

Highly toughened translucent glass matrix nanoceramics enhanced by amorphous Al_2O_3

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ABSTRACT: The introduction of glass matrix ceramics in dental restorations has revolutionized dental aesthetics. A key challenge in the development of dental glass ceramics is achieving nanocrystalline glass ceramics with superior mechanical properties without compromising translucency. In this study, ZrO_2 - SiO_2 glass ceramics doped with amorphous Al_2O_3 were investigated to address these requirements. The results indicate that the segregation of Al^{3+} at the grain boundaries of ZrO_2 crystallites and the nano-domains of amorphous Al_2O_3 significantly influences the microstructure, including the grain size and stabilization of tetragonal ZrO_2 , as well as the translucency and mechanical properties. The composition with 10 mol% Al_2O_3 exhibits the highest toughness of $8.05 \text{ MPa}\cdot\text{m}^{1/2}$ while maintaining excellent translucency. Moreover, the composition with 5 mol% Al_2O_3 demonstrates lower translucency but achieves a high flexural strength of 960 MPa. Overall, the mechanical properties of these translucent glass matrix ceramics surpass those of commercially available dental glass ceramics, highlighting their potential for dental restoration applications.

KEYWORDS: dental restorative material; nanocrystalline glass ceramics; ZrO_2 - SiO_2 ; translucency; mechanical properties

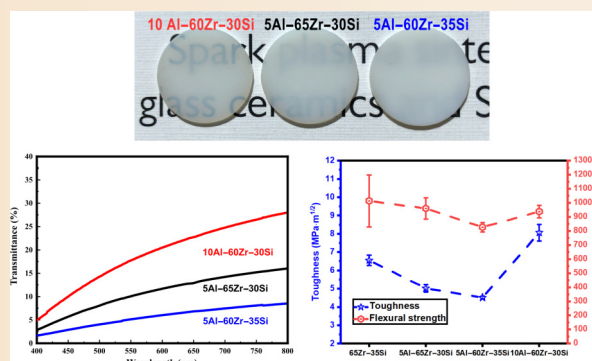
1 Introduction

The introduction of zirconia-based ceramics, particularly yttria-stabilized tetragonal zirconia polycrystalline containing 3 mol% yttria (3Y-TZP), has revolutionized dentistry, enabling the development of all-ceramic crowns and fixed dental prostheses (FDPs) [1,2]. However, since TZP ceramics are generally opaque, an esthetic porcelain veneer layer is normally deposited on the surface to improve their aesthetic appearance. This veneer layer is susceptible to debonding or chipping because it is more prone to subcritical crack growth, leading to clinical restoration failure [1]. Therefore, a material that is highly strong and that maintains good translucency is required for dental applications.

Translucent glass ceramics (GCs) have attracted considerable attention in recent years. Various types of glass ceramics with superior translucency have been developed and commercialized, including mica-based GC (Dicor, Leucite-based GC (IPS Empress) and lithium disilicate (IPS e.max Press) [3,4]. Unlike sintered ceramics, which normally require sintered aid to improve density, glass ceramics are inherently free of porosity [5] if prepared via controlled crystallization of bulk glasses. Additionally, since the composition of crystalline and amorphous glassy phases can be controlled by simply varying the raw powders

and thermal treatment temperature, their properties can be tailored to meet specific requirements [5]. Their surfaces can also be readily modified through acid etching (e.g., HF), making them suitable for bonding applications. Combination of these properties predestined them to be promising candidates for dental restoration. However, their brittleness and low fracture resistance remain significant limitations. Typical commercialized GCs have a toughness of 0.7 – $1.5 \text{ MPa}\cdot\text{m}^{1/2}$, while enamel has a toughness of 0.6 – $3 \text{ MPa}\cdot\text{m}^{1/2}$ and cortical bone has a toughness of 2 – $12 \text{ MPa}\cdot\text{m}^{1/2}$ [4]. The problems of poor damage tolerance limit their application only for inlays, onlays, and small anterior restorations. Various methods have been explored to improve the mechanical properties of glass ceramics. A typical example is the ceramics doped with ZrO_2 utilizing the phase transformation toughening effect of ZrO_2 . The incorporation of 11 – $16 \text{ wt\%}$ ZrO_2 into GCs (such as lithium silicate and mica-based GCs) could increase the toughness by approximately 60% [3,4].

Recently, ZrO_2 - SiO_2 nanocrystalline glass ceramics have been developed in which ZrO_2 nanocrystals are embedded into the amorphous SiO_2 matrix [4,6]. While maintaining high translucency, these ZrO_2 - SiO_2 glass ceramics have a high bending strength of up to 1014 MPa and an indentation fracture toughness of up to $6.5 \text{ MPa}\cdot\text{m}^{1/2}$. The toughening mechanism is attributed to



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a three-dimensional (3D) nanostructure formed by interconnected ZrO_2 nanocrystals at the grain boundaries [7]. In this structure, the crystalline phase bears the majority of stress, and the stress-induced phase transformation of ZrO_2 effectively inhibits crack propagation. To further enhance the properties of these glass ceramics, yttrium oxide has been introduced as a dopant. The yttrium ions were found to segregate at the grain boundaries (GBs) of ZrO_2 crystals, and this segregation increased the work of separation [8,9]. The maximum flexural strength achieved in this material is 673 MPa, while the toughness is $6.69 \text{ MPa}\cdot\text{m}^{1/2}$. The segregation of yttrium ions at the grain boundaries is of great interest. This segregation tendency is attributed to the charge and ionic radius mismatch between Y^{3+} and Zr^{4+} .

Owing to its high mechanical strength and good wear performance [10], Al_2O_3 , which is widely used in prosthetic bearings, has also shown potential for improving the mechanical properties of glass ceramics. The segregation of Al^{3+} at the grain boundaries is expected due to its size and charge mismatch with Zr^{4+} , as well as its low solubility in TZP [11]. Based on this understanding, Al_2O_3 was selected as a dopant in this study to modulate the transparency and mechanical properties of ZrO_2 - SiO_2 nanocrystalline glass ceramics through interface segregation of Al^{3+} ions. Three different compositions of Al_2O_3 - ZrO_2 - SiO_2 were synthesized and sintered using spark plasma sintering (SPS). The effects of Al_2O_3 dopant on the microstructure and optical and mechanical properties of the ZrO_2 - SiO_2 nanocrystalline material are systematically investigated and discussed.

