The zirconia-reinforced lithium silicate ceramic: lights and shadows of a new material

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This study aims to investigate the mechanical properties, composition and surface preparation for adhesive bonding of the recently introduced zirconia-reinforced lithium silicate (ZLS) glass-ceramic. One single block of ZLS was used to prepare the specimens (n=14). The fracture toughness (Ft) and the Vickers hardness (HV) were measured on specimens partially crystallized (PCs) (n=4) and fully crystallized (FCs) at 840°C for 8 min (n=4). The surface treatment was done using hydrofluoric-acid gel (HF) at different concentrations and times of action on FCs specimens (n=4). SEM-EDX was used to test elemental composition and crystalline phases (n=2). The new ZLS glass-ceramic showed significantly higher values of HV and Ft for FCs; PCs showed a brittle behavior. The surface etching should be made using HF at 4.9% for 20 s.

Keywords: Zirconia, Lithium silicate, Mechanical properties, Material properties, Surface characterization

INTRODUCTION

Metal-free restorations have emerged as a viable treatment option in fixed prosthodontics¹ showing increased aesthetic properties over metal ceramic restorations, with adequate mechanical behavior²-⁴. Metal-free prosthetic materials include a wide range of glass ceramics and polycrystalline materials, such as alumina and yttria-tetragonal zirconia polycrystal (Y TZP). YTZP has excellent mechanical properties, with a broad range of indications ranging from frameworks for monolithic multi-element bridges to frameworks for single crowns⁵-⁷. Although in the last years new high translucency stabilized zirconia have been introduced for monolithic full contour restorations, they remain predominantly opaque⁸,⁹. This aspect limits their use as monolithic restorations in the posterior region only¹⁰,¹¹. Veneered zirconia restorations, on the other hand, showed a considerable clinical rate of chipping and delamination of the veneering glass-ceramic¹²-¹⁴; while the fracture of the framework is reported as a minor complication¹⁵,¹⁰. The lithium disilicate (LS₂) glass ceramic is the most popular material used for all ceramic restoration. The LS₂ before thermal conversion is an amorphous glass matrix that after heat treatment becomes a crystalline material with about 70% of LS₂ orthorhombic crystal phase (Li₂Si₂O₅) this gives excellent mechanical properties and mimetic behavior¹⁷. These ceramics exhibit a translucency and aesthetic appearance superior to those high strength polycrystalline alternatives¹⁸. However, the mechanical properties limit their use in the molar area¹⁹-²⁹.

A new ceramic material for dental restorations has been lately introduced. The zirconia-reinforced lithium silicate (ZLS) is based on a lithium-metasilicate (Li₂SiO₃) glass ceramic and reinforced with about 10% of zirconium dioxide (ZrO₂)³⁰ that, after final crystallization process, leads to the formation of fine grained microstructure (Li₂O-ZrO₂-SiO₂). ZLS belongs to a newly generation of materials intended for CAD/CAM use that combines the positive mechanical characteristics of the zirconia with the glass-ceramic aesthetic appearance³⁰. Unlike the zirconia restorations, according to the manufacturer’s instructions, ZLS could be etched and cemented whit adhesive systems³⁰. It has been demonstrated that the fracture resistance of adhesively cemented monolithic CAD/CAM generated ceramic crowns is significantly higher than the conventional cementation one³¹.

ZLS is provided in a soft and easily formable partially crystalized state (PCs), to facilitate the CAD-CAM manufacturing; it is subsequently treated to obtain a fully crystalized state (FCs) with final color and appropriate mechanical properties. In that regard, the PCs state could influence the efficacy of marginal adaptation.

