

Using ZrO₂ or Al₂O₃ particles to enhance the mechanical properties of a LZSA glass-ceramic matrix

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ABSTRACT

Investigations of a range of glass ceramic compositions have been developed in the last decades. These materials show a good potential to be used at room temperature as a substitute to other ceramic materials, due to their lower sintering temperature and costs. The main reason that limits the use of these materials is their low mechanical strength. In this work a Li₂O-ZrO₂-SiO₂-Al₂O₃ (LZSA) glass powder was mixed with 30 wt. % of ZrO₂ or Al₂O₃ (submicron size), uniaxially pressed under 40 MPa and sintered at 650 °C/30 min. In some samples a second sintering step at 1000 °C during 30 minutes was also performed, in order to improve the mechanical properties by increasing the crystallized fraction. The sintered samples were characterized by bending strength measurements, X-ray diffraction and scanning electron microscopy analyses. Apparent densities values were determined by the Archimedes's method. The results obtained in this work indicate that the addition of ZrO₂ and Al₂O₃ (reinforcing particles) decreases the density of the glass-ceramic materials. X-ray diffraction analysis indicated an increase of the crystallized fraction in samples sintered at 1000 °C. Fracture strength values has showed to be dependent on the sintering temperature and also on the reinforcing crystalline particles.

Keywords: composite materials, mechanical properties, sintering, powder technology.

1 INTRODUCTION

Nowadays the industrial sectors are looking for the development of new materials that exhibit better properties and lower production costs. Some studies have been developed in order to investigate the potential of glass ceramics in structural applications [1 - 2]. The glass ceramic materials offer the possibility to be sintered at significant lower temperatures, as compared to other ceramic materials (aluminum and zirconium oxides), reducing the production costs. The disadvantage factor, that limits the application of this kind of material, is the low strength values that are not sufficient for structural applications. Mechanical properties of the ceramic materials can be improved due the incorporation of a second phase, as fibers, hard particles or whiskers [3 - 6]. Several works published in the literature report the improvement in properties of alumina-based composite materials [4 - 8]. Aspects such as microstructure, fracture strength and fracture toughness have been extensively investigated [9 - 11]. The results have showed that the presence of hard particles causes a pinning effect and a crack deflection mechanism, which further contribute to the final microstructure and mechanical performance of the alumina composite material, respectively. The incorporation of alumina and WC particles has also improved the mechanical properties of zirconium oxide materials [12 - 13]. The influence of SiC-platelets on the microstructure and mechanical properties of a cordierite glass ceramic material was also investigated [3]. The results have indicated that the crack deflection is the dominant mechanism which contributes to an improvement in the fracture toughness. In this work a glass ceramic material belonging to the Li₂O-ZrO₂-SiO₂-Al₂O₃ (LZSA) system reinforced with alumina and zirconia particles was investigated. The effect of the reinforcing element on the physical and mechanical properties were studied and compared with the reference materials (pure glass material). The objective of this study is to verify the possibility to obtain a glass ceramic composite material by conventional sintering process at low

temperatures and to investigate the potential use of aluminum or zirconium oxides as reinforcing elements in a LZSA matrix.

