Optimized sintering and mechanical properties of Y–TZP ceramics for dental restorations by adding lithium disilicate glass ceramics

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Abstract: The novel dental ceramics can be fabricated at lower temperatures when sol–gel derived lithium disilicate glass ceramics (LDGC) was used as an additive for yttria stabilized tetragonal zirconia polycrystalline (Y–TZP) ceramics. The effect of LDGC on the sintering, mechanical, and translucent properties of Y–TZP ceramics was investigated in the present study. The results showed that the LDGC additive effectively improved the densification of Y–TZP at 1100 °C, which was much lower than the sintering temperature for pure Y–TZP. When sintered at 1100 °C, the Y–TZP with 1 wt% LDGC reached a relative density of 95.45%, and possessed a flexural strength of 482.4 MPa and a fracture toughness of 5.94 MPa·m^{1/2}. Moreover, its translucency was also improved. While, the addition of LDGC could result in an escape of yttrium atoms from the grain lattice of zirconia, which induced the tetragonal–monoclinic transformation of zirconia and abnormal growth of monoclinic grains. The escaped yttrium atoms diffused into the intergranular glass phase. The results indicated that the novel Y–TZP–LDGC ceramics has a great potential to be used for all-ceramic restorations.

Keywords: yttria stabilized tetragonal zirconia polycrystalline (Y–TZP); lithium disilicate glass ceramics (LDGC); sintering; mechanical properties; dental restoration

1 Introduction

In recent years, all-ceramic restorations have attracted an increasing attention due to their unique characteristics of combining good mechanical properties, excellent

biocompatibility, and aesthetic performance together [1–3]. Currently, several kinds of ceramics have been used in clinical, including lithium disilicate glass ceramics, alumina-based ceramics, feldspathic ceramics, and zirconia ceramics [1,4,5]. Among these materials, yttria stabilized tetragonal zirconia polycrystalline (Y–TZP) has been considered as one of the most advantageous candidates for dental restorations, such as crown, inlay, onlay, and bridge, owing to its high flexural strength (900–1200 MPa) and fracture toughness

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(9–10 MPa·m^{1/2}) [6–9].

Zirconia was initially introduced as a biomaterial for the total hip replacement in 1988 [10]. At present, zirconia plays an important role in all-ceramic restoration system. It is well-known that zirconia has much higher fracture toughness than other ceramics used in dentistry, owing to the effect of transformation-toughening phenomena associated with the martensitic transformation, i.e., tetragonal to monoclinic phase (t-m) [6,10]. The volume expansion ranging from 3% to 5% of zirconia grains after this phase transition induced by localized stresses can result in the significant compressive stresses on the propagating cracks. The hindered crack propagation can effectively increase the fracture toughness of Y-TZP [11,12]. Y-TZP restorations are usually manufactured via a solid-state sintering at the temperature above 1500 °C [13,14]. The manufacturing temperature is higher, and the product's cost is more expensive, which will inevitably limit its commercial applications [15]. The most common method to decrease the manufacturing temperature for ceramics is to use sintering additives. Actually, several researches have reported about the performance of additives on the sintering properties of Y-TZP. Those results showed that the densification of Y-TZP could be effectively promoted due to the viscous flow of glass phase during sintering, such as CaO–Al₂O₃–SiO₂ (CAS) and Li₂O–Al₂O₃–SiO₂ (LAS) [13,16–20].

Lithium disilicate glass ceramics (LDGC) is polycrystalline material consisted of lithium disilicate crystalline grains and glassy phases [21]. Due to the glassy matrix and the interlocking microstructures of the needle-like lithium disilicate crystalline grains, LDGC presents a good translucency while maintaining a high strength (> 350 MPa) and a fracture toughness (2.5–2.8 MPa·m^{1/2}) [22]. These properties have a decisive influence on the reliability and esthetics of a restoration product. Currently, LDGC has been widely used for dental restorations, including inlays, crowns, and bridges [23–25]. Therefore, using LDGC as a sintering additive to improve the sintering performance of Y-TZP is worth of an expectation. Moreover, the addition of glass ceramics with excellent translucency is also a potential way to improve the characterized chalk color of Y-TZP [8,21,26].

In the present study, LDGC fabricated by sol-gel method was introduced into Y-TZP to optimize its mechanical and optical properties. The influence of LDGC addition on the sintering behavior, microstructure,

and mechanical properties of Y-TZP had been investigated thoroughly. The optical properties of LDGC added Y-TZP ceramics were also characterized.

