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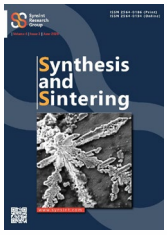

Research article

Influence of $K_2O/(CaO+ZnO)$ ratio on crystallization behavior, phase formation, and properties of transparent borosilicate glazes

Raziye Salami, Aida Faeghinia *, Zahra Khakpour, Mohammad Zakeri

Ceramics Department, Materials and Energy Research Center (MERC), Karaj, Iran

A B S T R A C T

The crystallization behavior of transparent borosilicate glass–ceramic glazes is strongly influenced by the composition of network-modifying oxides, which governs phase evolution and the resulting functional properties. In this study, the effect of the $K_2O/(CaO+ZnO)$ ratio on the thermal behavior, structural evolution, phase formation, microstructure, optical properties, and mechanical performance of transparent borosilicate glazes was systematically investigated. Glass frits with different $K_2O/(CaO+ZnO)$ ratios were prepared using the conventional melt-quenching method, applied onto ceramic substrates, and fired under identical conditions. The resulting glazes were characterized by differential thermal analysis (DTA), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), optical measurements, and Vickers microhardness testing. The results showed that decreasing the $K_2O/(CaO+ZnO)$ ratio significantly increased the glass transition temperature, indicating improved thermal stability of the parent glass, while only slightly affecting the crystallization peak temperature. Structural modifications of the borosilicate network promoted systematic changes in the crystalline phase assemblage, leading to the formation of anorthite, willemite, and calcium silicate phases with distinct crystal morphologies. Increased crystallization at lower $K_2O/(CaO+ZnO)$ ratios reduced the gloss of the fired glazes because of enhanced light scattering, whereas the formation of harder crystalline phases improved the microhardness of the glass–ceramic coatings. These findings demonstrate that the $K_2O/(CaO+ZnO)$ ratio is an effective compositional parameter for controlling the structure–property relationships of transparent borosilicate glazes and provides a practical strategy for optimizing their crystallization behavior and overall performance.

KEYWORDS

Transparent borosilicate glaze
Glass–ceramics
Crystallization
Phase evolution
Properties

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1. Introduction

Transparent glass–ceramic glazes have attracted considerable attention in ceramic tile manufacturing because they combine the aesthetic characteristics of conventional transparent glazes with enhanced mechanical and chemical performance. Unlike fully amorphous glazes, glass–ceramic glazes undergo controlled crystallization during firing, leading to the formation of crystalline phases dispersed within a residual glassy matrix [1, 2]. The nature, volume fraction, and morphology of these crystalline phases govern the final optical appearance, mechanical strength, hardness, and chemical durability of the glaze. Consequently, controlling crystallization has become one of the principal approaches for tailoring the performance of transparent ceramic glazes [1–3].

* Corresponding author. *E-mail address:* a.faeghinia@merc.ac.ir (A. Faeghinia)

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The crystallization behavior of glass–ceramic glazes is strongly influenced by the composition of the parent glass. In borosilicate glaze systems, the balance between network-forming oxides and network-modifying oxides determines the degree of structural polymerization; melt viscosity, glass stability, and ultimately the nucleation and growth of crystalline phases during thermal treatment [4, 5]. Among the network modifiers commonly employed in transparent glazes, K_2O, CaO, and ZnO play particularly important roles because they simultaneously influence glass structure, melting characteristics, crystallization kinetics, thermal expansion, and the development of functional properties [6].

ZnO is widely used in transparent ceramic glazes owing to its ability to improve gloss, chemical durability, and melt fluidity while also participating in the formation of crystalline phases such as willemite (Zn_2SiO_4) under appropriate firing conditions [7–9]. Likewise, CaO contributes to the crystallization of calcium-containing silicates and anorthite-based phases, which are known to improve the mechanical performance of glass–ceramic coatings. In contrast, K_2O primarily acts as an alkali network modifier that decreases the viscosity of the glass network and alters its degree of polymerization. Since these oxides influence the glass network through different structural roles, modifying their relative proportions can significantly affect crystallization behavior, phase assemblage, and the resulting microstructure [10–12].

Previous studies have extensively investigated the effects of ZnO addition, crystallization mechanisms in ZnO-containing glass–ceramic systems, and the influence of firing conditions on the formation of crystalline phases such as anorthite, wollastonite, and willemite [13, 14]. Considerable attention has also been devoted to improving the optical quality and mechanical performance of transparent glazes through compositional optimization. Nevertheless, comparatively less emphasis has been placed on understanding how the balance between alkali modifiers and divalent network modifiers governs the evolution of the glass structure and subsequently controls crystallization pathways [2, 15]. In particular, the influence of the K_2O/(CaO+ZnO) ratio on glass stability, phase evolution, microstructural development, and mechanical properties has not been systematically clarified.