2 EXPERIMENTAL PROCEDURE

A glass ceramic powder consisted of $\text{Li}_2\text{O-ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ (LZSA) with an average grain size of $4.0\ \mu\text{m}$ was selected as the matrix raw material. This material was prepared from a mixture of commercially available raw materials, melted at approximately $1500\ ^\circ\text{C}$ and quenched in water, in order to obtain a glass powder. Details about the preparation of the LZSA powders can be founded elsewhere [2]. Powders of alumina- α (Basserman) and ZrO_2 (Aldrich) with an average grain size of $1.64\ \mu\text{m}$ and $2.76\ \mu\text{m}$, respectively were used as reinforcing elements. Mixtures containing a fixed concentration of 30 wt. % of Al_2O_3 or ZrO_2 were prepared in a planetary ball milling. Subsequently, powders compacts were uniaxially pressed into prismatic bars ($5 \times 5 \times 30\ \text{mm}^3$) under 40 MPa. Specimens were sintered in air at 600 and $650\ ^\circ\text{C}$. Some samples were also submitted to a thermal treatment at $1000\ ^\circ\text{C}$, in order to improve the crystallization process. Glass ceramic powder without reinforcement was also prepared to be used as a reference material. The apparent density and porosity of the sintered specimens were measured using Archimedes water displacement method. The identification of crystalline phases was carried out by X-ray diffraction (XRD) on a diffractometer (Schimadzu XRD-600) operated at 40 kV with monochromatized $\text{CuK}\alpha$ radiation over a range 2θ from 20 to $80\ ^\circ$, at a scanning speed of $0.5^\circ/\text{min}$. A dilatometric study (BP Engineering RB-300) was carried out in air from ambient temperature up to $650\ ^\circ\text{C}$ with a heating rate of $10^\circ/\text{min}$. The mechanical strength of the sintered samples was determined as the average of five measurements for each composition, using a universal testing machine (Zwick, 2.5 kN) in a four-point bending geometry, with upper and bottom knives span of 40 and 20 mm, respectively, at a constant cross-head speed of $0.5\ \text{mm}/\text{min}$, according to EN 100 method.

3 RESULTS AND DISCUSSION

Figure 1 depicts the dilatometric curve obtained for pure LZSA. According to this Figure, the sintering process starts at around $560\ ^\circ\text{C}$. The effect of the reinforcing elements on the dilatometric behavior of LZSA is showed also in Figure 1. The Al_2O_3 or ZrO_2 incorporation causes a change on the onset of the sintering temperature. This is a clear evidence that the presence of both reinforcing elements delay the shrinkage process and, as a consequence, also the beginning of the sintering process of the reinforced LZSA glass material. The pure LZSA glass material was chosen to illustrate the typical thermal behavior of the investigated glass materials, which is shown in Figure 2. According to the DTA curve an endothermic inflection at around $600\ ^\circ\text{C}$ can be seen, corresponding to the glass transition. The exothermic peaks that occur between 700 and $850\ ^\circ\text{C}$ are characteristic of the glass crystallization, which is in agreement with the results of the X-ray diffraction analyses, showed in Figure 3, and with the results reported in the literature [1, 2].

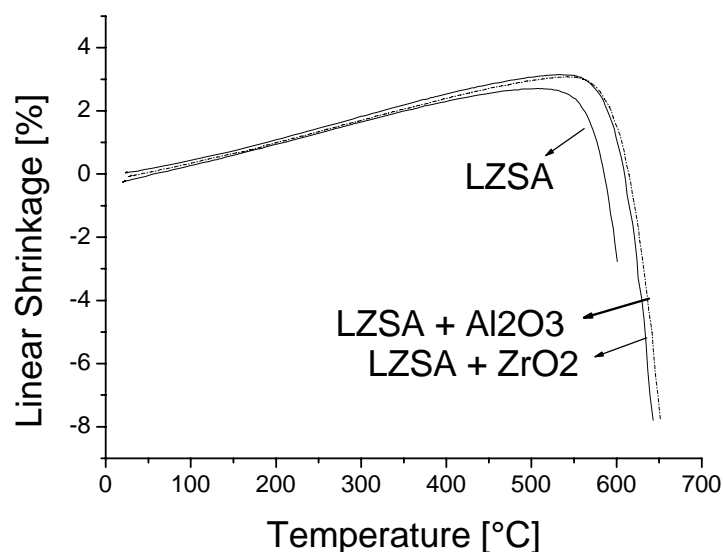


Figure 1: Influence of Al_2O_3 and ZrO_2 on the dilatometric behavior of LZSA glass.

