# LSA GLASS-CERAMIC TILES MADE BY POWDER PRESSING

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## ABSTRACT

A low cost alternative for the production of glass-ceramic materials is the pressing of the matrix glass powders and its consolidation simultaneously with crystallization in a single stage of sintering. The main objective of this work was to obtain LSA glass-ceramics with low thermal expansion, processed by pressing and sintering a ceramic frit powder. The raw materials were homogenized and melted (1480°C, 80min), and the melt was poured into water. The glass was chemically (XRF and AAS) and thermally (DTA, 10°C/min, air) characterized, and then ground (60min and 120min). The ground powders were characterized (PSD, laser diffraction) and compressed (35MPa and 45MPa), thus forming four systems. The compacts were dried (150°C, 24h) and sintered (1175°C and 1185°C, 10°C/min). Finally, the glass-ceramics were characterized by microstructural analysis (SEM and XRD), mechanical behaviour ($\sigma_{bending}$) and thermal analysis (α). The best results for thermal expansion were those for the glass-ceramics processed with smaller particle size and greater compaction pressure.

## 1. INTRODUCTION

Until the last 50 years the traditional ceramics, as they were known, were based on products from china ware, porcelain, bricks, roof tiles, floor and wall tiles and even glasses and ceramics for high temperature, which were based on clay as the primary raw material. However, the market needs for new products with improved properties have always stimulated the understanding of the fundamental nature of these materials and the phenomena that occur inside them and are responsible for their unique properties. Thus, these studies led to a new generation of materials, and the term "ceramics" have assumed a wider meaning. With the advent of electronic, computers, communication, aerospace and a range of other industries the ceramic market was improved [1-4].

These new classes of ceramic materials have found in the last 40 years the glass-ceramics as a keystone; glass-ceramics are ceramic materials prepared by melting and crystallization of glasses which can develop unique microstructures with small grain sizes, random orientation, residual crystalline phases and low porosity. These features allow obtaining materials with properties different from those observed in ceramics produced by conventional processes, and the glass-ceramics are characterized by a great diversity in their behaviour [5]. These materials have applications in several industrial sectors, for presenting a number of interesting properties such as high hardness, abrasion resistance, mechanical strength and resistance to thermal shock, and excellent chemical durability and low thermal and electrical conductivity [1,2,4].

The manufacture of glass-ceramic materials consists in the preparation of monolithic glass components, by applying the same technologies used in the manufacture of glasses, and later by the use of crystallization heat treatment of nucleation and crystal growth [6]. However, this technology requires large investments and can only be justified for large volumes of production. An alternative would be the production of glass-ceramic materials processed from powders and consolidated by sintering, though it is possible to use the same equipment from a traditional ceramic plant to the production of components with complex geometry. The process involves the following basic steps: (a) glass melting and its cooling, (b) spraying, (c) conformation by ceramic technology (uniaxial pressing, extrusion, slip casting, injection moulding, among others), (d) sintering for consolidation and crystallization [6].

According to the definition of glass-ceramics, their production seems to be easy; however few companies in the world dominate the technology and produce glass-ceramics with commercially acceptable properties. Thus, the main focus of this work is a preliminary study to obtain a glass-ceramic with low thermal expansion using a simple technique for powder consolidation: uniaxial pressing. The uniaxial pressing is a high productivity process and gives high green strength to the conformed product. Pressing is the manufacture process for ceramic tiles where the substrate is formed in presses, from a finely ground mixture, usually

containing a small amount of water or a binder, and is compressed into the final shape by pressure.

The LSA glass-ceramics ($SiO_2.Li_2O.Al_2O_3$) show great interest because they present many special properties, such as minimal thermal expansion (or even zero) in a large range of temperatures while present desirable optical properties as high transmissibility and high translucency. These properties make this kind of glass-ceramics satisfactory for many applications, particularly for technological applications [7-9]. This unusual combination of properties is obtained due to the formation of a crystalline solid solution of β-spodumene and β-quartz in the glass-ceramic matrix. The combination of the cited properties is obtained by the precipitation of a large volume fraction of crystalline phases into the glass-ceramics in a controlled morphology, with very small crystals (nm to nm).

