. Journal of the American Ceramic Society, 2004, 82(9): 2509-2513.
- [32] Rozhdestvenskaya V.I., Nikishova V.L., Lazebnik A.K. The crystal structure of frankamenite. Mineralogical Magazine, 1996, 60(6):897-905.

Author biography



Cairu Peng is a doctoral student at the School of Materials Science and Engineering, Beijing University of Technology, supervised by Professor Yingliang Tian and Associate Professor Zhiyong Zhao. Her research focuses on the resource utilization of solid waste.



Zhiyong Zhao is an associate professor at the School of Materials Science and Engineering, Beijing University of Technology, focusing on electronic glass, glass-ceramics, and the resource

recovery of solid waste.



Yingliang Tian is a professor at the School of Materials Science and Engineering at Beijing University of Technology, focusing on electronic glass, the resource recovery of solid waste, and glass melt properties.