2 Materials and methods

2.1 Material fabrication

Tetraethyl orthosilicate (TEOS; AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., China) and triethyl phosphate (TEP; AR, Sinopharm Chemical Reagent Co., Ltd., China) were honored as precursors of Si and P, respectively. The molar ratio of the glass components was designed according to 66.3SiO₂–27Li₂O–2.0Al₂O₃–1.8K₂O–1.7ZrO₂–1.2P₂O₅ system. First, nitric acid (2 mol/L) was added into deionized water to adjust pH value to 3, and then TEOS and TEP were added successively. The mixture was stirred under a rotation speed of 300 rpm at room temperature (~25 °C) until a complete hydrolysis was achieved. Meanwhile, lithium nitrate (LiNO₃; AR, Aladdin Industrial Corporation, China), zirconium nitrate pentahydrate (Zr(NO₃)₄·5H₂O; AR, Nine-Dinn Chemistry (Shanghai) Co., Ltd., China), potassium nitrate (KNO₃; AR, Sinopharm Chemical Reagent Co., Ltd., China), and aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O; AR, Sinopharm Chemical Reagent Co., Ltd., China) were sequentially added into deionized water according to the designed proportions, and mechanically stirred until dissolved completely. Second, the obtained aqueous solution was slowly added into the hydrolyzed solution prepared in the first step. The mixed solution was stirred for 24 h, and then held at 60 °C for 72 h to form a gel. After that, the gel was dried at 120 °C for 48 h. The dried gel was heat-treated at 600 °C for 1 h with a heating rate of 3 °C/min, and then calcined at 850 °C for 2 h in air atmosphere with a heating rate of 2 °C/min. Finally, the obtained glass ceramic powders were ground and screened with a 200-mesh sieve for the subsequent experiments.

Y-TZP with 0 wt%, 1 wt%, 3 wt%, and 5 wt% of LDGC were prepared in this study, with sample codes of 100Z, 99Z1LD, 97Z3LD, and 95Z5LD, respectively. Y-TZP powders (TZ-3YBE, Tosoh Co., Japan) and pre-prepared LDGC powders were mixed by ball milling in ethanol for 3 h. After ball milling, the mixed powders were dried and screened through 200-mesh sieve, and then compacted into rectangular

blocks with a dimension of 30 mm × 40 mm × 6 mm, followed by a cold isostatic pressing at 250 MPa. Finally, the compacts were sintered at 900–1100 °C for 2 h in air atmosphere with a heating rate of 5 °C/min.

2.2 Characterizations

Density of the samples was measured by the Archimedes method with distilled water as the medium. The differential scanning calorimetry (TG/DSC) analysis was conducted by a simultaneous TG/DSC apparatus (STA409 PC, Netzsch, Germany) with a heating rate of 10 °C/min under nitrogen atmosphere (50 mL/min). The morphology and chemical analyses of the samples were studied by scanning electron microscope (SEM; S-4800N, Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDS; Magellan 400, FEI, USA) after being polished and thermally etched at 1000 °C for 30 min. The grain size was measured from the SEM micrographs using Nano Measurer software according to the linear interception method. The number of measured grains is about 200. More detailed microstructural features were investigated by transmission electron microscope (TEM; JEM- 2100F, JEOL, Japan). The phase analysis was conducted by X-ray diffractometer (XRD; D/MAX-RBX, Rigaku, Osaka, Japan) with Cu K α radiation (λ = 0.15418 nm). Each group of the samples was tested for 3 times. The fraction of the monoclinic phase in ZrO₂, X_m , was calculated by using the Gravié and Nicholson method [27]:

$$X_m = \frac{I_{m(\bar{1}11)} + I_{m(111)}}{I_{m(\bar{1}11)} + I_{m(111)} + I_{t(101)}} \quad (1)$$

where I_t and I_m represent the integrated intensity (area under the peaks) of the tetragonal (101) and monoclinic (111) and ($\bar{1}11$) peaks, respectively. The monoclinic volume fraction, V_m , is then calculated by the method proposed by Toraya [28]:

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (2)$$

The theoretical densities of the composites can be calculated with the rule-of-mixtures:

$$\rho_t = \frac{\rho_l \rho_z}{(1 - x_l) \rho_l + x_l \rho_z} \quad (3)$$

where ρ_t is the theoretical density of the composite ceramic, ρ_l and ρ_z are the theoretical densities of LDGC (2.5 g/cm³) and Y-TZP (6.10 g/cm³) [29], respectively, and x_l is the weight percentage of the

LDGC additive in the composite ceramic.