2 Materials and characterization

2.1 Powder synthesis and glass ceramic sintering

The raw Al_2O_3 - ZrO_2 - SiO_2 powders were prepared by a sol-gel route. The sol solution was prepared by mixing solution A with B. Specifically, solution A was prepared by mixing and stirring tetraethyl orthosilicate (TEOS, Sigma-Aldrich, USA) with ethanol ($\text{EtOH} > 99\%$) and HCl (aqueous, 0.4 mol/L) to initiate hydrolysis and polycondensation of tetrahedra silica colloidal particles; while solution B was prepared by dissolving aluminium isopropoxide ($\text{C}_9\text{H}_{21}\text{AlO}_3$, Sigma-Aldrich, USA) into 1-propanol (99.7%, Sigma-Aldrich, USA) and tetrapropyl zirconate (TPZ, 70 wt% in 1-propanol, Sigma-Aldrich, USA). Three different compositions were prepared, namely, 5 mol% Al_2O_3 -65 mol% ZrO_2 -30 mol% SiO_2 , 5 mol% Al_2O_3 -60 mol% ZrO_2 -35 mol% SiO_2 , and 10 mol% Al_2O_3 -60 mol% ZrO_2 -30 mol% SiO_2 , which were designated as 5Al-65Zr-30Si, 5Al-60Zr-35Si, and 10Al-60Zr-30Si, respectively. A concentrated HCl solution was added to the mixed solution drop by drop to initiate final polymerization, and then the sol was aged in an oven at 60 °C for three days. Afterwards, the gel was dried at 120 °C for 24 h to remove water and organic solvents, followed by planetary ball milling for 45 min. The residual organics and chemisorbed hydroxyls were removed by calcination at 600 °C for 1 h.

The dense nanocrystalline glass ceramics were obtained by sintering in a spark plasma sintering system (SPS 825, Fuji Electronic Industrial Co., Ltd., Japan). The heat treatment process was as follows: the sintering die was heated to 366 °C within 2 min, then to 900 °C at a ramping rate of 120 °C/min, and subsequently to 1150 °C at a ramping rate of 30 °C/min. The sample was dwelled at 1150 °C for 5 min. A pressure of 60 MPa was applied during the sintering process. After sintering, the samples were polished to remove the residual surface graphite

paper. Finally, the samples were annealed in a furnace at 800 °C for 1 h to eliminate possible oxygen vacancies and residual stress.

2.2 Microstructure and property characterization

The phase compositions of the raw powders and SPS-sintered samples were characterized by an X-ray diffractometer (XRD; D8 Advance, Bruker, Germany). The grain sizes were calculated by the Scherrer equation. The volume percentages of the monoclinic and tetragonal phases were calculated via Profex software using Rietveld refinement. The surface morphology of the as-sintered samples and fracture surface after mechanical testing were observed by a scanning electron microscope (SEM; Merlin, Zeiss, Germany). To identify the ZrO_2 grain morphology, the as-sintered samples were soaked in a 48% HF bath for 2 min to remove the SiO_2 matrix. The nanoscale structures of the selected samples were analyzed by a transmission electron microscope (TEM; Titan 80-300, FEI Company, the Netherlands). Images were obtained by different imaging modes, including bright-field TEM (BF-TEM), high-resolution TEM (HR-TEM), and high-angle annular dark-field scanning TEM (HAADF STEM). The elemental distributions were obtained from energy-dispersive X-ray spectroscopy (EDS).

The light transmittance was defined as the ratio of the intensity of transmitted light to the incident light, which was recorded by an ultraviolet-visible (UV-Vis) spectrophotometer (UV-1800, Shimadzu, Japan). The samples were mirror-polished to a thickness of 1 mm before characterization.

The nano-hardness and elastic modulus were measured on a nanoindentation tester (Ultra nano-indenter, CSM Instruments, Switzerland) with an applied load of 8000 μN and a speed of 8000 $\mu\text{N}/\text{min}$. At least 20 indentations were performed on each sample. The microhardness was tested on a Vickers indentation tester (Buehler Micromet 2014, Lake Bluff, USA) under a load of 2 kgf. The crack lengths and diagonal lengths of indentation marks were measured by the software installed on the machine. The fracture toughness (K_{IC}) was calculated according to the equation proposed by Niihara and Palmqvist: $K_{\text{IC}} = 0.0264 H_V a (E/H_V)^{2/5} (l^{-1/2})$ [12], where H_V is the Vickers hardness; E is the elastic modulus obtained from nano-indentation; a is the average indentation half-diagonal; l is the average crack length originating from the indentation mark corners.

The flexural strength was measured with the piston-on-three ball method on a universal testing machine (Autograph AGS-H; Shimadzu, Japan). The flexural strength (S) is calculated by the equation: $S = -0.2387[P(X - Y)]/d^2$, where d is the sample thickness; X and Y are determined by the equations: $X = (1 + \gamma) \ln(B/C)^2 + [(1 - \gamma)/2] \ln(B/C)^2$ and $Y = (1 + \gamma) [1 + \ln(A/C)^2] + (1 - \gamma) \ln(A/C)^2$, where γ is Poisson's ratio (0.3); B is the radius of the piston tip (0.8 mm); C is the radius of samples; A is the radius of the supported circle (3.445 mm) [6].

3 Results and discussion

3.1 Characterizations of raw powders

The XRD patterns of the calcined powders are shown in Fig. 1(a). No sharp peaks were observed in all XRD patterns, with only a broad peak appearing at approximately 30°. No diffraction peaks of crystalline SiO_2 or Al_2O_3 were observed, indicating that SiO_2 and Al_2O_3 remained in an amorphous state. The microstructure of the calcined powders was further characterized by TEM, as shown in Figs. 1(b)–1(d). The nano-sized particles were agglomerated into micron-sized particles with polyhedral shapes (Fig. 1(b)). The particles demonstrated an amorphous structure, without lattice fringes, as observed in the HR-TEM image (Fig. 1(c)), and the

selected area electron diffraction (SAED) pattern demonstrated the amorphous nature of 10Al–60Zr–30Si powder (Fig. 1(c)). However, some nanocrystallites with sizes smaller than 10 nm were formed, with organized lattice fringes observed within the nanocrystallites (Fig. 1(e)). Figure 2 illustrates the elemental distribution of the powders, indicating a uniform distribution of Zr, Al, Si, and O elements.

Calcination, beyond its role in removing organic residues, plays a crucial role in modifying both the crystalline phase and morphology of ZrO_2 . In pure ZrO_2 , the tetragonal phase initially forms during heat treatment but transforms into the monoclinic phase as the temperature increases to 550 °C [13]. By controlling particle size or chemical impurities, tetragonal ZrO_2 can be stabilized at room temperature [14]. The tetragonal (t) phase can persist at low temperatures when the particle size is below a critical size (~ 30 nm diameter for pure ZrO_2), due to its lower surface energy compared to that of the monoclinic (m) phase [15]. Additionally, the $t \rightarrow m$ phase transformation temperature could be adjusted by the introduction of secondary compounds such as Y_2O_3 [16], CeO_2 [17], and CaO [18]. Amorphous SiO_2 could effectively stabilize the tetragonal phase at temperatures up to 1200 °C due to the strong confinement effect of amorphous silica and strong covalent Si–O–Zr interactions [13,14,19].