In the LSA glass-ceramic system the main phases of β-spodumene/β-eucryptite solid solution are produced in the glass-ceramic by controlled crystallization of a base glass with a composition range between 55% to 70% $SiO_2$, 15% to 27% $Al_2O_3$ and 1% to 6% $Li_2O$ (mass fraction), and the incorporation of specific additives [3].

Thus, the main objective of this study was to obtain the LSA glass-ceramic system ($LiO_2.SiO_2.Al_2O_3$) by melting the glass in the form of a ceramic frit, followed by glass grinding, granulation, compaction by uniaxial pressing and sintering simultaneously to the crystallization of the system [10].

## 2. EXPERIMENTAL PROCEDURE

The raw materials used to produce the LSA system in this study were lithium feldspar, lithium carbonate and titanium dioxide (as crystallization agent). The raw materials were dried, mixed in a laboratory eccentric mill (Servitech CT 42, high alumina grinders, 300mL, 5min) and the formulation was cast in an alumina crucible in a gas furnace to 1480°C for 80min for homogenization. The glass was poured into water under agitation to obtain a glass-ceramic frit, and the frit was dried in a stove (150°C, 24h). The frit chemical analysis was determined by X-ray fluorescence (Philips PW2400, molten sample) and by flame AAS (Unicam 969) to the determination of the lithium element.

After characterization the frit was ground in an eccentric mill (Servitech CT 42, high alumina grinders, 300mL) for 60min and 120min to obtain two particle size distributions. The particle size distributions were determined by laser diffraction (CILAS 1064, 10s-time reading) and thermal behaviour determined by optical dilatometry (HT Misura, 10°C/min, samples compressed to 25MPa with 9% moisture and 2 mm in diameter and height).

After milling the powder was compacted by uniaxial pressing (Gabbrielli hydraulic press, compacts with 32mm × 100mm) with the addition of 7wt% moisture

and compaction pressure of 35MPa and 45MPa. After pressing the compacts were again dried in a stove (150°C, 2h).

With the optical dilatometry results two main sintering temperatures were obtained, 1175°C and 1185°C, and the samples were sintered in a laboratory electric furnace (Jung LF0612) using these temperatures with 10°C/min heating rate in order to provide sintering simultaneous to crystallization.

Finally, the fired compacts were characterized by X-ray diffraction (Philips PW1830, CuKα (1.5418 Å), operating at 30kV and 15mA, with 2θ range between 0° and 75°, step of 0.05° and 1s reading time), scanning electron microscopy (Philips XL 30, 10kV, samples etched with 5vol% HF for 60s), dilatometry (BP RB 3000-20, 10°C/min, 25°C to 325°C) and mechanical resistance by three point bending method (EMIC DL 10000, 1mm/min).

## 3. RESULTS AND DISCUSION

Table 1 shows the chemical analysis of the frit (XRF and AAS), showing the main components of the oxide glass ($SiO_2$, $Al_2O_3$, $Li_2O$ and $TiO_2$), which are within the expected values for the final glass-ceramic.

| **Oxide** | $SiO_2$ | $Al_2O_3$ | $Li_2O$ | CaO | $K_2O$ | $Na_2O$ | $TiO_2$ | $ZrO_2$ |
|---|---|---|---|---|---|---|---|---|
| **Content (wt%)** | 64.7 | 22.4 | 6.8 | 0.5 | 0.8 | 1.0 | 1.8 | 0.6 |

*Table 1. Chemical analysis of the glass-ceramic (X-ray fluorescence and flame atomic absorption spectrometry).*

There are some other oxides as impurities, mainly $Na_2O$, who acts in the glass system as a softening agent. The presence of these oxides was considered negligible for the glass-ceramic under study.

Figure 1 shows the particle size distribution curves (and cumulative histograms) of the glass ground by one and two hours respectively. For the one hour ground glass the average particle diameter is 9.1μm, with 90% of the distribution below 22.0μm. For the two hours ground glass the average particle diameter is around 7.1μm, with 90% of the distribution below 16.7μm.