Understanding this compositional relationship is important because crystallization in glass–ceramic glazes is controlled not only by firing conditions but also by the structural characteristics of the parent glass. Variations in the K_2O/(CaO+ZnO) ratio are expected to modify the connectivity of the glass network, thereby altering the thermal stability of the parent glass, the sequence of phase formation, crystal morphology, and the balance between the residual glassy phase and crystalline constituents. These structural changes ultimately determine the mechanical performance and transparency of the final glaze [16–18]. Therefore, the present study investigates transparent borosilicate glazes with different K_2O/(CaO+ZnO) ratios to establish the relationships between glass composition, crystallization behavior, phase formation, microstructural evolution, and mechanical properties. Thermal analysis, FTIR spectroscopy, X-ray diffraction, scanning electron microscopy coupled with energy-dispersive spectroscopy, optical characterization, and Vickers microhardness measurements were employed to elucidate the structure–property relationships governing the development of transparent glass–ceramic glazes.

2. Experimental procedure

2.1. Raw materials, batch composition and glaze preparation

The investigated transparent borosilicate glazes were designed within the SiO_2–Al_2O_3–B_2O_3–CaO–K_2O–ZnO system to evaluate the influence of the K_2O/(CaO+ZnO) ratio (defined as the S ratio) on crystallization behavior, phase evolution, microstructural development, and mechanical performance. To isolate the compositional effect, the contents of the principal glass-forming oxides (SiO_2, Al_2O_3, and B_2O_3) were maintained constant, while the relative proportions of K_2O, CaO, and ZnO were systematically adjusted.

The parent glass composition corresponded to the molar formulation $2.5SiO_2$–$0.2Al_2O_3$–$0.15B_2O_3$–(CaO– K_2O–ZnO), in which the modifier composition was varied to obtain three different S ratios. The investigated compositions were designated F1, F2, and F3, corresponding to K_2O/(CaO+ZnO) ratios of 0.37, 0.31, and 0.24, respectively.

Commercial ceramic-grade raw materials were employed for glass preparation. High-purity silica (SiO_2) served as the primary glass former, providing the backbone of the borosilicate network. Alumina (Al_2O_3) was incorporated to improve the chemical durability and structural stability of the glass network, while boron oxide (B_2O_3) acted as a secondary network former to reduce melting temperature and promote glass formation. Calcium oxide (CaO) and potassium oxide (K_2O) were introduced as network-modifying oxides to tailor melt characteristics and crystallization behavior. Zinc oxide (ZnO), which exhibits both intermediate and network-modifying characteristics depending on glass composition, was incorporated to promote the formation of zinc-containing crystalline phases and to modify the crystallization characteristics of the transparent glaze.

The oxide batches were accurately weighed according to Table 1 and thoroughly homogenized before melting. The mixed batches were melted in alumina crucibles at temperatures ranging from 1450 to 1550 °C depending on composition. After complete melting and homogenization, the molten glass was rapidly quenched in water to produce glass frits with fully amorphous structures.

The obtained frits were subsequently dried and milled to obtain powders with particle sizes below 75 μm for glaze preparation. The glaze slurries were prepared by mixing the frit powder with water under identical processing conditions for all compositions to eliminate processing-related variations. The prepared slurries were then applied onto biscuit-fired wall-tile substrates and fast-fired at 1060 °C for 45 min.

Table 1. Nominal compositions of the oxides used in the samples with different S ratios (Reused from Ref. [19], licensed under CC BY 4.0).

Sample	K_2O	SiO_2	Al_2O_3	B_2O_3	CaO	ZnO	S ratio
F1	7.5	60.1	8.2	4.2	12.7	7.1	0.37
F2	6.5	60.1	8.2	4.2	15.2	5.8	0.31
F3	3.5	61.67	8.2	4.2	17.7	4.3	0.24

2.2. Characterization

DTA was performed to determine the characteristic thermal behaviour of the glasses, including the glass transition temperature (T_g), crystallization peak temperature (T_p), and melting temperature (T_m). These characteristic temperatures were subsequently used to evaluate the glass-forming ability and thermal stability of the investigated compositions. The structural evolution of the parent glasses was examined by Fourier-transform infrared spectroscopy (FTIR: Nexus 670, Thermo Nicolet). The X-ray diffraction (XRD: PHILIPS PW1730) analysis was employed to identify the crystalline phases formed during heat treatment and to evaluate the influence of composition on phase evolution. The morphology of the crystallized glazes was characterized using field emission scanning electron microscopy (FESEM: MIRA3 TESCAN). The optical appearance of the fired glazes was evaluated by optical characterization to assess the effect of crystallization on glaze transparency. Finally, the mechanical performance of the glazes was evaluated by Vickers microhardness testing.

3. Results and discussion

3.1. Thermal behavior and glass stability

The thermal behavior of the parent borosilicate glasses was studied by differential thermal analysis to evaluate the influence of the S ratio on glass transition, thermal stability, and crystallization. The DTA curves of the investigated compositions are presented in Fig. 1, while the characteristic temperatures determined from the thermograms are summarized in Table 2.

All investigated glasses exhibited the characteristic thermal events of a typical glass–ceramic precursor, consisting of an endothermic glass transition followed by an exothermic crystallization peak. These thermal events indicate that the quenched frits were successfully obtained in an amorphous state and possessed sufficient thermal stability to undergo controlled crystallization during subsequent heat treatment. Although the crystallization peak remained within a relatively narrow temperature range for all compositions, significant differences were observed in the glass transition temperature as the S ratio was varied. A progressive decrease in the S ratio resulted in a pronounced increase in the glass transition temperature, with T_g increasing from 618 °C for F1 to 704 °C for F2 and reaching 772 °C for F3, whereas the T_P increased only slightly from 928 °C to 945 °C. This trend demonstrates that modifying the relative proportions of K_2O, CaO, and ZnO has a considerably greater influence on the structural relaxation of the glass network than on the temperature at which bulk crystallization occurs. The increase in T_g with decreasing S ratio suggests that replacing part of the alkali modifier (K_2O) with the combined CaO–ZnO modifiers produces a thermally more stable glass network that requires higher temperatures to initiate cooperative atomic rearrangement.