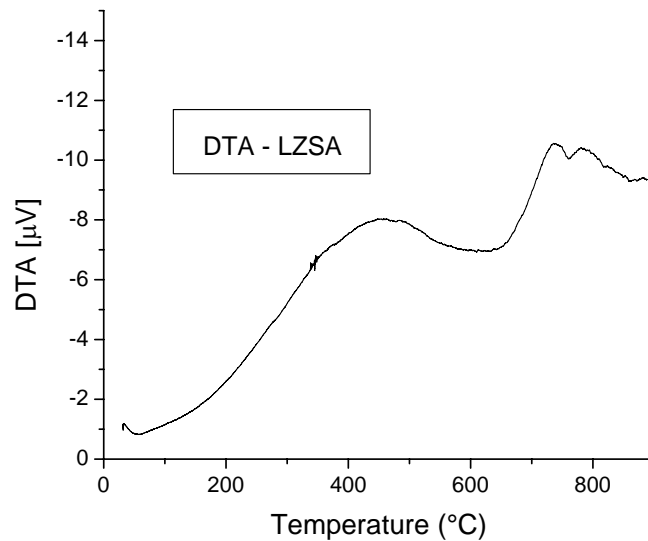


Figure 2: Differential thermal analysis (DTA) of LZSA glass material.

Table 1 summarizes the evaluated parameters of LZSA with Al_2O_3 or ZrO_2 . It can be noted that the increase of the sintering temperature from 600 to 1000 °C reduces the densification of pure LZSA glass material, which is probably related to the volatility of the LZSA glass at high temperatures. The increase of the porosity values observed in the LZSA glass material with additions of Al_2O_3 and ZrO_2 at 650 °C can be attributed to the difficulty to sinter the LZSA glass material with the incorporation of alumina particles. The presence of rigid particles of Al_2O_3 or ZrO_2 in the LZSA glass material probably reduces the mobility of the LZSA grain boundaries during the sintering process and prevents full densification. Similar behavior was also founded for other composite systems such as Al_2O_3 + carbides [6, 9, 11] and ZrO_2 +WC [13]. Contrary to that, the reinforcing materials show an improvement of the densification by increasing the temperature. The ZrO_2 reinforcing material presents a decrease of the porosity values from 20.35 to 8.25 %, showing a good potential to be used as reinforced element in the LZSA glass matrix. The increase of the sintering temperature to 1000 °C has reduced the porosity of the Al_2O_3 -LZSA composite material, but not to the adequate porosity level as observed for the ZrO_2 -LZSA material.

Table 1: Porosity, density and strength values obtained in this work

	Density [g/cm ³]	Porosity [%]	Flexural Strength [MPa]
LZSA(650 °C)	2.56	1.41	90 ± 8
LZSA (650 °C + 1000 °C)	2.48	2.21	85 ±7
LZSA + 30 wt. % Al_2O_3 (650 °C)	1.81	28.05	-----
LZSA + 30 wt. % Al_2O_3 (650 °C + 1000 °C)	2.15	18.84	40 ±4
LZSA+ 30 wt. % ZrO_2 (650 °C)	2.41	20.35	-----
LZSA+ 30 wt. % ZrO_2 (650 °C + 1000 °C)	2.91	8.25	120 ±10

X-ray diffraction pattern of the materials investigated in this work is shown in Figures 3 and 4. The LZSA glass material clearly showed a behavior change between 650 and 900 °C. The first material shows a

characteristic amorphous behavior, presenting mainly the presence of $ZrSiO_4$ and ZrO_2 peaks. The X-ray pattern of the material sintered at $650\text{ }^\circ\text{C}$ showed a reduction of the amorphous behavior and a crystallization process with the presence of β -spodumene. The increase of the temperature to $1000\text{ }^\circ\text{C}$ has induced the disappearance of the amorphous characteristic, with the material showing only well defined crystalline peaks. Figure 4 shows the X-ray pattern of the reinforced material sintered at $650\text{ }^\circ\text{C}$ and submitted to a crystallization treatment at $1000\text{ }^\circ\text{C}$. The X-ray analyzes didn't show the presence of an amorphous characteristic. The sintered composite materials show well defined crystalline peaks. The incorporation of Al_2O_3 and ZrO_2 to the material has caused the presence of Al_2O_3 and $ZrSiO_4$ and ZrO_2 .