2.3 Mechanical properties

Both flexural strength and elastic modulus were tested on a universal testing machine (Instron 5566, Instron Co., USA), and measured by the three-point bending method with a loading rate of 0.5 mm/min and a support span of 20 mm. The samples were cut and polished into rectangular bars with the size of 3 mm × 4 mm × 26 mm. Six bars were tested for each group. The flexural strength was calculated by

$$\sigma_f = \frac{3Pl}{2bh^2} \quad (4)$$

where σ_f is the flexural strength, P is the breaking load, l is the length of the support span, and b and h are the width and thickness of the bar, respectively.

The fracture toughness was determined by single-edge-notched beam method with a loading rate of 0.05 mm/min and a sample span of 20 mm. This test was also carried out on a universal test instrument (Instron 5566, Instron Co., USA). The fracture toughness was calculated by

$$K_{IC} = \frac{3Pl}{bw^{3/2}} \times \frac{1.99\alpha^{1/2} - \alpha^{3/2}(1 - \alpha)(2.15 - 3.93\alpha + 2.70\alpha^2)}{2(1 + 2\alpha)(1 - \alpha)^{3/2}} \quad (5)$$

$$\alpha = \frac{a}{w} \quad (6)$$

where K_{IC} is the fracture toughness, P is the load, l is the span length, a is the depth of the notch, and w and b are the width and thickness of the bar, respectively.

The Vickers hardness was determined by a Vickers indentation hardness tester (TUKON-2100B, Instron Co., USA). For each sample, 5 indentations with a load of 1 kg were measured on finely polished surface for 10 s.

3 Results and discussion

3.1 Phase characterization

The fabricated LDGC powder was studied by means of SEM, XRD, and DSC techniques. Figure 1 shows the SEM micrograph, XRD pattern, and DSC profile of the as-prepared powder. The powder, showing particle aggregation in the SEM micrograph, consists of both amorphous phase and crystallization phase, which is characteristic of glass ceramics, where the diffraction

Fig. 1 (a) SEM micrograph, (b) XRD, and (c) DSC profile of the fabricated LDGC powder.

peaks of crystalline can be readily indexed to lithium disilicate (PDF #72-0102). The DSC profile shows that the melting point of LDGC is 980 °C, which means that LDGC powder will be melted into liquid phase when the sintering temperature is higher than 980 °C.

XRD profiles of the Y–TZP–LDGC samples with different content of LDGC addition sintered at different temperatures are shown in Fig. 2. It is obvious that there coexist the dominant crystalline phase of tetragonal ZrO₂ (t-ZrO₂; PDF #80-0965) and the residual phase of monoclinic ZrO₂ (m-ZrO₂; PDF #86-1451). The fraction of m-ZrO₂ is calculated and listed in Table 1. Generally, the m-ZrO₂ fraction increases as a function of the LDGC content. This trend is most evident for the 1100 °C sintered samples. After sintering at 1100 °C, the m-ZrO₂ fractions are only 14.0 and 13.2 vol%, in the samples 100Z and 99Z1LD (0 and 1 wt% of LDGC, respectively). However, when the amount of LDGC addition is 3 wt%, the fraction of m-ZrO₂ increases to 32.7 vol%

sharply. Finally, the m-ZrO₂ fraction reaches at 31.3 vol% in the sample with 5 wt% LDGC addition after sintering at 1100 °C.

3.2 Relative density and mechanical properties

The relative density (Fig. 3(a)) and mechanical properties, including flexural strength (Fig. 3(b)), elastic modulus (Fig. 3(c)), and hardness (Fig. 3(d)), were also studied with those samples sintered at different temperatures. The results are shown in Fig. 3. The theoretical density of the Y–TZP–LDGC composites is calculated from the theoretical densities reported for tetragonal Y–TZP and LDGC. When the sintering temperature is 900 °C, the relative density of Y–TZP is 50.66%. However, with 5 wt% LDGC addition, the relative density increases linearly to 61.24%, as shown in Fig. 3(a). When sintered at 1000 °C, the relative density of Y–TZP without LDGC is 56.93%. With 3 wt% LDGC addition, the relative density of the composite rapidly

Fig. 2 XRD patterns of the samples with different LDGC content sintered at different temperatures: (a) 900 °C, (b) 1000 °C, and (c) 1100 °C.