The observed behavior can be understood by considering the different structural roles of the modifying oxides in borosilicate glasses. Potassium oxide acts primarily as a monovalent network modifier that introduces non-bridging oxygen atoms and facilitates structural mobility within the silicate network [20]. Increasing the proportion of K_2O therefore promotes a less polymerized structure with lower viscosity and lower resistance to structural relaxation [21]. In contrast, increasing the relative amounts of CaO and ZnO suppresses this effect. Calcium ions possess higher field strength than potassium ions and establish stronger electrostatic interactions with non-bridging oxygen atoms, thereby increasing network rigidity. Zinc oxide may additionally behave as an intermediate oxide depending on the local glass structure, contributing to stronger short-range ordering and improving the resistance of the glass network to thermal deformation [22, 23]. Consequently, decreasing the S ratio enhances the thermal stability of the parent glass, as reflected by the systematic increase in T_g. In comparison with the substantial variation in T_g, the crystallization peak temperature exhibited only a modest increase among the investigated compositions. This observation suggests that although the modifier ratio strongly influences the initial stability of the glass network, the subsequent crystallization process is governed by a combination of structural and kinetic factors. Once the glass transition has occurred, the activation energy required for crystal growth appears to be affected to a much smaller extent by changes in the S ratio. The relatively limited shift in T_p also indicates that all compositions remain suitable for controlled crystallization under the selected firing conditions.

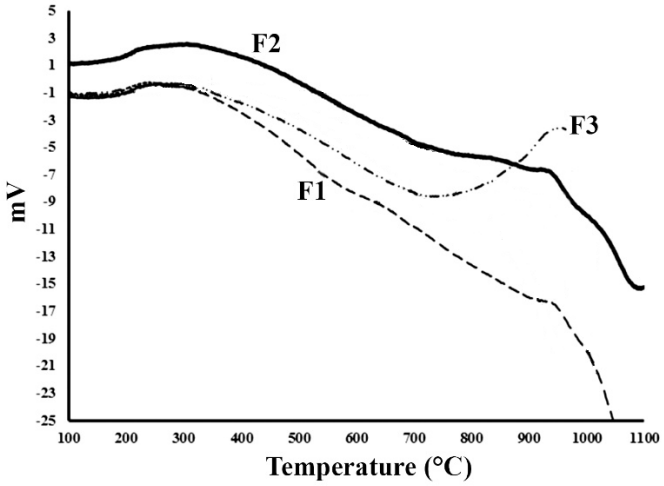

Fig. 1. DTA curves of transparent borosilicate glasses with different S ratios.

Table 2. Characteristic thermal parameters (Reused from Ref. [19], licensed under CC BY 4.0).

Samples	T_g, °C	T_P, °C	T_P-T_g
F1	618	928	310
F2	704	930	226
F3	772	945	173

The thermal stability parameters summarized in Table 2 further support this interpretation. As the S ratio decreased, the temperature interval between glass transition and crystallization increased, indicating an improvement in the thermal stability of the parent glass. A wider processing window implies that the glass can tolerate higher temperatures after softening before the onset of rapid crystallization, providing greater flexibility during industrial firing. Such behavior is advantageous for transparent glass–ceramic glazes because excessive or premature crystallization may adversely affect surface quality and optical appearance, whereas controlled crystallization promotes the development of uniformly distributed crystalline phases that enhance mechanical performance.

The DTA results therefore demonstrate that the K_2O/(CaO+ZnO) ratio is an effective compositional parameter for tailoring the thermal characteristics of transparent borosilicate glazes. Increasing the relative proportion of CaO and ZnO significantly improves glass stability by increasing the glass transition temperature while only slightly affecting the crystallization temperature. These findings indicate that the compositional modification primarily alters the stability of the parent glass rather than fundamentally changing its crystallization mechanism. Such changes in thermal behavior are expected to influence the subsequent evolution of the glass network, the formation of crystalline phases, and the development of the final microstructure, which are examined in the following sections through FTIR, X-ray diffraction, and microstructural analyses.

3.2. Structural evolution of the glass network

Fourier-transform infrared spectroscopy was employed to investigate the structural evolution of the borosilicate glass network as a function of the S ratio. Since the crystallization behavior of glass–ceramic systems is strongly governed by the short-range structure of the parent glass, FTIR analysis provides valuable information regarding changes in network connectivity induced by compositional modification. The FTIR spectra of the investigated glass compositions are presented in Fig. 2.

