

**HIGH PERFORMANCE $ZrSiO_4$
REINFORCED LZSA GLASS-CERAMICS
MATRIX CERAMIC FLOOR TILES**

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1. INTRODUCTION

The need from the market by new products that show better performance has extraordinarily stimulated the scientific investigation focused in the application of materials with interesting properties and low costs. This interest increases when exists the possibility to manufacture components by using technological know-how. Glass-ceramics are relatively new materials specially used because of their exceptional characteristics such as high bend, abrasion and scratch strengths; high hardness; wide range of coefficient of thermal expansion (CTE), even negatives resulting in high thermal shock resistance and high chemical resistance. These characteristics basically depend on the nature, size and distribution of the formed crystals as well as on the residual glassy phase.^[1] Glass-ceramic materials find great applications in different engineering areas as well as in some domestic uses. These materials are interesting not only by their excellent properties but also because of the possibility to produce them by using low cost raw materials and also using some residues such as slag from steel plants, glass wastes, fly ashes which can be transformed into products with optimized properties for a given application.^[2] The classical fabrication of glass-ceramic materials consists of the preparation of monolithic glass components by using the same technologies used in the glass fabrication followed by heat-treatment for crystallization.^[3,4] However, this technology requires great investments and can be justified only for great production volumes.^[2] A viable alternative could be the production of glass-ceramics processed from glass powders and consolidated by sintering since it is possible the utilization of the same equipments of a traditional ceramic plant to produce components with complex shapes. In the last years the technological importance of this relatively new class of glass-ceramic, obtained by sintering and controlled crystallization of parent glass powders has increased. Oliveira^[5-11] studied a sintered glass-ceramic material belonging to the LZS ($\text{Li}_2\text{O-ZrO}_2\text{-SiO}_2$) with the same or better typical characteristics and properties than those of some commercial glass-ceramics and other traditional ceramics products or natural stones. The good properties showed by the LZS glass-ceramic are due to the formed crystalline phases (ZrSiO_4 and $\text{Li}_2\text{Si}_2\text{O}_5$). Montedo^[12] modified the LZS glass-ceramic system by partially substituting zirconium oxide by alumina so that the resulting LZSA ($\text{Li}_2\text{O-ZrO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$) glass-ceramic showed a CTE lower than that of the LZS glass-ceramic system. In the powder technology extrusion is a processing forming method that can be used for the production of sintered glass-ceramic materials, which is the subject of this work. Extrusion is a very productive forming technique used for mass production of large and even small components. The traditional building materials like bricks and roof tiles, refractories, porcelain electrical insulators and transparent ceramic pipes are produced by extrusion. The substrates can be extruded so that components with thickness lower than 1 mm with complex shapes and produced at low costs can be obtained.^[13] Plasticity, property that glassy materials do not exhibit, is the capability of a material to be deformed without rupture by the action of an applied load and to retain the achieved deformation when the applied load is removed.^[14] This property is a decisive factor for the extrusion process and it directly interferes on the quality of the extruded products. To provide plasticity to a ceramic, organic and inorganic binders can be used. However, the utilization of organic binders may increase the process costs since a very long heat-treatment for binder extraction is applied. Furthermore, there is the possibility of defects generation such as internal porosity and cracks caused by the decomposition of carbon residues. An alternative to solve these problems could be the utilization of an inorganic binder as bentonite, which in this case will be incorporated to the finished material. In this context, this work has as main objective to characterize a ZrSiO_4 particulate-reinforced LZSA glass-ceramic matrix with bentonite as binder and formed by extrusion for ceramic floor tile applications.