3.2 Phase composition and microstructure of sintered samples

Figure 3(a) shows the XRD patterns of the sintered samples. Strong diffraction peaks were found at approximately $2\theta = 30^\circ$, 50° , and 60° , corresponding to (101), (112), and (211) lattice planes of t- ZrO_2 , respectively. This indicated that the samples were mainly composed of t- ZrO_2 . A small amount of m- ZrO_2 was also observed. There were no diffraction peaks for crystalline SiO_2 and

Al_2O_3 , indicating that these two components exhibited an amorphous structure. The volume fraction of the monoclinic phase was calculated using the Rietveld refinement, and the results are summarized in Fig. 3(b). The 5Al–65Zr–30Si sample showed the highest amount of monoclinic phase, at 4.2%. The monoclinic phase decreases with increasing amount of doped Al^{3+} , reaching a minimum in 10Al–60Zr–30Si at 2.2%. A similar trend was also found for the grain size of t- ZrO_2 (Fig. 3(c)), in which the grain size decreased from 44.6 ± 3.6 to 38.0 ± 0.6 nm with increasing amounts of doped Al^{3+} . Figure 4 presents the surface morphology of the samples characterized by SEM. To identify the shape and size of ZrO_2 crystals, the amorphous SiO_2 matrix was removed by HF for observation. The particles exhibited nearly spherical morphologies, with a uniform size distribution and smaller grains interconnected.

The nanoscale structure of the sintered 10Al–60Zr–30Si sample was characterized via TEM. In STEM-HAADF mode, the ZrO_2 crystallites appeared as bright ellipsoidal grains due to the higher atomic number of zirconium, which led to stronger electron scattering (Fig. 5(a)). These nanocrystallites were homogeneously distributed within the amorphous SiO_2 matrix and exhibited a Gaussian size distribution, ranging from 15 to 55 nm, with an average size of 33.3 nm. Figures 5(b) and 5(c) show HR-TEM images of the sample. Lattice fringes with a spacing of 3.03 Å within the grains are observed, which are indexed as (101) lattice plane of ZrO_2 crystalline. A distinct intergranular interface with a thickness of approximately 0.8 nm was identified between adjacent grains (Fig. 5(c)). This interfacial layer thickness is close to the equilibrium thickness of the intergranular glass phase proposed by Clarke, where a thickness of 0.7 nm is predicted for TZP/ SiO_2 systems [20,21]. The formation of such an interfacial layer (also referred to as an interfacial glassy film (IGF)) is believed

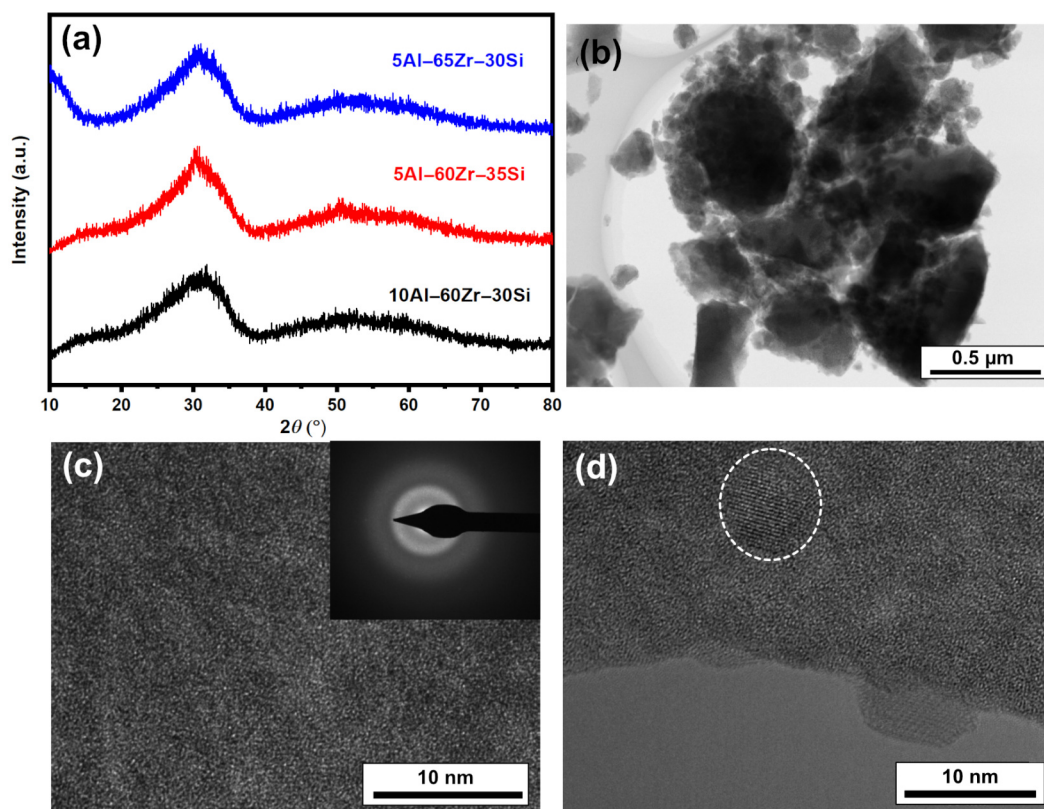


Fig. 1 Structural characterization of calcined powders: (a) XRD patterns of calcined powders; (b) BF-TEM image of calcined 10Al–60Zr–30Si powder; (c, d) HR-TEM images of calcined 10Al–60Zr–30Si powder (inset of (c): SAED pattern).