The aims of the present study were to evaluate the mechanical properties as Vickers hardness (Hv) and fracture toughness (Ft) in PCs and FCs of ZLS ceramic, as well as the elemental composition and the surface reaction to different acid-etching procedures. The null hypothesis (H₀) under test considered any difference between PCs and FCs for Hv and Ft.
MATERIALS AND METHODS

Sample preparation
Square-shaped specimens 3.5×3.0×1.0 mm thick (n=14) were cut from one non-crystallized block (lot 36021, Shade A2) of Vita Suprinity (VITA Zahnfabrik, DeguDent, Germany). The specimens for mechanical test (n=8) were divided into two groups: as received by milling center or PCs (n=4) and heat-treated or FCs (n=4). The crystallization protocol was made in accordance with the manufacturer’s indications at 840°C for 8 min in a ceramic furnace (Programat EP 510, Ivoclar Vivadent, Schaan, Liechtenstein). The specimens were embedded in resin (Acrylic VLXB, Kemet International, Kent, UK), polished to a high-luster finish and clamped in position before the indentation tests.

Vickers indentation
Twenty indentations were made on each group (five on each sample). The indentations were made using a diamond Vickers pyramid (angle 136° and area-depth ratio A=24.5 h*c) fixed with the load cell at a universal testing machine (Lloyd 30K, Lloyd Instruments, Segensworth, UK) under constant load of 50 N for 5 s in a controlled displacement mode at 0.5 mm/S (Fig. 1). To determine the stress intensity present at the crack tip due to the indentation, the crack tip profile was determined using a scanning electron microscope (SEM) Zeiss EVO 50 XVP with LaB6 (Carl Zeiss SMT, Cambridge, UK). The length of radial cracks emanated from each of the four indented corner sources were measured using Image-Pro Plus ver. 6.0 (Media Cybernetics, Bethesda, USA). To ensure accuracy, the software was calibrated for each experimental image using a software feature named “Calibration Wizard” which reported the number of pixel between two selected points (scale bar). The linear remapping of the pixel numbers was used to calibrate the distance in microns.

Hardness Vickers (Hv) was calculated from the standard formula for force divided by contact area:

\[ H_v = \frac{1.8544 \cdot P}{d^2} \]  

where \( P \) is the indenter load in N and \( d \) is the length of the diagonal in mm.

Fracture toughness
Fracture toughness of the material was estimated using cracks produced by hardness indents. It was represented by the term \( K_{IC} \) and was defined as the critical value of the stress intensity factor at a crack tip necessary to produce catastrophic failure under simple uniaxial loading32); the “I” stands for mode one (uniaxial) and the “C” stands for critical. To determine fracture toughness the Palmqvist equation was used33):

\[ K_{IC} = \beta_0 \left( \frac{P}{l} \right)^{1/2} \]  

where \( P \) was the applied load, \( l \) was the crack length from the tip of the indentation to the crack end, and \( \beta_0 \) was an empirical parameter, usually set equal to 7 for a Vickers indenter33). Palmqvist cracks were characteristic in that they have an \( l^{-0.5} \) dependence. The units of \( K_{IC} \) are MPa m^{1/2}.

SEM fractography
All the experimentally fractured specimens were coated with a very thin layer of gold by vacuum sputter using an Emitech K 550 (Emitech, Ashford, Kent, UK) and analyzed under a scanning electron microscope (SEM) Zeiss EVO 50 XVP with LaB6 (Carl Zeiss SMT) equipped with tetra solid-state detector for backscattered electrons (BSE). The fractographic patterns were evaluated as follow: the mirror area, that appears as a flat shiny area; the mist area, that

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Fig. 1  Schematic representation of HV 50 indentation test.  
In (a) cross sectional view, in (b) plane view. \( P= \)applied load; \( l= \)crack length; \( d= \)diameter of indentation.
appears to be slightly rougher; the hackle area, ridges and grooves radiating from the indentation point as well as layers resulting from branching of the fracture path. Different magnifications were used to analyze the fractures because some patterns were easier to recognize at higher magnifications and others were more apparent at lower magnifications.

**EDS analysis**

The compositional analysis of ZLS was performed on two randomly chosen FCs specimens by means of a SEM equipped with an energy dispersive spectrometer detector (EDS; INCA, Oxford Instruments, Oxon, UK). Uncoated specimens were placed on the aluminium stubs and investigated using a tetra solid-state BSE detector. SEM operating conditions included 30 kV accelerating voltage, 10 mm working distance and a 1.2 nA probe current. The images were captured with 20 scans using a line average technique.