Table 1 Volume fraction of monoclinic ZrO₂ phase in the sintered Y–TZP–LDGC samples (vol%)

Sample	900 °C	1000 °C	1100 °C
100Z	13.2 ± 0.2	11.5 ± 1.2	14.0 ± 2.6
99Z1LD	14.4 ± 0.6	18.1 ± 0.7	13.2 ± 1.1
97Z3LD	16.5 ± 0.8	29.2 ± 0.8	32.7 ± 0.7
95Z5LD	19.3 ± 0.7	28.6 ± 0.1	31.3 ± 0.5

Fig. 3 Relative density and mechanical properties of samples sintered at different temperatures: (a) relative density, (b) flexural strength, (c) elastic modulus, and (d) hardness.

increases up to 85.94%. After sintered at 1100 °C, the relative density of samples greatly increases from 81.58% to 95.45% with only 1 wt% of LDGC addition. However, with a further increase of LDGC addition, the relative density gradually decreases, for example, 91.25% with 5 wt% LDGC addition.

The flexural strength increases from 37.0 to 76.6 MPa, the elastic modulus from 13.2 to 31.8 GPa, and the hardness from 0.6 to 1.5 GPa, for the samples sintered at 900 °C with LDGC addition increasing from 0 to 5 wt%. The flexural strength of samples with 5 wt% LDGC addition achieves a maximum value of 363.7 MPa, and the elastic modulus and hardness reach to 77.4 and 7.85 GPa, respectively, when the sintering temperature reaches at 1000 °C. While the flexural strengths are 483.8 and 482.4 MPa, when the LDGC additions are 0 and 1 wt% at 1100 °C, respectively. However, the flexural strength decreases with more of LDGC content. Consistent with flexural strength, the highest elastic modulus and hardness also reach at 81.9 and 11.13 GPa, respectively, when the LDGC addition is 1 wt%. When the LDGC content is further increasing,

the elastic modulus and hardness gradually decreased. Furthermore, a similar tendency is observed in the fracture toughness at 1100 °C as shown in Table 2. The sample 99Z1LD, with 1 wt% LDGC addition, presents the highest fracture toughness of $5.94 \text{ MPa}\cdot\text{m}^{1/2}$.

The fracture surfaces of samples sintered at 1100 °C were studied by SEM as shown in Fig. 4. In Fig. 4(a), it could be found that there are pores at the triple-junction among ZrO_2 grains. In sample 99Z1LD, the pores among ZrO_2 grains disappeared, which means 99Z1LD has a higher relative density than 100Z. In samples 97Z3LD and 95Z5LD, macro pores can be observed on the fracture surfaces. The existence of these pores reduces the relative density and has a negative effect on the mechanical properties of the samples.

It is noted that the addition of LDGC contributes to the densification of Y-TZP. The melt-out effect of added LDGC at grain boundaries can facilitate the atom diffusion and promote the densification of samples through liquid sintering. In addition, the increment of temperature can reduce the viscosity of glass phase, which can also promote the atom diffusion and thus

Table 2 Fracture toughness of the samples sintered at 1100 °C

Sample	100Z	99Z1LD	97Z3LD	95Z5LD
Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	4.98 ± 0.32	5.94 ± 0.67	3.91 ± 0.36	3.70 ± 0.10

Fig. 4 SEM micrographs of the fracture surfaces of samples sintered at 1100 °C: (a) 100Z, (b) 99Z1LD, (c) 97Z3LD, and (d) 95Z5LD. The insets show the morphologies at a higher magnification.

facilitate the densification. Therefore, with the increment of LDGC addition and sintering temperature, the relative density of the samples gradually increased. However, when the LDGC addition is more than 3 wt%, the relative density of the samples sintered at 1100 °C will be decreased. This is induced by the pores within the ceramics (Figs. 4(c) and 4(d)) and the volumetric expansion caused by the t–m transformation of ZrO_2 grains [18,30].