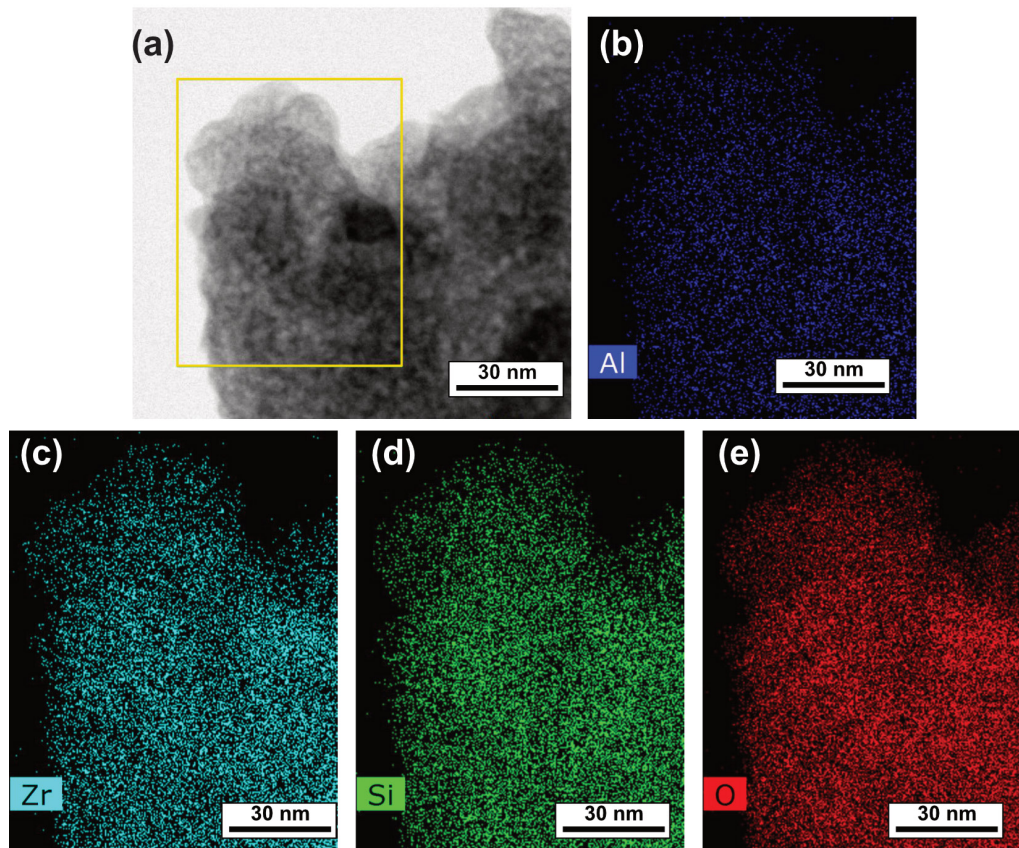


Fig. 2 STEM-EDX results of calcined 10Al-60Zr-30Si powder: (a) BF-TEM image; (b) Al, (c) Zr, (d) Si, and (e) O maps.

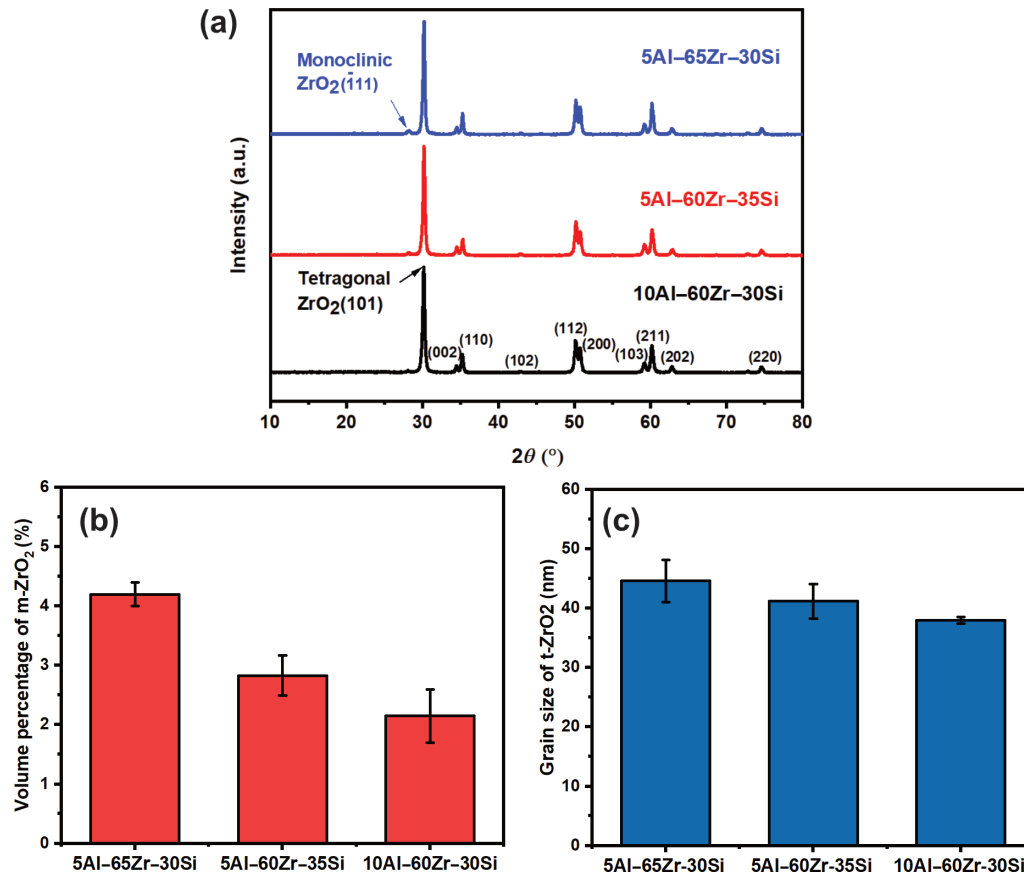


Fig. 3 (a) Representative XRD patterns of SPS-sintered Al_2O_3 -doped ZrO_2 - SiO_2 glass ceramics; (b) volume percentage of monoclinic ZrO_2 phase; and (c) grain size of tetragonal ZrO_2 . Both volume percentage and grain size were calculated using Rietveld refinement.