The FTIR spectra samples exhibit the characteristic absorption bands of borosilicate glass networks, confirming that the prepared frits possess similar structural units while differing in their degree of network modification. The broad absorption band located in the high-wavenumber region is assigned to the asymmetric stretching vibrations of Si–O–Si bridges, which constitute the primary framework of the silicate network. Additional bands observed at intermediate and lower wavenumbers correspond to symmetric Si–O stretching vibrations, Si–O–Al linkages, bending vibrations of Si–O–Si bonds, and structural units associated with borate groups. These features are consistent with the formation of homogeneous borosilicate glasses before crystallization. Although no new absorption bands appeared with changing composition, noticeable variations in the intensity and position of several characteristic bands were observed as the S ratio decreased. These spectral changes indicate that modifying the relative proportions of K_2O, CaO, and ZnO alters the local environment of the glass network without fundamentally changing its structural framework. The gradual evolution of the spectra therefore reflects changes in network connectivity rather than the formation of new structural species.

The increase in the relative proportion of CaO and ZnO at lower S ratios resulted in a more rigid glass network, which is consistent with the thermal behavior discussed in the previous section. Potassium oxide primarily acts as a monovalent network modifier, breaking Si–O–Si bridges through the formation of non-bridging oxygen atoms and consequently reducing network connectivity. Therefore, compositions containing higher K_2O contents are expected to exhibit a more depolymerized structure with greater structural flexibility. In contrast, replacing part of the K_2O with CaO and ZnO modifies the glass network differently. Calcium ions possess higher ionic field strength and establish stronger interactions with oxygen atoms, while ZnO may partially behave as an intermediate oxide by participating in the local glass structure. As a result, decreasing the S ratio promotes a more stable and less easily relaxed network, in agreement with the observed increase in glass transition temperature. The FTIR results also provide insight into the subsequent crystallization behavior of the investigated glazes. Structural rearrangement during heat treatment requires the

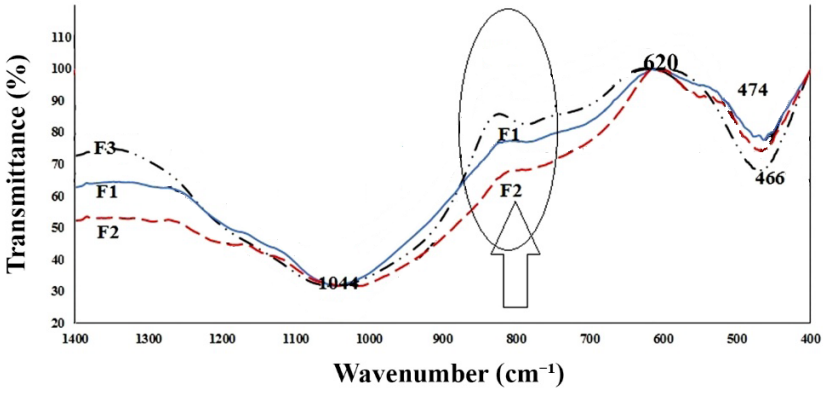

Fig. 2. FTIR spectra of transparent borosilicate glasses with different S ratios (Reused from Ref. [19], licensed under CC BY 4.0).

migration of network-modifying cations and the reorganization of silicate structural units into energetically favorable crystalline configurations. A more polymerized and thermally stable glass network generally delays structural relaxation but provides a more controlled environment for crystal nucleation and growth during firing. Consequently, the compositional modifications identified by FTIR are expected to influence not only the onset of crystallization but also the nature and distribution of the crystalline phases formed in the glass–ceramic system. An important observation is that the spectral variations are gradual across the F1, F2, and F3 compositions, indicating that the effect of the K_2O/(CaO+ZnO) ratio is evolutionary rather than abrupt. This behavior suggests that the structural modification of the parent glass proceeds continuously as the balance between alkali and divalent modifiers changes. Such progressive structural evolution is consistent with the corresponding changes observed in the DTA results, where a systematic increase in glass transition temperature was accompanied by only a slight shift in crystallization temperature. Together, these findings demonstrate that the primary influence of the S ratio is to modify the stability and connectivity of the glass network rather than to fundamentally alter the crystallization mechanism.

3.3. Phase evolution of the glass–ceramic glazes

The influence of the S ratio on the crystallization behavior of the transparent borosilicate glazes was investigated by XRD. The diffraction patterns obtained after firing are presented in Fig. 3. XRD analysis provides direct evidence of the crystallization products developed during firing and reveals how compositional modification controls phase selection in the glass–ceramic system.

All fired specimens exhibited diffraction peaks superimposed on a broad amorphous halo, indicating that crystallization occurred within a residual glassy matrix rather than resulting in complete devitrification. This confirms that the selected firing schedule successfully produced glass–ceramic glazes in which crystalline phases were uniformly developed while preserving the continuous glass phase required for transparent coatings. The coexistence of crystalline and amorphous phases demonstrates that the investigated compositions followed a controlled crystallization process rather than extensive bulk crystallization.