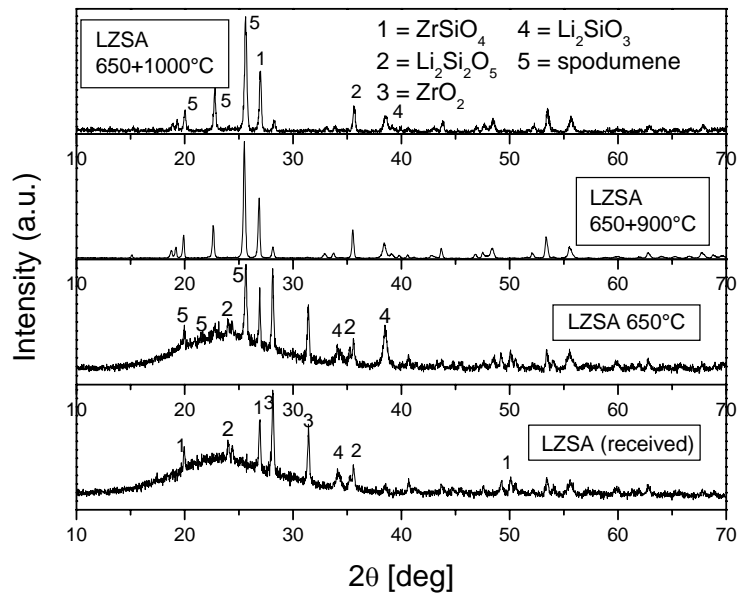


Figure 3: X-ray diffraction of LZSA glass material.

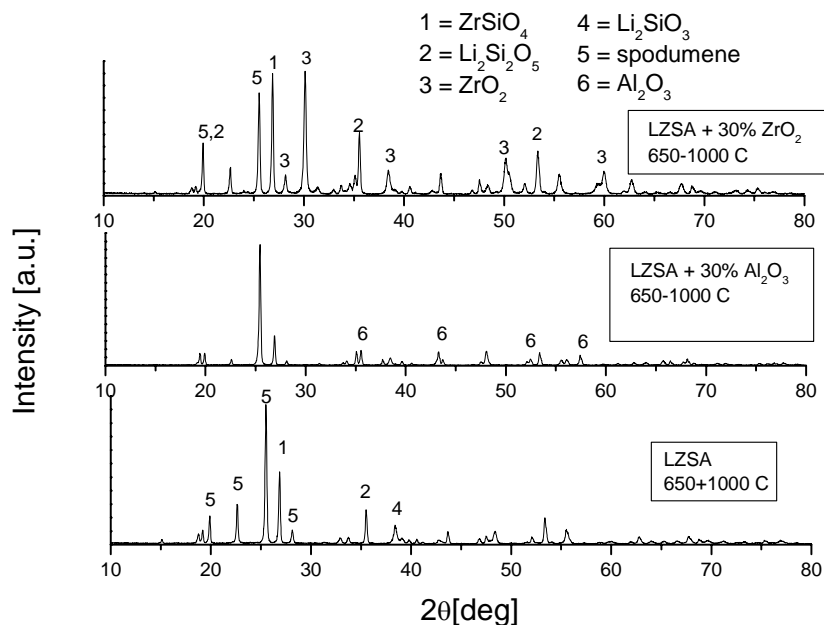


Figure 4: X-ray diffraction of LZSA glass material with Al_2O_3 and ZrO_2 additions sintered at $650\text{ }^\circ\text{C}$ and submitted to a crystalline treatment at $1000\text{ }^\circ\text{C}$.