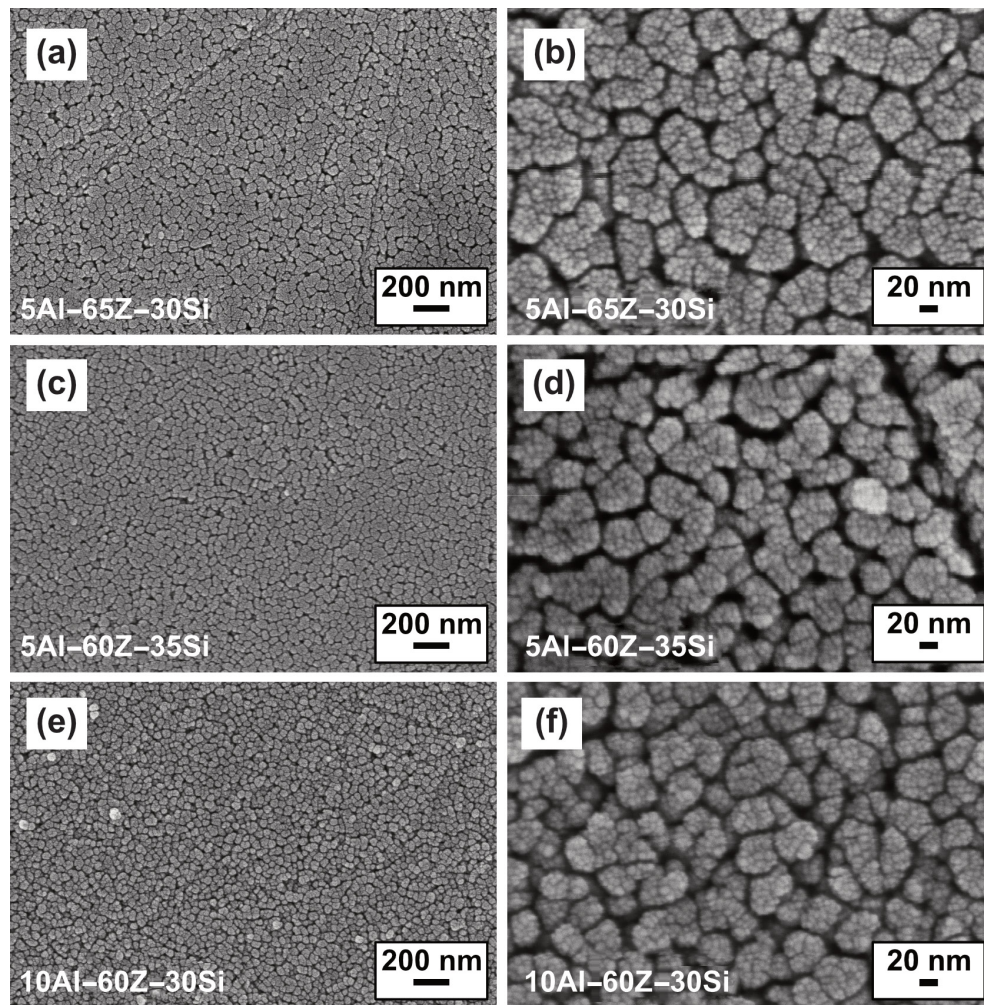


Fig. 4 Surface morphology of glass ceramics sintered by SPS after etching with HF.

to be attributed to the balance between the attractive van der Waals-dispersion force and repulsive structural force [21].

3.3 Optical performance

The transmittance results of the annealed samples are presented in Fig. 6. Notably, this method can only qualitatively compare the transmittance difference within the same sample group under same testing conditions, as the transmittance is strongly influenced by the distance between the detector and tested samples. The transmittance clearly increases with increasing wavelength (λ). This trend could be explained by Mie theory, where the scattering coefficient is inversely proportional to λ^{-4} [22]. Thus, severe scattering occurs at lower wavelengths, resulting in lower transmittance. Among the samples, 10Al-60Zr-30Si sample exhibits the highest transmittance, while 5Al-60Zr-35Si shows the lowest transmittance. The optical images (inset of Fig. 6) further highlight the differences in translucency: 10Al-60Zr-30Si sample has white translucent appearance, whereas 5Al-65Zr-30Si exhibits lower translucency.

To obtain a transparent material, it is crucial to reduce light scattering caused by pores, grain boundary, and second phase [22]. In glass ceramics, the birefringence of the crystal and the refractive index difference between the amorphous matrix and crystals are the main factors causing light scattering. In this study, the refractive indices of t-ZrO₂, SiO₂, and Al₂O₃ are 2.15, 1.46, and 1.76, respectively. It has been reported that a refractive index

difference of 0.09 can cause significant scattering [23], indicating that the high translucency of the annealed 10Al-60Zr-30Si samples could not be explained by the refractive index difference. The grain size, on the other hand, is another critical factor influencing scattering. The scattering coefficient increases sharply with increasing grain size and reaches a maximum when the grain size is close to the wavelength [22]. Klimke *et al.* [24] reported that the in-line transmittance of t-ZrO₂ increased from 50% to 70% when the grain size was reduced from 40 to 20 nm. Therefore, in our study, 10Al-60Zr-30Si, with the smallest grain size, exhibits better translucency. In addition, porosity can be detrimental to transmittance, and even 0.01 vol% porosity within the ceramics could induce huge scattering [22]. In this study, the density of the samples was measured by the Archimedes method, and we did not observe any significant differences between the different groups. The density of all the samples was above 99.9%. Furthermore, no visible pores can be observed from the fracture surface (Fig. 8) or TEM image (Fig. 5), indicating the high density of SPS-sintered Al₂O₃-ZrO₂-SiO₂ samples.

Furthermore, annealing has been shown to improve the translucency of samples. This enhancement in translucency and reduction in discoloration can be attributed to the elimination of color centers. Aliovalent ions with lower valence states (such as Mg²⁺, Y³⁺, and Al³⁺) could induce the formation of both cation and oxygen vacancies through the substitution of Zr⁴⁺. The substitution of Al³⁺ ions could be expressed in the following equation:

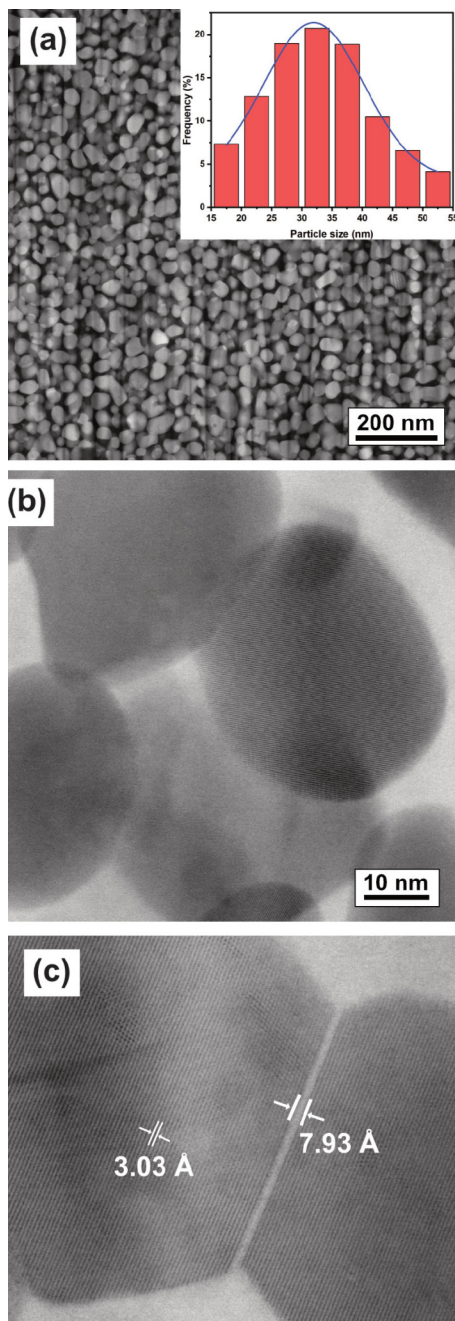


Fig. 5 Representative TEM images of sintered 10Al-60Zr-30Si sample: (a) BF-TEM image (inset: grain size distribution); (b, c) HR-TEM images of sample showing positions of grains within silica matrix and grain boundaries.

$\text{Al}_2\text{O}_3 \xrightarrow{\text{ZrO}_2} 2\text{Al}'_{\text{Zr}} + \text{V}_{\text{O}} + 3\text{O}_{\text{O}}$ [23]. These vacancies trap one or two electrons to form color centers [25]. These color centers are defects that cause selective absorption and therefore reduce the transmittance of the samples. Moreover, during SPS in a graphite die under vacuum, a reducing atmosphere (CO/CO_2) is generated, leading to the formation of oxygen vacancies [26]. The reducing atmosphere and high electric current are the driving forces behind the formation of color centers [25,27]. These color centers can be removed by annealing in air or an oxygen atmosphere at an adequate temperature [27,28].