**Surface treatments**

To examine the effects of different acid etching concentrations and times on FCs ZLS surface; four specimens of 3.9×3.0×1.0 mm were used. After preparation, the specimens were embedded in resin (Acrylic VLXB, Kemet International), and wet polished up to 1000-grit silicon carbide paper and polishing liquid on a grinding device (TMA2, Grottammare, Italy). The acid-etching procedure was performed at room temperature using hydrofluoric acid gel at 4.9% (Ivoclar Vivadent) for either 20 and 40 s and hydrofluoric acid gel at 9.5% (Bisco, Schaumburg, IL, USA) for either 20 and 40 s. The evaluation was performed by a means of SEM.

**Microstructure analysis**

The samples prepared for the surface treatments evaluation, have been further investigated for ZLS microstructure analysis. Ten SEM images (30,000× and 80,000×) per sample were used to determine the dimension of crystals. The measure (length of crystals) was made using Image-Pro Plus vers. 6.0 (Media Cybernetics). The software was calibrated for each experimental image using the calibration function. The number of pixel forming the scale bar reported on each digital SEM image was used for linear remapping of the distance in nanometers. The mean and standard deviation were determined considering more than 400 crystals counted.

**Statistical analysis**

Statistical inference was performed by means of the computerized statistical package (Sigma Stat 3.5, SPSS, Ekrath, Germany). The differences among the variables were made, after evaluating the normality and the equal variance tests. The unpaired t-test was used to evaluate the comparisons between the means. A p value of under 0.05 was considered statistically significant.

**RESULTS**

**Vickers indentation**

The Hv50 values (mean±SD) were 6.8±0.5 GPa for PCs group, and 7.6±0.7 GPa for FCs group. The t-test discovered statistically significant differences in the mean values among the groups (p<0.001) (Fig. 2).

**Fracture toughness (Ft)**

The Ft (mean±SD) measured as K1C were 2.8±0.9 MPa m$^{1/2}$ for PCs group and 4.7±0.8 MPa m$^{1/2}$ for FCs group. The t-test discovered statistically significant differences in the mean values among the groups (p<0.001) (Fig. 3).
SEM fractography
SEM observation revealed a different fractographic pattern around the indentation sites. FCs ZLS showed some area of plastic deformation associated to the minor area of intergranular delamination cracks and linear cracks with several bridging (Fig. 4). PCs ZLS showed symmetric mirror regions that would suggest a tensile field stress followed by a mist region with peripheral radial hackle regions (Fig. 5).

EDS analysis
The microanalytical investigation of the ZLS considered in the present study showed a chemical composition of silicon (Si)=59 wt%, lithium (Li)=20 wt%, zirconium (Zr)=12 wt%, phosphorus (P)=4.2 wt%, potassium (K)=2.5 wt%, aluminum (Al)=1.5 wt% and other minor components=0.8 wt% (Fig. 6).

Surface treatments
At room temperature the application of HF gel at 4.9% for 20 s showed the best results with preservation of microstructure, while increasing the etching time to 40 s the surface degradation of ZLS microstructure appears evident. At the same time, the increase of hydrofluoric acid concentration to 9.5% either for 20 and 40 s produces a progressive surface degradation with a large destructuring of the ZLS material (Fig. 7).

Microstructure
The microstructure observed in the ZLS (Fig. 8) before the heat treatment for crystallization (PCs state) showed an extremely homogeneous fine structure material made by nanoparticles of 150.4±28.5 nanometers.

After heat treatment at 840°C for 8 min was obtained an FCs state characterized by a homogeneous fine crystalline structure with an average crystal size of

Fig. 4  SEM images of indentations in a fully crystallized specimen.
In (a) the indentation test at ×500 magnifications with in evidence (*) the area imaged in (b) at ×10,000 magnifications. In (b) the material appear formed by Nano dimensioned grains (more or less 500 nm), which forms a bridged zones directly along the crack wall (withe arrows).