The XRD results reveal that the crystalline phase assemblage changes systematically with the S ratio. As the relative proportions of CaO and ZnO increased and the S ratio decreased, noticeable differences were observed in both the intensity and distribution of diffraction peaks, indicating that compositional modification altered the crystallization pathway of the parent glass. These observations confirm that the relative proportions of network-modifying oxides play a decisive role in determining which crystalline phases become thermodynamically favorable during firing. The principal crystalline phases identified in the investigated glazes include anorthite ($CaAl_2Si_2O_8$), willemite (Zn_2SiO_4) and calcium-containing silicate phases, whose relative abundance varies according to the glass composition. The formation of these phases is consistent with the availability of Ca, Zn, Al and Si within the parent borosilicate glass and reflects the redistribution of modifier cations during crystallization. Because these crystalline phases possess different crystal structures and growth characteristics, changes in their relative proportions are expected to exert a significant influence on the subsequent microstructure and mechanical properties of the glass–ceramic glazes. The progressive decrease in the S ratio promotes the participation of CaO and ZnO in crystallization, resulting in a gradual evolution of the phase assemblage. This behavior agrees well with the DTA results, where decreasing the S ratio significantly increased the glass transition temperature while only slightly affecting the crystallization peak temperature. The higher thermal stability of compositions containing lower S ratios suggests that the parent glass undergoes greater structural ordering before crystallization begins. Consequently, once nucleation is initiated, the available modifier cations are redistributed in a manner that favors the development of calcium- and zinc-containing crystalline phases.

The presence of willemite is particularly significant because ZnO not only modifies the glass network but also serves as an essential constituent of this crystalline phase. During heat treatment, Zn-containing structural units within the parent glass provide favorable conditions for the nucleation and growth of willemite crystals. Similarly, the availability of calcium and aluminosilicate structural units facilitates the formation of anorthite, while additional calcium silicate phases develop depending on the local chemical environment established by the modifier composition. The coexistence of these crystalline phases demonstrates that crystallization proceeds through multiple competitive pathways whose relative contributions are governed primarily by the S ratio.

The gradual variation in diffraction peak intensity among the investigated compositions indicates that the modifier ratio influences not only the type of crystalline phases but also their relative amounts. Increasing the proportion of CaO and ZnO promotes more extensive crystallization of modifier-rich phases, whereas higher K_2O contents

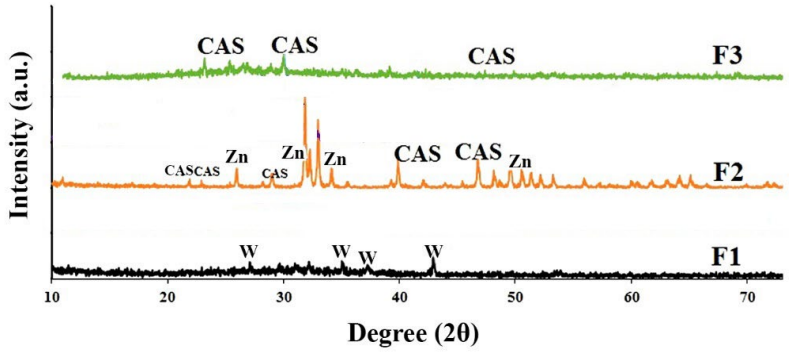

Fig. 3. XRD patterns of transparent borosilicate glazes with different S ratios after firing (Reused from Ref. [19], licensed under CC BY 4.0).

favor the retention of a larger amorphous fraction within the fired glaze. This observation is consistent with the structural role of K_2O as an alkali modifier that lowers melt viscosity and enhances structural mobility, thereby influencing both nucleation kinetics and crystal growth during firing. In contrast, the higher field strength of Ca^{2+} and the intermediate structural behavior of Zn^{2+} contribute to a more stable parent glass, ultimately directing crystallization toward specific silicate phases.

An important feature of the XRD results is that no undesirable secondary crystalline phases were detected within the investigated compositional range. This indicates that systematic adjustment of the S ratio modifies the relative abundance of desirable crystalline phases without fundamentally changing the crystallization mechanism or producing unstable reaction products. Such controlled phase evolution is particularly advantageous for transparent glass–ceramic glazes because excessive formation of unwanted crystalline phases may deteriorate both optical quality and mechanical performance.

3.4. Microstructural development

The microstructural evolution of the fired transparent borosilicate glazes was investigated by scanning electron microscopy to establish the relationship between the S ratio, crystalline phase development, and final glaze morphology. The FESEM images of F1 and F3 are presented in Fig. 4.

All investigated compositions exhibited crystalline regions with polyhedral morphologies, which are characteristic of pyroxene-related crystalline phases such as wollastonite, anorthite, and calcium silicate phases. The formation of these crystalline phases within the residual glassy matrix confirms the glass–ceramic nature of the developed glazes. The morphology and distribution of the crystals were strongly influenced by the modifier oxide balance, demonstrating that the S ratio plays a significant role in controlling crystallization behavior.

The SEM observations were consistent with the XRD results, showing that variations in the S ratio modified both the amount of crystallized phase and the type of crystalline morphology developed. Comparison of the SEM images with the XRD patterns indicated that the degree of crystallinity increased for the compositions with lower S ratios. In particular, the F3 composition exhibited a higher crystalline fraction compared with F1, which is associated with the formation of calcium aluminosilicate phases, mainly anorthite. The increased contribution of CaO and ZnO in low-S-ratio compositions provides favorable conditions for the formation of stable crystalline silicates during firing.