3.4 Mechanical properties

The mechanical properties of the studied samples are illustrated in Fig. 7. For comparison, the properties of samples with a

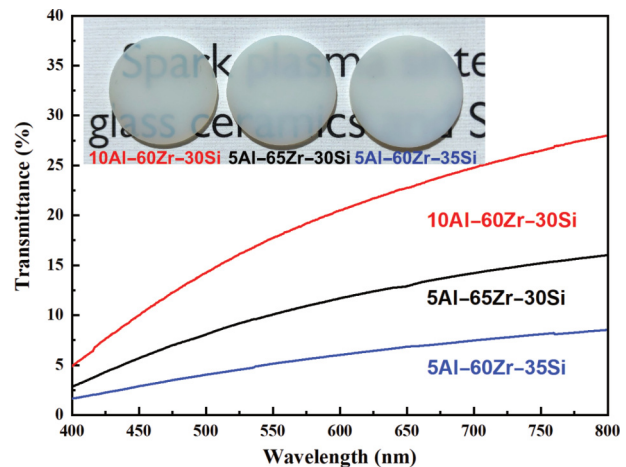


Fig. 6 Transmittance of SPS sintered glass ceramics (inset: optical appearance of annealed samples).

composition of 65 mol% ZrO_2 –35 mol% SiO_2 were also included [6]. Among the samples, the 10Al-60Zr-30Si samples exhibited the highest nano-hardness and elastic modulus, which were 12.87 ± 0.44 and 164.1 ± 2.9 GPa, respectively. In contrast, the 5Al-60Zr-35Si samples, which contained the lowest amounts of Zr and Al, showed the lowest hardness and elastic modulus values, which were 10.82 ± 0.15 and 135.1 ± 2.5 GPa, respectively. This difference is primarily due to ZrO_2 grains being harder than SiO_2 amorphous matrix. Moreover, according to the Hall-Petch theory, smaller grain sizes increase hardness by inhibiting dislocation motion, as smaller grains increase the energy required for dislocations to bypass neighboring grains [29]. Consequently, the 10Al-60Zr-30Si samples with the smallest grain size exhibited higher hardness values than the 5Al-65Zr-30Si samples.

The fracture toughness followed a similar trend as the hardness and elastic modulus. The 10Al-60Zr-30Si samples exhibited the highest fracture toughness of $8.06 \pm 0.45 \text{ MPa}\cdot\text{m}^{1/2}$, while the 5Al-65Zr-30Si and 5Al-60Zr-35Si samples showed lower toughness values of 5.02 ± 0.21 and $4.51 \pm 0.08 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The flexural strength of the 5Al-65Zr-30Si samples ($960 \pm 75 \text{ MPa}$) was comparable to that of the 10Al-60Zr-30Si samples ($938 \pm 44 \text{ MPa}$). Conflicting results between fracture toughness and flexural strength were also found in other zirconia-toughened ceramics; that is, structural materials with higher flexural strength normally exhibited lower toughness [30,31]. This phenomenon is attributed to the stress-induced tetragonal to monoclinic phase transformation and the R-curve behavior of zirconia. R-curve behavior refers to the increase in fracture resistance (toughness) as a crack grows due to mechanisms such as phase transformation or microcracking. In zirconia, this is driven by the stress-induced phase transformation near the crack tip, which creates a zone that shields the crack from propagating easily. According to Swain and Rose [30], the toughness increment is proportional to $\sqrt{h}$ (h is the height of the transformation zone), whereas the crack propagation length (ΔL) is proportional to h . This means that the materials start to weaken (crack growth $\propto h$), while the toughness continues to increase ($\Delta K \propto \sqrt{h}$). Thus, the maximum strength is limited by the critical stress that induces phase transformation.

To further analyze the toughening behavior, the fracture morphology of the 10Al-60Zr-30Si samples was observed, as presented in Fig. 8. During crack propagation, the released fracture energy propagates through the bulk in the form of Rayleigh waves, leading to interference of the propagation wave with the stress field at the crack tip, resulting in complex crack

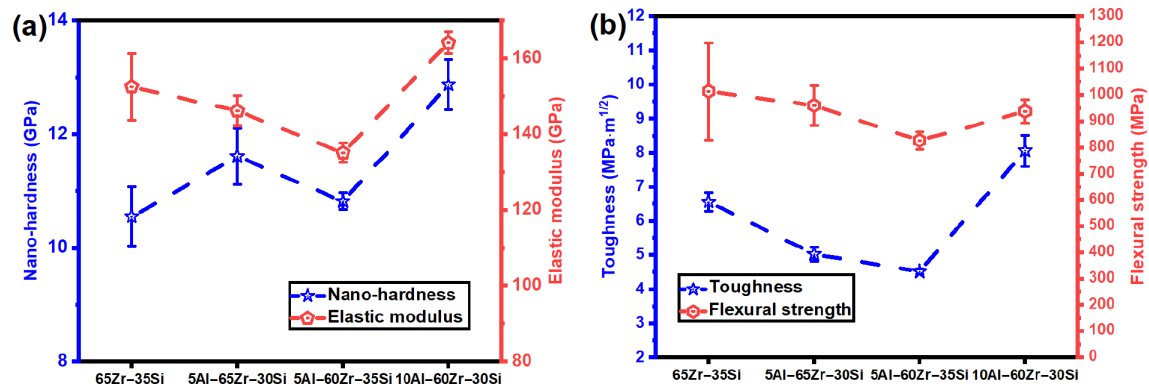


Fig. 7 Mechanical properties of Al₂O₃-ZrO₂-SiO₂ glass ceramics: (a) nano-hardness and elastic modulus; (b) toughness and flexural strength.

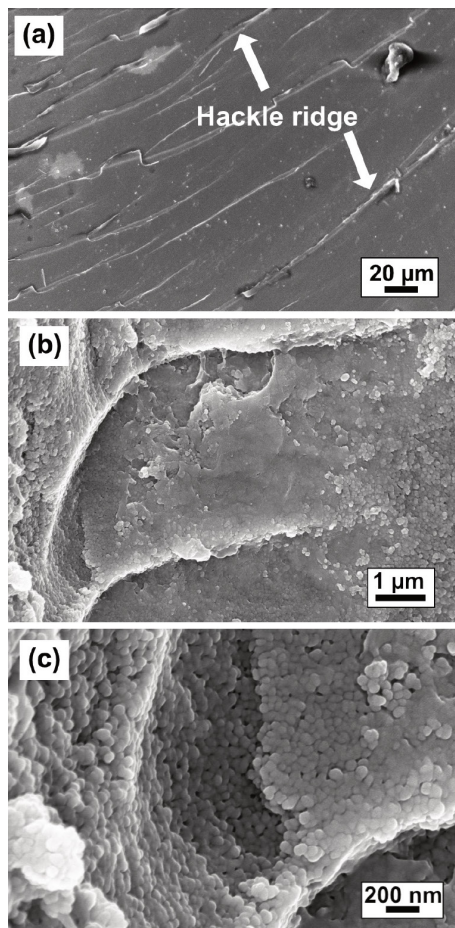


Fig. 8 Representative fracture morphologies of 10Al-60Zr-30Si samples: (a) fracture morphology at low magnification showing bifurcate river-pattern zone; (b, c) high-magnification fracture surface etched with HF gel.