Fig. 5  SEM images of indentations in a partially crystallized specimen.
In (a) the indentation test at ×500 magnifications with in evidence (*) the area imaged in (b) at ×10,000 magnifications. In (b) the material structure appear glassy (amorphous) and the crack walls were without bridged zones (withe arrows).
DISCUSSION

The present investigation mainly concerned with the changes of mechanical properties taking place within the microstructure of the ZLS during the heating “crystallization” process. The vickers hardness appeared significantly decreased in the PCs group ($p<0.001$) as well as the fracture toughness ($p<0.001$) consequently the approximately of 854.5±155.0 nanometres. The crystals appeared embedded in a second phase.

Fig. 6 SEM-EDX evaluation.
In (a) the surface of the material at ×500 magnifications with the line along which the analytical scan was performed. In (b) the energy dispersive spectroscopic lines of the elements recognized.

Fig. 7 SEM images of surface treatments.

GEL HF 4.5% 20 SEC  GEL HF 4.5% 40 SEC

GEL HF 9.5% 20 SEC  GEL HF 9.5% 40 SEC
hypothesis under test (H0) was rejected.

Guazzato et al.\textsuperscript{34} evaluating the fracture toughness of zirconia-based dental materials found values ranging from 4.8±0.5 MPa m\textsuperscript{1/2} to 7.4±0.6 MPa m\textsuperscript{1/2} and hardness values between 11±0.9 GPa and 13±0.3 GPa. In the present study FCs ZLS presented values of fracture toughness of 4.7±0.8 MPa m\textsuperscript{1/2} and Vickers hardness of 7.6±0.7 GPa.

On the other hand, for pressable lithium-disilicate ceramics it was reported fracture toughness of 1.13±0.02 MPa m\textsuperscript{1/2}, and hardness value of 5.38±0.28 GPa\textsuperscript{35}, while the CAD/CAM lithium disilicate ceramic it was reported values of fracture toughness ranging from 2.27±0.16 MPa m\textsuperscript{1/2} to 2.37±0.28 MPa m\textsuperscript{1/2} and values of Vickers hardness of 6.02±0.2 GPa\textsuperscript{36}. Otherwise, the fracture toughness of the dental enamel was reported as ranging between 0.7±0.2 MPa m\textsuperscript{1/2} and 1.77±0.2 MPa m\textsuperscript{1/2} while, the hardness values showed 4.7±0.3 GPa\textsuperscript{37}.

The collected data prove that ZLS exhibits superior mechanical properties compared to lithium-disilicate glass ceramics and comparable to those of existing zirconia-based ceramics. The comparison with enamel also show that the material is suitable for oral function, even in the posterior regions where the masticatory forces range between 600 and 900 N\textsuperscript{38}.

The CAD/CAM processing procedures commonly used for metal-free restorations are based on the milling of a soft and easily formable, partially crystallised phase. Subsequently the restoration in the established shape is thermally treated to obtain the final mechanical properties and color shade required for oral applications\textsuperscript{3,39}. In the PCs, ZLS appears to be brittle, as demonstrated by this study. Consequently, technicians and practitioners during laboratory phases should take account of the lower mechanical properties showed by this material and limit as much as possible the corrections on the restorations during the marginal adaptation process of the crowns.

Indentation cracking is a valuable method to determine the surface fracture toughness of hard brittle materials because it is easy to perform, while causing negligible surface damage\textsuperscript{40,41}. Fracture toughness (K\textsubscript{IC}) represents the intrinsic properties of a material to resist crack propagation under an induced stress, and it is an appropriate parameter for indicating the structural performance of brittle materials\textsuperscript{42}. It is a
measure of the maximum energy a material could absorb before fracture takes place. Fracture occurs when the intensity of the stress field reaches this threshold. Fracture toughness depends strongly upon composition and the microstructure of the material: the crack-microstructure interactions can affect crack propagation and hence the fracture toughness. A variety of toughening mechanisms are possible within a ceramic's microstructure. These mechanisms include crack deflection, zone shielding, contact shielding, stress dispersion in the crack tip and particle bridging. All these mechanisms aim at different approaches to increase the energy required for crack propagation.