2. EXPERIMENTAL PROCEDURES

A glass composition belonging to the system LZSA was prepared from commercially available raw materials. Details of the preparation and characterization are described in a previous publication.^[12] In order to obtain compacts by extrusion commercial ZrSiO_4 (average particle size of 4.5 μm) from 10 to 70 wt-%, in 10% intervals and 7 wt-% bentonite (average particle size of 2.8 μm) were added to the glass powder and mixed and humidified with water (23 wt-%). Subsequently, the mixtures were stored for 12 h to moisture homogenization and then they were extruded in a Netzsch extruder MA 01 so that compacted samples with nominal dimensions of 80 (length) x 25 (width) x 5 (thickness) mm were obtained and used for the experiments. Thermal linear shrinkage (TLS) and CTE of compacted and sintered samples, respectively, were measured using a dilatometer (Netzsch dilatometer Model DIL 402PC) at $10^\circ\text{C}\cdot\text{min}^{-1}$ in air, using alumina as reference material, for rectangular samples of 20 mm length, 5 mm width and 5 mm thickness. The crystallization temperature of the glass powder and mixtures were measured using differential thermal analysis, DTA (Netzsch, STA EP 409) in air at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ using powdered specimens of about 30 mg in an alumina sample holder with an empty alumina crucible as reference material. The obtained extruded compacted samples, after 48 h at 20°C , were dried at $110 \pm 5^\circ\text{C}$ and then isothermally sintered in an electric furnace at $10^\circ\text{C}\cdot\text{min}^{-1}$ in air for 10 min at temperatures in the range of 500-1300°C. After sintering, samples were air-quenched to room temperature. The theoretical density (ρ_t) of the sintered samples was measured by using a pycnometer and the apparent density (ρ_{ap}) was measured by the Archimedes principle in water immersion at 20°C . Taking in account the apparent density and theoretical density measurements, the relative density (ρ_r) and porosity were calculated. After sintering, samples were transversally cut, grounded and polished with 1 mm alumina paste and then etched in 2% HF for 25 s. Subsequently, all the samples were coated with a thin Au film for scanning electron microscopy (SEM) observations (Model Philips XL-30). To investigate the crystalline phases formed during heat-treatments, powdered samples were analyzed with a Philips PW 3710 X-ray (Cu $K\alpha$) powder diffractometer (XRD). Bending strength (σ_b) of green and sintered samples was performed in an EMIC test machine (Model DL 2000) according to ISO 10545-4. Deep abrasion (D_a) of sintered samples was performed (Gabrielli test machine Model CAP) according to ISO 10545-6. Chemical resistance (CR) was evaluated by weight loss of the test piece ($80 \times 25 \times 5 \text{ mm}^3$) after 650 h immersed in a 1% H_2SO_4 and NaOH solutions, respectively at 20°C . In order to determine the hardness of the obtained materials, samples were mounted in epoxy resin and surfaces were ground smooth, and then polished with 1 mm alumina paste. Subsequently, microhardness measurements were performed with a Vickers automatic hardness tester at a load level of 4.903 N. A total time of 15 s was used for each indentation. Each value of hardness is the average of ten measurements with the respective standard deviation.

3. RESULTS AND DISCUSSION

DTA curves are shown in Fig. 1. According to this figure it can be seen that the crystallization temperature of the investigated compositions take place at about 780°C . However, as the reinforcing crystalline phase (zircon- ZrSiO_4) added increased the crystallization peak intensity decreases.