morphologies [32,33]. Therefore, fracture morphologies are important for an in-depth understanding of the mechanism. The samples exhibited a high density without any visible pores. Bifurcate hackle ridges can be observed on the surface (Fig. 8(a)), which are caused by the high crack propagation velocity. According to linear elastic fracture mechanics, the toughness is closely related to propagation velocity, where $\Delta K \propto \sqrt{G}$ (G is the energy flux, which increases with velocity) [33]. Therefore, this configuration may indicate the presence of localized plasticity at the crack tip. Figure 8(c) shows the fracture surface at a higher magnification. The samples were etched with HF to remove the SiO₂ matrix and identify the ZrO₂ crystals. The nan-sized spherical ZrO₂ particles are visible on the surface.

3.5 Elemental distribution

The elemental distribution was analyzed via STEM-EDS mapping, and the results are presented in Fig. 9. The distribution of Zr and Si elements confirmed that the nanoparticles and the matrix corresponded to ZrO₂ and SiO₂ (Fig. 9(a)), respectively. Most of the Al elements were distributed in small domains, and these domains were attached to the surface of ZrO₂ nanoparticles (Fig. 9(b)). In addition, Al segregation was observed at the grain boundaries between ZrO₂ grains, forming a thin layer approximately 1 nm in depth (Fig. 9(c)). High-resolution DF-TEM images of the interface region between ZrO₂ crystallites and the surrounding amorphous matrix are presented in Fig. 10. The bright contrast in the lattice fringes corresponds to the ZrO₂ crystalline phase, with the outer layer showing amorphous Al₂O₃ segregation. The darkest region represents the amorphous SiO₂ matrix.

The driving force for the segregation of Al³⁺ at grain boundaries is of great interest. Similar grain boundary segregation of aliovalent cations in tetragonal zirconia has been reported and is explained by space charge theory [9,34]. In TZP systems doped with divalent or trivalent cations (such as Mg²⁺, Al³⁺, and Y³⁺), these aliovalent dopants substitute for Zr⁴⁺ and create oxygen vacancies. Therefore, to maintain the neutrality of the bulk material, dopants must segregate to the surface to compensate for the charge difference. As a result, dopants with lower valence states exhibit strong segregation at the grain boundaries. Moreover, the occurrence of Al³⁺ domains in the outer layer of ZrO₂ grains (Figs. 9(a) and 9(b)) could be attributed to the low solubility of Al₂O₃ in ZrO₂ at room temperature [11], thus forming Al³⁺ clusters during the cooling process of SPS.

The segregation of Al³⁺ at the grain boundaries plays an important role in stabilizing the tetragonal ZrO₂ phase and inhibiting grain growth during sintering. Since the monoclinic phase is thermodynamically more stable at room temperature, ZrO₂ is expected to undergo a martensitic transformation from the tetragonal phase to the monoclinic phase during cooling. However, this phase transformation involves a volume expansion of approximately 4%, resulting in crack formation and thus a catastrophic effect on the material performance [14,35]. Thus, it is crucial to stabilize the tetragonal phase at room temperature. The aliovalent substitution of Al³⁺ for Zr⁴⁺ creates oxygen vacancies, which reduce the driving force for the tetragonal-to-monoclinic transformation. On the other hand, the segregation of Al³⁺ at the grain boundaries could also inhibit grain growth due to reduced grain boundary mobility. In solute drag theory, cation solute determines grain boundary mobility, indicating that solute segregation makes grain boundary migration more difficult [34]. Therefore, 10Al-60Zr-30Si samples with high amounts of Al³⁺