The formation of different calcium silicate polymorphs can also be related to the volatility of potassium oxide during firing. Evaporation of K_2O from the glaze surface may promote the transformation of wollastonite into para-wollastonite. The lower K_2O content in F3 therefore contributes to the observed differences in crystalline phases and morphology. This observation highlights the important role of alkali modifier concentration in controlling not only the glass structure but also the final crystalline phase assemblage.

3.5. Optical properties

The optical properties of the transparent borosilicate glazes were evaluated through gloss measurements and colorimetric analysis using the CIE system. The measured optical parameters of the fired glazes are summarized in Table 3.

The optical behavior of the investigated glazes was strongly correlated with their crystallization behavior and phase assemblage. Among the investigated compositions, F1 and F2 exhibited higher gloss values, whereas F3 showed significantly reduced gloss due to the increased formation of crystalline calcium silicate phases. Since surface smoothness is strongly affected by crystallization, the development of larger crystalline regions and increased crystal content results in increased light scattering and reduced specular reflection. The lower gloss observed for F3 is associated with the formation of anorthite and wollastonite phases. These crystalline phases increase surface roughness and modify the interaction between incident light and the glaze surface, resulting in a whiter and more opaque appearance. Therefore, the decrease in gloss is not simply a consequence of firing behavior but is directly related to the extent and nature of crystallization controlled by the S ratio. The F2 composition contained willemite crystals; however, the possible formation of anorthite in this system also contributed to a reduction in gloss compared with F1. The presence of zinc-containing crystalline phases and calcium aluminosilicates indicates that intermediate S ratios promote a more complex crystallization behavior, where several crystalline phases coexist and influence optical scattering.

The CIE color parameters further confirmed the tendency of the developed glass–ceramic glazes toward white coloration. The L*, a*, b* values indicated that the investigated compositions exhibited a

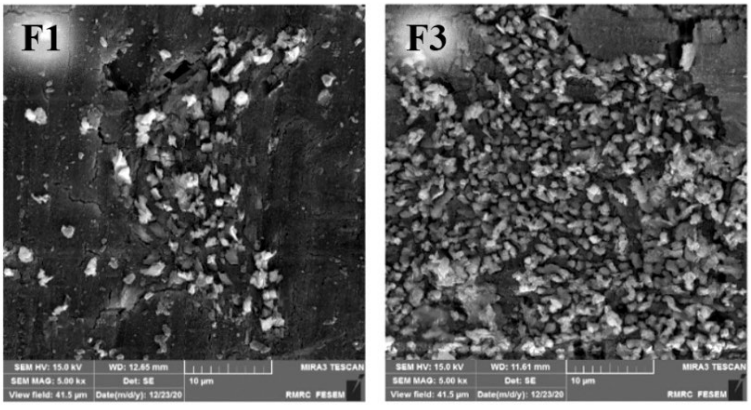

Fig. 4. FESEM micrographs of F1 and F3 (Reused from Ref. [24], licensed under CC BY 4.0).

predominantly white appearance, with the whiteness index of the relevant compositions reaching approximately 65%. The optical response therefore reflects the balance between residual glass transparency and crystalline phase formation. These results demonstrate that the S ratio provides an effective approach for controlling the transparency–crystallinity balance in borosilicate glazes. While increased crystallization can improve mechanical properties, excessive formation of crystalline phases such as anorthite and wollastonite reduces gloss and transparency. Therefore, optimization of the S ratio is essential for achieving the desired combination of optical quality and functional performance.

3.6. Mechanical performance

The mechanical performance of the transparent borosilicate glazes was evaluated through Vickers microhardness measurements. The hardness values of F1, F2, and F3 were 730 ± 14, 744 ± 20, and 817 ± 35 Hv, respectively. The microhardness values exhibited a clear dependence on the S ratio and the resulting crystalline phase assemblage. Among the investigated compositions, F3 showed the highest hardness value of 817 ± 35, whereas F1 exhibited the lowest hardness value of 730 ± 14 Hv. This behavior demonstrates that increasing the relative contribution of CaO and ZnO promotes the formation of harder crystalline phases and improves the mechanical resistance of the glaze. The superior hardness of F3 is attributed primarily to the formation of anorthite, which possesses a higher hardness compared with the calcium silicate phases present in other compositions. The higher proportion of divalent cations in the residual glass phase also contributes to the increased hardness of F3 compared to F2. The stronger interaction of Ca^{2+} and Zn^{2+} with the glass network increases structural rigidity and enhances resistance to indentation. In contrast, the lower hardness observed for F1 is related to the higher amorphous fraction and the presence of wollastonite, which has a lower hardness value compared with anorthite. The higher $K_2O/(CaO+ZnO)$ ratio reduces the extent of crystallization and results in a softer glass–ceramic structure dominated by the residual glass phase. The correlation between microhardness, phase evolution, and microstructure confirms that the mechanical performance of transparent borosilicate glazes is governed by composition-controlled crystallization. Lower S ratios promote the development of rigid crystalline phases, particularly anorthite, resulting in improved hardness. Therefore, controlling the S ratio provides an effective method for tailoring the mechanical properties of glass–ceramic glazes while maintaining control over their optical characteristics.

Table 3. Optical parameters and gloss values of the glazes prepared with different S ratios.