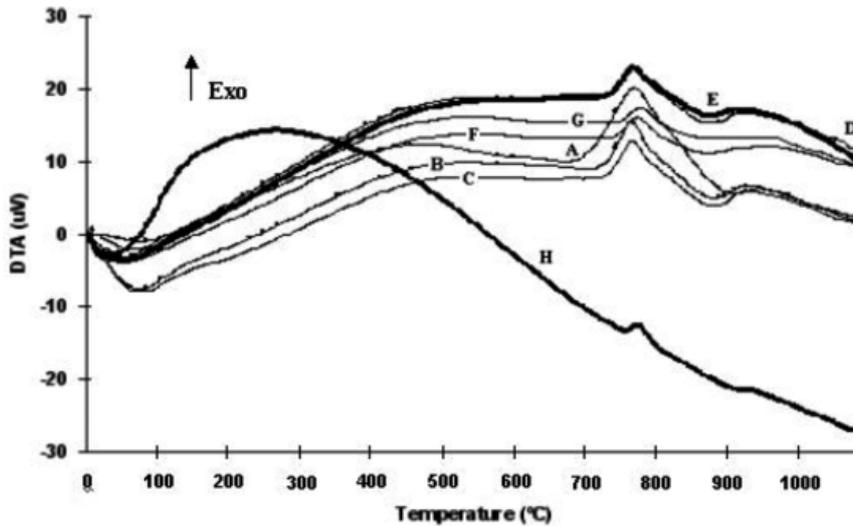


Figure 1. DTA curves of LZSA glass-ceramic (A) and composites (B – 10 wt-% ZrSiO₄); (C – 20 wt-% ZrSiO₄); (D – 30 wt-% ZrSiO₄); (E – 40 wt-% ZrSiO₄); (F – 50 wt-% ZrSiO₄); (G – 60 wt-% ZrSiO₄); (H – 70 wt-% ZrSiO₄).

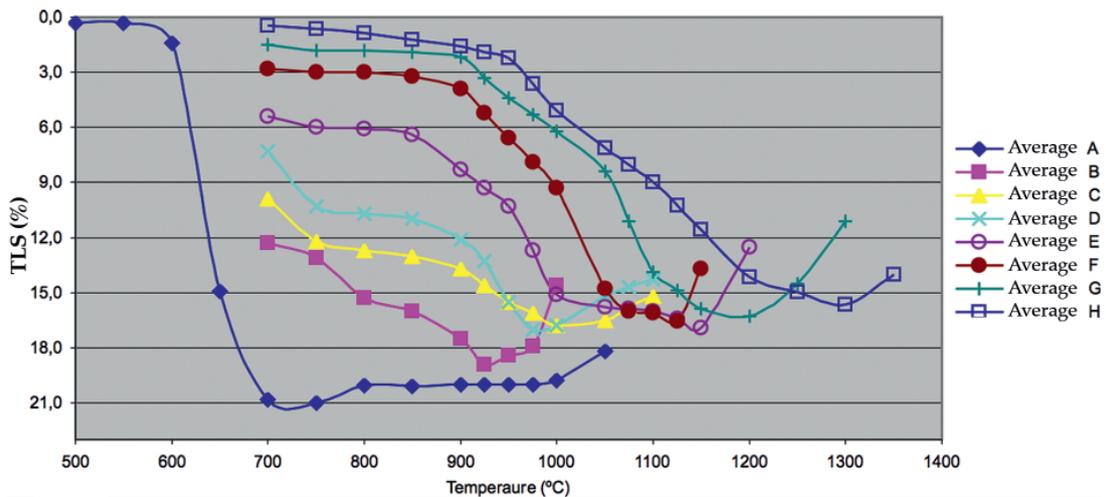


Figure 2. TLS curves of LZSA glass-ceramic (◆) and composites (■ 10 wt-% ZrSiO₄); (▲ 20 wt-% ZrSiO₄); (X 30 wt-% ZrSiO₄); (o 40 wt-% ZrSiO₄); (• 50 wt-% ZrSiO₄); (+ 60 wt-% ZrSiO₄); (□ 70 wt-% ZrSiO₄).

This happens because the glass-ceramic matrix fraction decreased respect to the reinforcing phase what means that lower crystal fractions were formed from de glass-ceramic matrix. Moreover, it can be said that the reinforcing crystalline phases did not interfered in the crystallization peak position. On the other hand, according to the TLS curve (Fig. 2), densification is apparently affected by zircon additions i.e., as the zircon was added thermal shrinkage decreased and the shrinkage rate for all studied compositions tends to zero at 730, 925, 1000, 975, 1150, 1125, 1200 and 1300°C, respectively. This behavior is related to the reduction of the formed viscous liquid phase as the zircon was added. The sintered samples were then subjected to deep abrasion, porosity, bending strength and microhardness measurements according to results as shown in Table I. From Table I it can be seen that the deep abrasion values are affected by the zircon particle additions decreasing from A to B compositions and increasing from B to D compositions. It can be also noticed that the bending strength increased from A to B compositions and decreased from B to C compositions. These deep abrasion and bending strength variations resulted from compositional and sintering