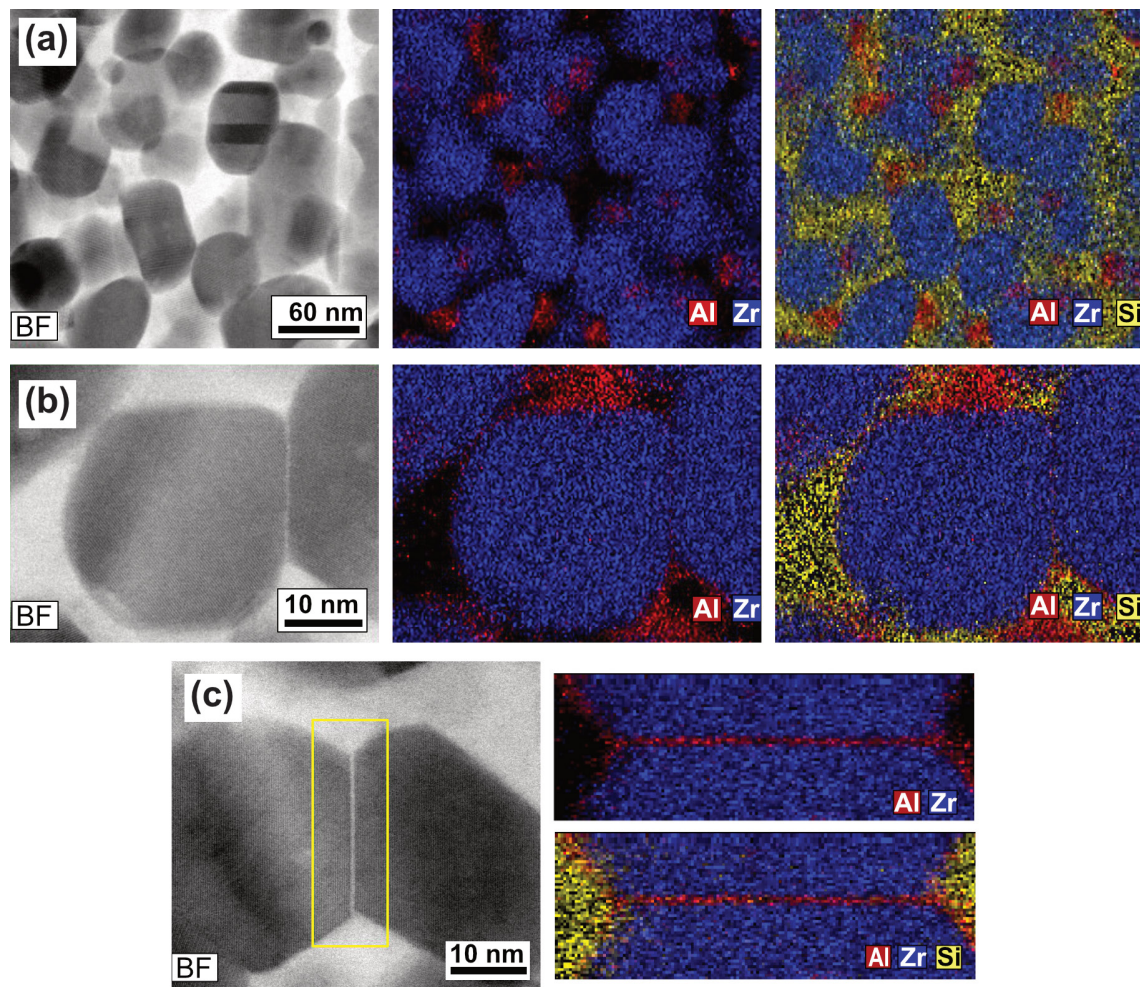


Fig. 9 STEM-EDS mapping of 10Al-60Zr-30Si samples showing elemental distribution; BF-TEM images correspond to the area where EDS mapping was carried out: (a) low magnification, (b) high magnification, and (c) high magnification focusing on the interface.

segregation exhibit good stabilization effects and strong inhibitory effects on grain growth, resulting in a low volume percentage of m-ZrO₂ and small grain sizes (Fig. 4).

3.6 Relationships between Al³⁺ segregation and toughening mechanism

The segregation of Al³⁺ at the grain boundaries affects not only the phase structure but also the grain boundary energy, which in turn affects the mechanical properties of the bulk. In previously reported ZrO₂-SiO₂ glass-ceramics, an ordered three-dimensional (3D) structure of ZrO₂ nanocrystalline was formed, resulting in high flexural strength [7]. This structure employs high fracture strength while maintaining high toughness (with a strength of 1014±185 MPa and a toughness of 6.55±0.29 MPa·m^{1/2}). Since the applied stress transfers the load effectively to ZrO₂ crystalline through the interfacial layer, the stress-induced t → m phase transformation toughening of ZrO₂ crystalline is initiated within this 3D structure [7]. The strain fields produced by phase transformation leads to intergranular fracture with crack deflection, resulting in reduced intensity of local crack tip stress and the driving force for crack propagation [36–38]. In this study, Al³⁺ segregation could lead to enhanced crack deflection due to the reduced grain size and change in bonding strength between the amorphous interfacial layer and ZrO₂ crystallites. However, this could not be the main reason for the toughening mechanism in this study because the 5% Al₂O₃-doped samples exhibit lower

toughness than the non-doped samples. The higher toughness of 10Al-60Zr-30Si could be attributed to the amorphous Al₂O₃ domains formed at the outer layer of the ZrO₂ crystalline. These domains could act as “platelets”, which could block crack propagation through crack deflection [10].

In this study, the mechanical properties are improved significantly ($K_{IC} = 8.06 \text{ MPa}\cdot\text{m}^{1/2}$) by doping 10 mol% of Al₂O₃ into 60% ZrO₂-30% SiO₂, which is superior to commercially available dental glass ceramics. Dental materials are subjected to a lot of stress due to chewing and grinding, making mechanical properties such as toughness and strength essential to avoid fracture and failure of the dental restoration. Several groups of glass ceramics have been developed, including mica-based, leucite-based, and lithium disilicate glass ceramics [4]. However, their low mechanical strength limits their application in posterior bridges or abutments (mica-based GCs have a toughness of 0.8–1.5 MPa·m^{1/2} and strength of 300–450 MPa; leucite-based GCs have a toughness of 0.7–1.3 MPa·m^{1/2} and strength of 160–255 MPa; lithium disilicate has a toughness of 0.8–1.5 MPa·m^{1/2} and strength of 300–450 MPa [4]. The flexural strength of those GCs is generally three- or four-point bending strength, which could be different than the biaxial strength. However, even considering this difference, the amount of GCs prepared in this study is still higher. Therefore, the Al₂O₃-ZrO₂-SiO₂ GCs with higher mechanical strength and fracture toughness show great potential for dental applications.

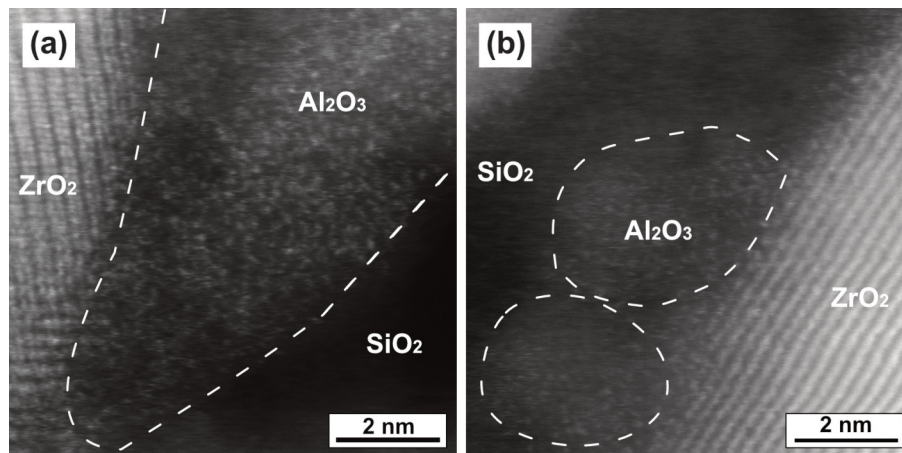


Fig. 10 (a, b) HRTEM images of 10Al-60Zr-30Si samples showing segregation of Al_2O_3 . Amorphous areas with brighter contrast marked with dashed lines are amorphous Al_2O_3 .

4 Conclusions

In this study, we developed highly translucent and toughened ZrO_2 - SiO_2 glass matrix nanoceramics enhanced by amorphous Al_2O_3 through SPS. The content and segregation of Al^{3+} at the grain boundaries of ZrO_2 nanocrystalline play important roles in determining the microstructure and mechanical properties of ZrO_2 - SiO_2 glass ceramics. ZrO_2 nanocrystals are embedded within the amorphous SiO_2 matrix, while Al^{3+} segregates at the grain boundaries of ZrO_2 nanocrystals. Some Al^{3+} domains were also observed, which is attributed to the low solubility of Al_2O_3 . Increasing Al and Si contents reduces the monoclinic phase fraction and grain size due to the improved stabilization effect and inhibition of grain growth. The 10 mol% Al_2O_3 samples, with the lowest grain size of 38 nm, exhibited the best translucency and the highest toughness of $8.05 \text{ MPa}\cdot\text{m}^{1/2}$, highlighting their potential for dental applications. Moreover, the 5Al-65Zr-30Si samples exhibit a better flexural strength of 960 MPa. The strengthening mechanisms are attributed to the combined effect of 3D architecture of ZrO_2 and segregation of Al ions at the grain boundaries, which alter the bonding energy and thus mechanical properties.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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