Sample	c*	b*	a*	L*	Gloss
F1	11.27	-5.95	9.56	51.57	86.1
F2	1.77	0.47	1.70	74.41	83.2
F3	2.33	-0.04	2.33	76.53	67.30

4. Conclusions

This study investigated the effect of the $K_2O/(CaO+ZnO)$ ratio on the crystallization behavior, phase evolution, microstructural development, optical properties, and mechanical performance of transparent borosilicate glass–ceramic glazes in the SiO_2–Al_2O_3–B_2O_3–ZnO–CaO–K_2O system. The results demonstrated that decreasing the $K_2O/(CaO+ZnO)$ ratio significantly enhanced the thermal stability of the parent glass, as evidenced by the increase in glass transition temperature, while only slightly affecting the crystallization peak temperature. FTIR analysis revealed that modifying the relative proportions of K_2O, CaO, and ZnO altered the connectivity and stability of the borosilicate glass network without changing its fundamental structural framework, thereby influencing the subsequent crystallization process. XRD analysis showed that the modifier ratio governed the crystalline phase assemblage formed during firing, promoting the development of anorthite, willemite, and calcium silicate phases with varying relative abundances depending on composition. These compositional changes were further confirmed by FESEM observations, which revealed systematic variations in crystal morphology, phase distribution, and the degree of crystallization, indicating a strong correlation between glass composition and microstructural evolution. The optical properties were also closely associated with the crystallization behavior, where increased formation of crystalline phases, particularly anorthite and wollastonite, reduced the gloss of the fired glazes due to enhanced light scattering. Furthermore, the microhardness increased with decreasing $K_2O/(CaO+ZnO)$ ratio, and the highest hardness was obtained for the composition containing the lowest S ratio owing to the formation of harder crystalline phases and a more rigid glass network. Overall, the results demonstrate that the $K_2O/(CaO+ZnO)$ ratio is an effective compositional parameter for tailoring the structure–property relationships of transparent borosilicate glass–ceramic glazes, providing a practical approach for optimizing the balance between crystallization behavior, microstructure, optical characteristics, and mechanical performance in advanced ceramic glaze systems.

CRediT authorship contribution statement

Raziye Salami: Conceptualization, Methodology, Writing – original draft.
Aida Faeghinia: Supervision, Funding acquisition.
Zahra Khakpour: Supervision, Writing – review & editing.
Mohammad Zakeri: Project administration, Resources.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

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Declaration of generative AI and AI-assisted technologies in the writing process

The authors declare that ChatGPT (OpenAI GPT-5.5) was used for language editing, grammatical corrections, and stylistic improvement of this manuscript. Following the AI-assisted revisions, the authors carefully reviewed and edited the entire manuscript and take full responsibility for its accuracy, originality, and scientific content.

References

[1] S. Wang, X. Li, C. Wang, M. Bai, X. Zhou, et al., Anorthite-based transparent glass-ceramic glaze for ceramic tiles: Preparation and crystallization mechanism, J. Eur. Ceram. Soc. 42 (2022) 1132–1140. https://doi.org/10.1016/j.jeurceramsoc.2021.11.036.

[2] Z. Bao, S. Wang, L. Miao, Y. Xu, Z. Cheng, X. Wang, Preparation, properties and formation mechanism of transparent anorthite-based glass-ceramic glaze with high hardness, Ceram. Int. 50 (2024) 26182–26192. https://doi.org/10.1016/j.ceramint.2024.04.359.

[3] O.J. Akinribide, G.N. Mekgwe, S.O. Akinwamide, F. Gamaoun, C. Abeykoon, et al., A review on optical properties and application of transparent ceramics, J. Mater. Res. Technol. 21 (2022) 712–738. https://doi.org/10.1016/j.jmrt.2022.09.027.

[4] C. Fu, D.B. Dingwell, W. Song, High temperature composition-controlled spreading dynamics of volcanic melts, Chem. Geol. 713 (2026) 123436. https://doi.org/10.1016/j.chemgeo.2026.123436.

[5] V.E. Eremyashev, A.A. Osipov, G.G. Korinevskaya, D.E. Zhivulin, E.I. Danilina, Structural Features and Properties of Multicomponent Sodium-Cesium/Rubidium Aluminoborosilicate Model Matrix Glasses of Basis Composition, J. Struct. Chem. 65 (2024) 725–739. https://doi.org/10.1134/S0022476624040097.

[6] M. Leśniak, M. Gajek, J. Partyka, M. Sitarz, Structure and thermal properties of the fritted glazes in SiO2–Al2O3–CaO–MgO–Na2O–K2O–ZnO system, J. Therm. Anal. Calorim. 130 (2017) 165–176. https://doi.org/10.1007/s10973-017-6183-x.

[7] G. Acikbas, N. Calis Acikbas, N. Dizge, P. Belibagli, Multi-functional ceramic glazes with nano ZnO/Cu–ZnO incorporation, Ceram. Int. 50 (2024) 43800–43810. https://doi.org/10.1016/j.ceramint.2024.08.233.

[8] R. Yao, R. Zhang, T. Lang, Y. Zhou, Y. Shi, et al., Transparent zinc silicate/ zinc oxide crystallized glass-ceramics for water remediation application under visible light, Ceram. Int. 49 (2023) 10420–10427. https://doi.org/10.1016/j.ceramint.2022.11.224.