When the sintering temperatures are 900 and 1000 °C, the relative density of Y–TZP–LDGC samples increases with the increment of LDGC content, and the flexural strength, elastic modulus, and hardness of the samples increase accordingly. After sintering at 1100 °C, the sample with 1 wt% LDGC addition has the highest values of relative density, elastic modulus, hardness, and fracture toughness at the same time. The above results show that the flexural strength, elastic modulus, and hardness of Y–TZP–LDGC samples follow the same trend and strongly correlate with the variation of relative density, which indicate that the density is a dominate factor for the mechanical properties of Y–TZP–LDGC samples. It is well-known that the lower density of the ceramic indicates more internal pore defects inside (Fig. 4). The pore defects can cause the stress concentration and reduce the cross-sectional area of the material, which is unfavorable for the mechanical properties [11,12]. In addition, the volume expansion caused by t–m transformation may result in pores and micro-cracking, and thus the increasing

m- ZrO_2 content has adverse effects on the mechanical properties. Moreover, the excessive intergranular glass phase may negatively affect the mechanical properties of Y–TZP, since the mechanical properties of LDGC are lower than that of Y–TZP. Therefore, after sintering at 1100 °C, although the density of 97Z3LD and 95Z5LD is higher than that of 100Z, the flexural strength of them is lower than that of 100Z [15,31].

For zirconia-based materials, stress-induced t–m transformation is the primary toughening–reinforcing mechanism. Therefore, the content of t- ZrO_2 plays an important role in the fracture toughness of Y–TZP–LDGC samples. In the present work, the density of samples is increased with the addition of LDGC, but the content of t- ZrO_2 will be reduced. For the samples sintered at 1100 °C, the relative density of 99Z1LD is higher than that of 100Z, while its m- ZrO_2 content is close to that of 100Z, and thus the fracture toughness of 99Z1LD is higher than that of 100Z. Although the relative density both of 97Z3LD and 95Z5LD is higher than that of 100Z, the fracture toughness of them is lower than that of 100Z, which may be caused by the higher m- ZrO_2 content.

3.3 Microstructural characterization

Figure 5 shows the SEM micrographs of the original surfaces of samples sintered at 1100 °C. In Fig. 5(a), the sample 100Z has a uniform grain size and some pores can be observed on its surface (indicated by yellow open circles). With 1 wt% LDGC addition, pores

Fig. 5 SEM micrographs of the original surfaces of samples sintered at 1100 °C: (a) 100Z, (b) 99Z1LD, (c) 97Z3LD, and (d) 95Z5LD. Yellow open circles indicate the pores, and arrows indicate the glass phase.

disappear on the sample surface. When the LDGC addition increases to 3 wt%, a thin glass phase appears at the grain boundaries (by the yellow arrow). As the LDGC addition further increases to 5 wt%, zirconia grains are gradually wrapped by the glass phase, and the thickness of the glass phase at the grain boundary is increased obviously. These results indicate that the LDGC gradually melts and fills the gaps among the ZrO_2 grains during the sintering process.

Figure 6 shows SEM micrographs of the polished and thermal etched surfaces of Y–TZP–LDGC samples sintered at 1100 °C. It is clear in Fig. 6(a) that the size of ZrO_2 grains is uniform, and there are some

intergranular pores in the sample. When 1 wt% LDGC is added, the intergranular pores disappear, without obvious changes in ZrO_2 grain size (Fig. 6(b)). When the LDGC addition is more than 3 wt%, it is remarkable that there shows a bimodal size distribution of ZrO_2 grains (Figs. 6(c) and 6(d)); smaller ones are at nano scales (about 100 nm), while the larger ones are around 1–4 μm as indicated by white circles. Besides, the average diameter of both larger and smaller ZrO_2 grains increases gradually with the increasing content of LDGC addition. The shape of smaller ZrO_2 grains turns accordingly from polygon into roundness. Table 3 summarizes the average grain size of the samples

Fig. 6 SEM micrographs of the samples sintered at 1100 °C: (a) 100Z, (b) 99Z1LD, (c) 97Z3LD, and (d) 95Z5LD. The insets show the morphologies at a higher magnification. White circles indicate the larger grains.

Table 3 Average grain size of the samples sintered at 1100 °C

Sample	100Z	99Z1LD	97Z3LD	95Z5LD
Average grain size (nm)	90 ± 33	107 ± 39	112 ± 43	120 ± 40

sintered at 1100 °C.