temperature differences. In fact, by comparing B and E compositions, for example, it can be observed that the deep abrasion resistance decreased even with higher zircon content. However, B composition shows porosity lower than E composition indicating a higher densification degree. This occurred because LZSA frit content in B composition is higher and in the sintering temperature more viscous liquid phase is formed according to microstructural evaluation. The more significant result related to the deep abrasion and bending strength among the studied compositions is related to the G composition sintered at 1200°C. Microhardness values also tend to increase as the zircon content increases so that H composition sintered at 1300°C showed the highest value (9.4 GPa). This occurred because H composition has a higher zircon content and also because it was sintered at a higher temperature. Table II shows the measured properties of the studied G composition sintered at 1150°C for 10 min compared with some reference materials. As the holding time increased from 10 to 60 min at 1125°C the relative density and the deep abrasion resistance tend gradually to increase from 93.6 to 94.1% and from 65 to 56 mm³, respectively. The small increase in the relative density promoted a significant improvement on the bending strength (from 153 to 220 MPa), probably because by increasing the holding time at the sintering temperature the viscosity of the glass-ceramic matrix decreased providing further densification. As expected, deep abrasion and bending strength also decreased.

Comp.	T (°C)	D _a (mm ³)	Porosity (%)	σ _f (MPa)	HV _{500g} (GPa)
A	725	134 ± 5	5.5 ± 0.4	60 ± 8	6.4 ± 0.2
B	950	73 ± 6	6.4 ± 0.4	77 ± 10	6.2 ± 0.4
C	950	90 ± 4	7.2 ± 0.2	76 ± 7	6.3 ± 0.3
D	950	116 ± 6	8.5 ± 0.2	104 ± 8	6.4 ± 0.4
E	1100	80 ± 3	10.2 ± 0.3	118 ± 5	6.4 ± 0.4
F	1125	69 ± 4	10.7 ± 0.2	162 ± 7	7.5 ± 0.3
G	1200	51 ± 3	8.8 ± 0.2	180 ± 8	8.1 ± 0.3
H	1300	60 ± 3	9.2 ± 0.2	144 ± 11	9.4 ± 0.3

Table I. Evaluated properties of formulated and prepared materials sintered at selected temperatures (T) for 10 min.

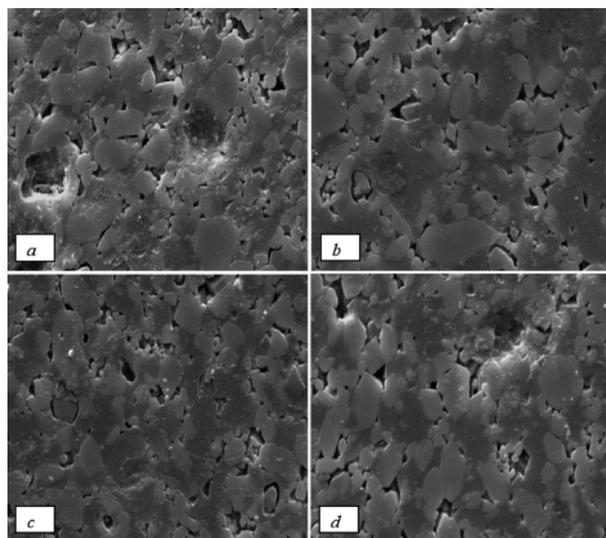


Figure 3. SEM photographs related to G comp. sintered at 1125 (a), 1150 (b) and 1175°C (c) for 10 min and at 1175°C (d) for 60 min.