In the present study, the SEM observation after indentation revealed the presence of both a very fine microstructure with bridged zones directly along the crack wall in the FCs specimens. This phenomenon could be related among other, to a strong interface between the zirconia enriched matrix and very fine crystals of lithium silicate. The combination of a brittle ceramics matrix enriched with high strength ceramic particles or dispersed oxides can result in a material with relatively high toughness. Therefore, the toughening mechanisms in ceramic composite behave like concrete. The PCs group, instead, present brittle fracture that is a primary area of concern in this material. The lower fracture toughness reported by this group could be due to the prevalence and the influence of the silicate glass matrix on the reinforcement phase.

The microstructure organization before and after crystallization treatment appeared to be extremely different (Fig. 8 a and b) showing the presence inside the bulk material of a multicomponent system due to nucleation process following the heat treatment. Moreover, in none of the evaluated conditions was possible to identify the zirconia particles. This observation is in agreement with the report by Krüger et al. The improved mechanical properties of the ZLS can be attributed to a very fine grained structure which is favourable for enhanced strength.

The thermal crystallization treatment appeared to be a crucial aspect for mechanical and optical properties of the material, as consequence, the influence of the heat rate, the final temperature and the time of treatment are objectives for further study.

The surface morphology of ZLS ceramic, subjected to hydrofluoric acid-etch treatments, appeared confirm to those reported in the literature. As reported by Yen et al., hydrofluoric acid can react preferentially with the silica phase in a glassy matrix. As a result, the surface of the ceramic becomes rough, which is required for micromechanical retention. Nevertheless acid concentration and duration of action must be strictly controlled.

Further analysis will be necessary to evaluate the clinical performance of ZLS.

CONCLUSIONS

The results of this study showed that the ZLS material significantly increases both the $F_t$ and the $HV$ values after crystallization treatment ($p<0.001$). As consequence, at partially crystallized state, the material appeared to be significantly more brittle with a tendency to develop cracks inside the material bulk. Therefore, it is suggested to take care during the manipulation process for marginal adaptation; while, the best surface treatment preparation was obtained with a 4.9% solution gel of HF applied at room temperature for 20 s.

REFERENCES

1) Zarone F, Russo S, Sorrentino R. From porcelain-fused-to-metal to zirconia: clinical and experimental considerations. Dent Mater 2011; 27: 85-96.
2) Sailer I, Fehér A, Fiser F, Gauckler LJ, Lüthy H, Hämerle CH. Five-year clinical results of zirconia frameworks for posterior fixed partial dentures. Int J Prosthodont 2007; 20: 383-388.
3) Guzzato MPK, Sara G, Swain MV. Strength, reliability, and mode of fracture of bilayered porcelain/core ceramic. Int J Prosthodont 2004; 17: 142-149.
4) Pjetursson BE, Sailer I, Zwahlen M, Hämerle CH. A systematic review of the survival and complication rates of all-ceramic and metal-ceramic reconstructions after an observation period of at least 3 years. Part I: Single crowns. Clin Oral Implants Res 2007; 18: 73-85.
5) Stevenson B, Ibbetson R. The effect of substructure on the colour of samples/restorations veneered with ceramic: a literature review. J Dent 2010; 38: 361-368.
6) Traini T, Gherlone E, Farabita SF, Caputi S, Piattelli A. Fracture toughness and hardness of a Y-TZP dental ceramic after mechanical surface treatments. Clin Oral Investig 2014; 18: 707-714.
7) Bachhav VC, Aras MA. Zirconia-based fixed partial dentures: a clinical review. Quintessence Int 2011; 42:173-182.
8) Zhang Y. Making yttria-stabilized tetragonal zirconia translucent. Dent Mater 2014; 30: 1195-1203.
9) Traini T, Gherlone E, Parabita SF, Caputi S, Piattelli A, Ferrini F. A 3 years prospective study of survival for zirconia-based single crowns fabricated from intraoral digital impressions. J Dent 2014; 42: 1151-1155.
10) Larsson C, Wennerberg A. The clinical success of zirconia-based crowns: a systematic review. Int J Prosthodont 2014; 27: 33-43.
11) Sailer I, Pjetursson BE, Zwahlen M, Hämerle CH. A systematic review of the survival and complication rates of all-ceramic and metal-ceramic reconstructions after an observation period of at least 3 years. Part II: Fixed dental prostheses. Clin Oral Implants Res 2007; 18: 86-96.
12) Heintze SD, Rousson V, Survival of zirconia- and metal-supported fixed dental prostheses: a systematic review. Int J Prosthodont 2010; 23: 493-502.
34) Guazzato M, Albakry M, Ringer SP, Swain MV. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics. Dent Mater 2004; 20: 449-456.