According to liquid phase sintering theory, liquid phase can wet the solid particles, with resulting in capillary pressure in the space between particles, which can promote the densification by rearranging the particles to denser packing and increasing the mass transfer rate through dissolution–reprecipitation mechanism [13,31–33]. Therefore, the intergranular pores eliminate in sample 99Z1LD and the relative density of Y–TZP increases with a small amount of LDGC addition. Furthermore, the increased mass transfer rate is conducive to grain growth. Thus, the average grain size of samples is increased as shown in Table 3.

In fact, the LDGC additive mostly distributes at grain boundaries during sintering process. Therefore, the thickness of glass phase grain boundary increases with more addition of LDGC. This thick glass phase grain boundary would hinder the mutual contacts between grains and subsequently increase the diffusion path of grain boundary, resulting in limited mass transfer and low grain-growth rate. Therefore, when LDGC addition is more than 1 wt%, further increase in LDGC content leads to a decrease in relative density. Additionally, the similar result is also observed by Tekeli in SiO₂/8YSCZ (8 mol% yttria-stabilized cubic zirconia) composites, in which the overdose SiO₂ addition has been proved to retard the densification of 8YSCZ by hindering the grain growth [34,35].

The detailed microstructure on micron and nano

scale was analyzed by TEM imaging, electron diffraction as well as chemical analysis. Figure 7 gives the TEM bright field micrographs of 99Z1LD and 97Z3LD samples sintered at 1100 °C. It can be concluded that the grain size of 99Z1LD sample is uniform and the phase of marked grain is demonstrated to be tetragonal ZrO₂ (Figs. 7(a) and 7(b)). However, two types of ZrO₂ grains with different sizes are present in sample 97Z3LD (Figs. 7(c) and 7(d)), which is consistent with the SEM results (Fig. 6(c)). Furthermore, the selected area electron diffraction (SAED) patterns have confirmed that the larger ZrO₂ grains are the monoclinic phase, while smaller ones are cubic (Figs. 7(c)–7(f)).

Elemental mapping results on polished surface of the 1100 °C sintered samples are shown in Fig. 8. Si distribution reveals the existence of LDGC addition. At this magnification, element distribution of Zr, Y, and Si looks homogeneous in the sample of 99Z1LD. However, for 97Z3LD and 95Z5LD samples, it is obvious that the distribution of all the elements is non-uniform, and larger size grains lacking of Y and Si elements (white dashed ellipse in Figs. 8(b) and 8(c)) are observed, which further confirm the formation of larger-size ZrO₂. Elemental analysis was also performed to fully understand the distribution of glass addition at a higher magnification in TEM. The Si distribution in Fig. 8(d) indicates that the glass addition is mainly distributed along ZrO₂ grain boundaries. Meanwhile, the linear variation of element content in

Fig. 7 TEM images of (a) 99Z1LD and (c, d) 97Z3LD sintered at 1100 °C; (b, e, f) SAED patterns of the marked grains with numbers.

Fig. 8 SEM elemental mappings of the polished surfaces of (a) 99Z1LD, (b) 97Z3LD, and (c) 95ZZ5LD sintered at 1100 °C; (d) TEM elemental mappings and (e) line scan of 97Z3LD sintered at 1100 °C.

Fig. 8(e) shows that the glass addition at the grain boundary riches in yttrium. Therefore, it can be concluded that the Y element may diffuse from the larger-size ZrO_2 into intergranular glass. The consequence is that the lack of Y in larger-size ZrO_2

will directly induce the phase transition from t- ZrO_2 to m- ZrO_2 . It is well-known that Y_2O_3 is the stabilizing agent of the zirconia. The content and distribution of Y have a direct influence on the phase form of zirconia [36]. Thus, it is reasonable to suppose that the lack of

Y in larger-size ZrO_2 will directly induce the phase transition from t- ZrO_2 to m- ZrO_2 .

Several studies have shown that the introduction of bio-glass (such as 64S, $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-MgO}$, and $\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5$) into Y-TZP can induce a t-m transformation and lead to an increase in the m- ZrO_2 fraction [30,31,37]. It was explained that this could be caused by the inhomogeneous spreading of liquid phase during the sintering process. In fact, it is difficult to achieve the uniform mixing of precursor powders due to the agglomeration of LDGC powders (Fig. 1(a)). The recrystallization of the inhomogeneous intergranular glass phase and the mismatch in coefficient of thermal expansion between the glass phase and zirconia matrix will cause considerable localized stress and structure changes during cooling process, which may also induce the undesirable phase transition [18].