Table 1 shows the flexural strength values determined in this work. The LZSA glass material shows a better behavior at lower sintering temperatures. It can be noted that the strength of LZSA is decreased with increasing temperature. This behavior can be related to the decrease of the densification of this material that is associated to the lithium evaporation that takes place at high temperatures, showing that the temperature of 1000 °C is too high to sinter the pure LZSA material. The presence of 30 wt. % Al_2O_3 caused a significant decrease on the strength of the LZSA glass material, which can be attributed to the increase on the porosity level of the composite material as compared to the LZSA glass material at the same conditions. The presence of ZrO_2 shows a divergent behavior. The LZSA + 30 wt. % ZrO_2 sintered at 650 °C and submitted to a crystallization treatment at 1000 °C causes an improvement of the mechanical property. Strength values ranged from 85 to 120 MPa. It was not possible to measure the strength of the composite materials (with ZrO_2 or Al_2O_3) sintered at 650 °C, because they were very fragile. The mechanical property observed in this work has showed to be a simultaneous function of the four effects: the sintering temperature, the porosity level, the second phases and the presence of crystallized phases. By increasing the temperature some parameters are improved and others become worse.

Figure 5a and 5b show a typical microstructure of the pure LZSA material and LZSA + 30 wt. % ZrO_2 , sintered at 650 °C and submitted to a crystallization treatment at 1000 °C. The LZSA glass material shows a β -spodumene grain size of approximately 2 μm and ZrSiO_2 (white particles). The LZSA+ ZrO_2 material shows a similar microstructure, with various small particles around the grain boundary.

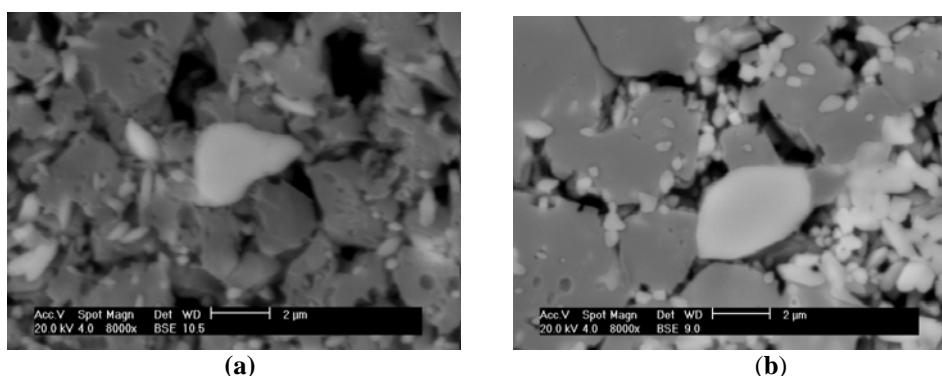


Figure 5: Micrograph of pure LZSA (a) and LZSA + 30 wt. % ZrO_2 (b) sintered at 650 °C and submitted to a crystallization treatment at 1000 °C.

4 CONCLUSIONS

The results obtained from the characterization of pressureless sintered LZSA with alumina or zirconium oxide revealed that:

- 1- The addition of ZrO_2 and Al_2O_3 reduces the densification process of the LZSA glass material.
- 2- The flexural strength values have shown to be dependent on the presence and type of a second phase and on the sintering temperatures.
- 3- The presence of ZrO_2 and Al_2O_3 shows a divergent behavior. The addition of ZrO_2 improves the mechanical behavior of the LZSA glass material at 1000 °C, but the incorporation of Al_2O_3 decreases the strength values.
- 3- The X-ray diffraction analysis shows the presence of ZrSiO_2 , ZrO_2 , Al_2O_3 and β -spodumene.
- 4- The material shows a dependence of the crystallization process on the sintering temperature. At 650 °C the LZSA material still shows an amorphous characteristic. The increase of the temperature to 1000 °C improves the crystallization process, showing the material no amorphous behavior.

5 ACKNOWLEDGEMENTS

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