Fig. 3 shows micrographs related to G samples sintered at 1125, 1150 and 1175°C for 10 min and at 1175°C for 60 min. From the figure light areas attributed to zircon particles and dark areas attributed to the residual glassy phase can be seen according to microprobe chemical analysis. It can be verified yet from Fig. 3 that zircon particles show good interaction with the glass-ceramic matrix, i.e., zircon (reinforcing) particles were well wetted by the matrix so that the formed interface showed small apparent porosity. According to Montedo^[12] the LZSA glass-ceramic frit shows preponderantly, after crystallization, β -spodumene, zircon, lithium disilicate and α -quartz crystalline phases. The first formed crystalline phases (G composition), after heat-treatments, were zircon and β -spodumene. The formation of these crystalline phases, probably, with fine grains and uniformly distributed in the glass-ceramic matrix, contributes to improve the mechanical strength as well as to decrease its coefficient of thermal expansion. Moreover, other crystalline phases, in small amounts, as lithium metasilicate and ZrO_2 were detected.

PROPERTIES	G	LZS	LZSA	M	GR	NP
ρ_{ap} (g/cm ³)	3.04	2.65	2.52	2.69	2.64	2.70
Total porosity (%)	5.5±0.2	8.8	5.5±0.4	-	-	-
σ_f (MPa)	220±10	163±9	60±8	14±4	27 ± 5	50
HV500g (GPa)	7.17±0.4	6.05 ± 0,4	6.4±0.2	-	-	-
Deep abrasion (mm ³)	51 ± 3	35 ± 2	134±5	650 ± 15	142 ± 1	126 ± 1
CTE (10 ⁻⁶ °C ⁻¹)	3.9	8.0 – 10.0	7.1	19.0	19.8	-
Chemical resistance						
Acids (wt%)	< 0,01	< 0,01	-	5.74	0.15	0.08
Alkalics (wt%)	< 0,01	< 0,01	-	8.99	0.03	0.05

Table II. Measured properties of the studied G composition sintered at 1150°C for 10 min compared with some reference materials. LZS and LZSA are sintered glass-ceramics; M: Marble; GR: Granite; NP: Neopariès.

Porosity is lower than LZS glass-ceramic and bending strength and microhardness are higher than those found for the considered reference materials. Deep abrasion resistance is very high if compared with the reference materials. Only the LZS glass-ceramic shows a better performance. This behavior can be attributed to the relatively high hardness of zircon, that in the LZS system is the major formed crystalline phase, and in particular the material toughness and/or stiffness as a consequence of the formed interface and the reinforcing particles, which actuate as a barrier to the crack propagation, increases the material critical stress and so its mechanical resistance. The chemical resistance in comparison with the reference materials is superior. The relatively low CTE can be explained since zircon but in particular β -spodumene have a low CTE ($4 \times 10^{-6} \text{°C}^{-1}$ and $0.4 - 2 \times 10^{-6} \text{°C}^{-1}$, respectively)^[15] against $11 \times 10^{-6} \text{°C}^{-1}$ for lithium disilicate^[16] based glass-ceramics.

4. CONCLUSIONS

An optimized extruded 60 wt% zircon particulate-reinforced LZSA glass-ceramic matrix added with 7 wt% bentonite as binder and humidified with 23 wt% water was obtained by sintering and crystallization. Sintering and densification started at about 640°C and its rate was reduced at 700°C due to the crystallization process. After crystallization (850°C) densification increased again by reduction of the glassy phase viscosity as the temperature increased. This new densification occurred at 1150°C. A

further temperature increase, i.e., from 1150 to 1250°C resulted in a material expansion caused by the melting of the glass-ceramic matrix. On heating, the compacts first crystallize into zircon and b-spodumene and then into lithium metasilicate and ZrO_2 . The microstructure consisted of fine crystals uniformly distributed and randomly oriented through out the glassy phase as well as a residual porosity. The extruded samples, after sintering at 1150°C for 10 min, showed a thermal linear shrinkage of about 14% which corresponds to a relative density of 94,5% and deep abrasion resistance and bending strength of about 51 mm³ and 220 MPa, respectively. The chemical resistance was superior to the tested reference materials and the measured relatively low CTE ($3.9 \times 10^{-6} \text{C}^{-1}$) indicates that the obtained material exhibit good thermal shock resistance. Finally, it can be concluded that the extrusion technology is a potential candidate to produce sintered materials for a number of applications including small formats ceramic floor tiles for heavy traffic.

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