Although it has been reported for several times that the m- ZrO_2 fraction of Y-TZP increases when glasses used as the additive, the phenomenon of Y segregation has been rarely reported [13,16,18,30,31,35]. Yttrium silicates (Y-Si-O), or the $\text{Y}_2\text{O}_3\text{-SiO}_2$ binary system, including $\text{Y}_2\text{Si}_2\text{O}_7$, Y_2SiO_5 , and $2\text{Y}_2\text{O}_3\cdot 3\text{SiO}_2$, have been widely investigated and used as high-temperature structural ceramics [38–40]. Y_2SiO_5 can be obtained by calcining Y_2O_3 and SiO_2 when lithium used as an additive [38,41]. In the $\text{Y}_2\text{O}_3\text{-SiO}_2$ binary system, the additive of lithium can lower the reaction temperature of $\text{Y}_2\text{O}_3\text{-SiO}_2$ by eutectic reactions. Apparently, the introduction of lithium is beneficial to the formation of Li-Si-Y-O liquid phase and can promote the reaction between Y_2O_3 and SiO_2 . In addition, the previous work has shown that several yttrium silicates, including $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$, Y_2SiO_5 , and $\text{Y}_2\text{Si}_2\text{O}_7$, are obtained in the $\text{Y}_2\text{O}_3\text{-SiO}_2$ system with a lithium additive, after a calcination at 1025 °C [41]. This might be the reason why Y element diffuses away from ZrO_2 grains to the intergranular lithium-containing glass phase.

The t- ZrO_2 fraction depends both on the grain size and Y content in samples at room temperature. For 3Y-TZP (3 mol% yttria-stabilized tetragonal zirconia) used in the present work, the critical grain size of t- ZrO_2 is about 1 μm , which means the grains larger than 1 μm would transfer to m- ZrO_2 during the cooling process [10]. This is in good agreement with the TEM results observed in the present work (Figs. 7(d) and 7(e)). Moreover, the Y segregation in the Y-TZP-LDGC samples should be noted. It is easy to find that there is more Y in smaller grains, and less in

larger grains. Since the zirconia stabilized by higher Y content (about 8 mol%) can be cubic phase at room temperature [34,42], c- ZrO_2 grain is observed in the region of smaller grains with higher Y concentration (Figs. 7(d) and 7(f)) [34]. Due to the limited total content of Y in the starting powders, the content of c- ZrO_2 grains is too low to be detected by the XRD analysis.

3.4 Translucency

As can be seen from Fig. 9, the significant difference in translucency is identified among the Y-TZP-LDGC samples sintered at 1100 °C. The optical images show that the additive of LDGC has a significant impact on the translucency of the samples. Specifically, the addition of 1 wt% LDGC can greatly increase the translucency of the sample. However, with a further increase of LDGC, the translucency gradually decreases.

Limited translucency is a major drawback of Y-TZP and directly influences the appearance of dental restorations [8,43,44]. The main factor affected the translucency of Y-TZP is the light scattering, mainly at pores, grain boundaries, or second phases. In the present Y-TZP-LDGC system, the addition component LDGC performs an excellent translucency. According to the above results, the additive of LDGC can eliminate the pores in Y-TZP (as shown in Figs. 5 and 6). Therefore, the addition of LDGC improves the translucency of Y-TZP. However, when the addition is more than 1 wt%, the density of samples decreases dramatically, and the translucency will be correspondingly decreased.

4 Conclusions

The present work investigates the influence of LDGC addition on the sintering, mechanical, and translucent properties of Y-TZP ceramics. The results show that the addition of LDGC can significantly promote the densification of Y-TZP ceramics through liquid phase

Fig. 9 Optical images of the samples sintered at 1100 °C (the sample thickness is 0.3 mm).

sintering at relatively lower temperatures. Meanwhile, the addition of LDGC can also cause the yttrium atoms to escape from the zirconia grain lattice to the intergranular glass phase, resulting in an increase of m-ZrO₂ fraction in Y-TZP ceramics and a decrease of mechanical properties at the same time. Moreover, the diffusion of Y atoms from zirconia grain lattice can also result in an abnormal growth of monoclinic grains. When sintered at a relatively low temperature of 1100 °C, Y-TZP added with 1 wt% LDGC would possess a flexural strength of 482.4 MPa and a fracture toughness of 5.94 MPa·m^{1/2}. It also exhibits a better translucency, which is a promising material for all-ceramic dental restorations.

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