35) Gorman CM, Horgan K, Dollard RP, Stanton KT. Effects of repeated processing on the strength and microstructure of a heat-pressed dental ceramic. J Prostheth Dent 2014; 112: 1370-1376.

36) Coldea A, Swain MV, Thiel N. In-vitro strength degradation of dental ceramics and novel PICN material by sharp indentation. J Mech Behav Biomater Dent 2013; 26: 34-42.

37) Garrido MA, Giráldez I, Ceballos L, Rodríguez J. On the possibility of estimating the fracture toughness of enamel. Dent Mater 2014; 30: 1224-1233.

38) Wallimo A, Nystrom M, Kononen M. Bite force and dentofacial morphology in men with severe dental attrition. Scand J Dent Res 1994; 102: 92-96.

39) Li RW, Chow TW, Matulina JP. Ceramic dental biomaterials and CAD/CAM technology: State of the art. J Prosthodont Res 2014; 58: 208-216.

40) Soderholm KJ. Review of the fracture toughness approach. Dent Mater 2010; 26: e63-77.

41) Leonardi A, Furgiuele F, Syngellakis S, Wood RJK. Analytical approaches to stress intensity factor evaluation for indentation cracks. J Am Ceram Soc 2009; 92: 1093-1097.

42) Oh WS, Zhang NZ, Anusavice KJ. Effect of heat treatment on fracture toughness K(II) and microstructure of a fluorocarbon-based glass-ceramic. J Prosthodont Res 2007; 16: 439-444.

43) Bhat M, Kaur B, Kumar R, Bamzai KK, Kotru PN, Wanklyn BM. Effect of ion irradiation on dielectric and mechanical characteristics of ErFeO3 single crystals. Nucl Instr Meth Phys Res B 2005; 234: 494-508.

44) Quinn JB, Sundar V, Lloyd IK. Influence of microstructure and chemistry on the fracture toughness of dental ceramics. Dent Mater 2003; 19: 603-611.

45) Tang X, Nakamura T, Usami H, Wakabayashi K, Yatani H. Effects of multiple firings on the mechanical properties and microstructure of veneering ceramics for zirconia frameworks. J Dental Res 2012; 40: 372-380.

46) Yoshimura HN, Gonzalez CC, Cesar PF, Miranda JR WG. Relationship between elastic and mechanical properties of dental ceramics and their index of brittleness. Ceram Int 2012; 38: 4715-4722.

47) Swain MV. Toughening mechanisms for ceramics. Mater Forum 1989; 13: 237-353.

48) Albakry M, Guazzato M, Swain MV. Influence of hot pressing on the microstructure and fracture toughness of two pressable dental glass-ceramics. J Biomed Mater Res B Appl Biomater 2004; 71: 99-107.

49) Krüger S, Deubener J, Ritzberger C, Höland W. Nucleation kinetics of lithium metasilicate in ZrO2-bearing lithium silicate glasses for dental application. Int J Appl Glass Sci 2013; 4: 9-19.

50) Stangel I, Nathanson D, Hau CS. Shear strength of the composite bond to etched porcelain. J Dent Res 1987; 66 : 1460-1465.

51) Gulser AU, Yilmaz F, Yenisey M, Güler E, Ural C. Effect of acid etching time and a self-etching adhesive on the shear bond strength of composite resin to porcelain. J Adhes Dent 2006; 8 ; 21-25.

52) Yen TW, Blackman RR, Baez RJ. Effect of acid etching on the flexural strength of a feldspathic porcelain and a castable glass ceramic. J Prosthodont Dent 1993; 70: 224-233.

53) Sorensen JA, Engelman MJ, Torres TJ, Avera SP. Shear bond strength of composite resin to porcelain. Int J Prosthodont 1991; 4: 17-23.