[9] R.F. Samigullina, I. V. Ivanova, N.A. Zaitseva, T.I. Krasnenko, Solid-state synthesis of the Zn2SiO4:Mn phosphor: Sequence of phase formation, localization and charge state of Mn ions in the intermediate and final reaction products, Opt. Mater. (Amst). 132 (2022) 112788. https://doi.org/10.1016/j.optmat.2022.112788.

[10] Z. Yang, Q. Lin, S. Lu, Y. He, G. Liao, Y. Ke, Effect of CaO/SiO2 ratio on the preparation and crystallization of glass-ceramics from copper slag, Ceram. Int. 40 (2014) 7297–7305. https://doi.org/10.1016/j.ceramint.2013.12.071.

[11] H. Shendy, G.A. Khater, M.G. Shahien, A.M. Zayed, Preparation of innovative glass-ceramic materials based on mica schist within the CaO–MgO–Al2O3–SiO2 system, Open Ceram. 17 (2024) 100545. https://doi.org/10.1016/j.oceram.2024.100545.

[12] Y. Yu, S. Wang, Y. Xu, P. Wang, Y. Zhao, et al., Effect of K2O on the glass structure, crystallization behavior, and properties of non-stoichiometric cordierite glass-ceramics, Ceram. Int. 52 (2026) 19149–19164. https://doi.org/10.1016/j.ceramint.2026.03.013.

[13] L. Chen, Y. Dai, Structure, physical properties, crystallization and sintering of iron-calcium-aluminosilicate glasses with different amounts of ZnO, J. Non. Cryst. Solids. 452 (2016) 45–49. https://doi.org/10.1016/j.jnoncrysol.2016.08.017.

[14] G. Chen, Effect of ZnO addition on properties of cordierite-based glass-ceramics, J. Mater. Sci. Mater. Electron. 18 (2007) 1253–1257. https://doi.org/10.1007/s10854-007-9283-8.

[15] J. Partyka, K. Thomas, P. Katarzyna, K. Karolina, K. Dawid, The impact of nano-quartz and the CaO/MgO molar ratio on the surface and mechanical properties of transparent glazes, Ceram. Int. 51 (2025) 39983–39991. https://doi.org/10.1016/j.ceramint.2025.06.231.

[16] H. Yuan, S. Shen, X. Tong, Q. Li, Y. Huang, et al., Ternary modifier engineering (Na2O–K2O–CaO) in lithium disilicate glass-ceramics: Crystallization pathways, microstructure, and mechanical performance, Ceram. Int. 52 (2026) 22492–22502. https://doi.org/10.1016/j.ceramint.2026.03.312.

[17] D. Kim, H.-J. Kim, S.-I. Yoo, Effect of ZnO/K2O ratio on the crystallization sequence and microstructure of lithium disilicate glass-ceramics, J. Eur. Ceram. Soc. 39 (2019) 5077–5085. https://doi.org/10.1016/j.jeurceramsoc.2019.05.032.

[18] J.J. Reinosa, F. Rubio-Marcos, E. Solera, M.A. Bengochea, J.F. Fernández, Sintering behaviour of nanostructured glass-ceramic glazes, Ceram. Int. 36 (2010) 1845–1850. https://doi.org/10.1016/j.ceramint.2010.03.029.

[19] A. Faeghinia, Z. Khakpour, R. Salami, M. Zakeri, K, Ca, and Zn Ratios Affect Glass Frit Properties, Adv. Ceram. Prog. 11 (2025) 1–11. https://doi.org/10.30501/acp.2025.491648.1172.

[20] M. Kumar, A. Kumar, K. Singh, Effect of K2O/SrO on structural, thermal, optical, and mechanical properties of SiO2 –B2O3 –SnO2 glass for IT/LT-SOFC applications, RSC Adv. 16 (2026) 26083–26098. https://doi.org/10.1039/D5RA10040B.

[21] N. Ma, H. Liang, Z. Luo, L. He, A. Lu, Effect of partial substitution of K2O by MgO on the structure, and thermal, physical, optical properties and crystallization behaviour of K2O–MgO–B2O3–P2O5 glasses, Ceram. Int. 50 (2024) 32306–32321. https://doi.org/10.1016/j.ceramint.2024.06.038.

[22] Z. Jin, H. Yang, J. Lv, L. Tong, G. Chen, Q. Zhang, Effect of ZnO on Viscosity and Structure of CaO–SiO2–ZnO–FeO–Al2O3 Slags, JOM. 70 (2018) 1430–1436. https://doi.org/10.1007/s11837-017-2660-8.

[23] R. Oueslati-Omrani, A. Agrebi, I. Khattech, A.H. Hamzaoui, The influence of ZnO additions on the structural, optical and thermochemical studies of Li2O-ZnO P2O5 phosphate glasses, J. Non. Cryst. Solids. 614 (2023) 122408. https://doi.org/10.1016/j.jnoncrysol.2023.122408.

[24] R. Salami, A. Faeghinia, Z. Khakpour, M. Zakeri, Effect of ZnO particle size on the sintering behavior, phase evolution, and optical properties of transparent borosilicate glazes, Synth. Sinter. 6 (2026) 26–34. https://doi.org/10.53063/synsint.2026.61300.