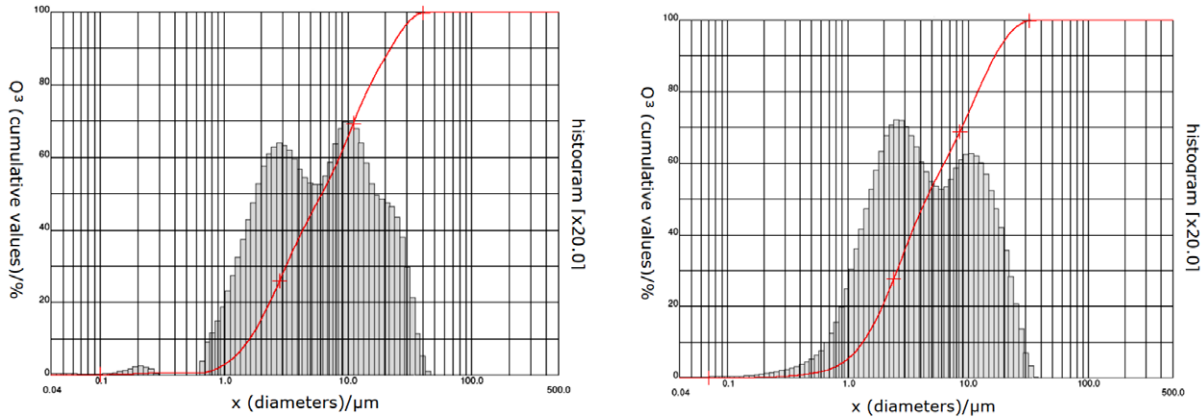


*Figure 1. Particle size distributions for 1h and 2h crushed glasses, respectively.*

The optical dilatometric curves, figure 2, show that the 1h ground glass presents the beginning of shrinkage at 669°C and the maximum rate of sintering near 1185°C. For the glass ground during 2h the beginning of shrinkage occurs at 647°C, and the maximum rate of sintering occurred at approximately 1175°C. This behaviour can be explained by the higher reactivity of the 2 hours ground glass due to the smaller particle size ($D_{50}$=7.1µm) which is related to the increased time of grinding.

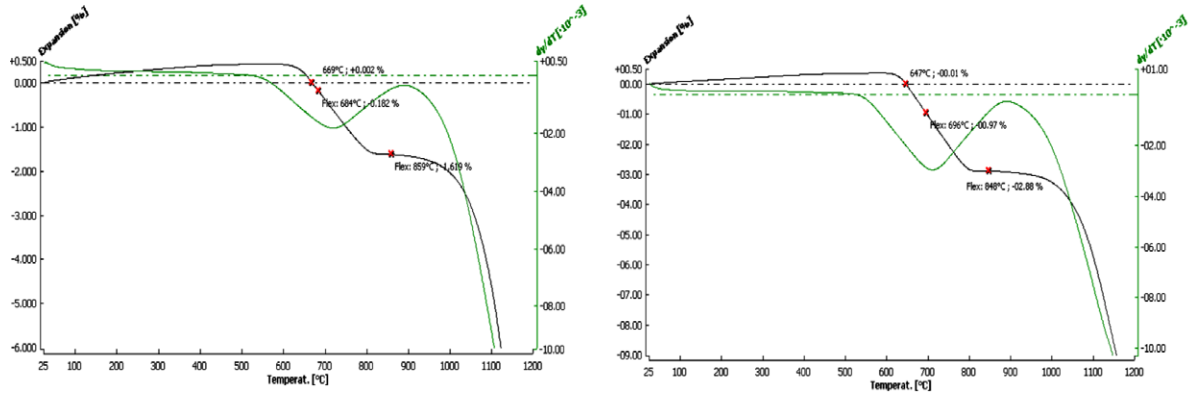


*Figure 2. Dilatometric curves for the 1h and 2h crushed glasses, respectively.*

After base glass (frit) characterization, the glass-ceramics were obtained by powder pressing (35MPa and 45MPa) the ground base glass (1h and 2h) and subsequent sintering (1175°C and 1185°C). The coefficients of thermal expansion ($CET_{(25\text{-}325)}$) of the glass-ceramics were determined by dilatometry, which is the property of greatest interest in the system under study, as the LSA glass-ceramics are used in situations where low coefficient of thermal expansion is desired. The determination of the $CET_{(25\text{-}325)}$ was performed with glass-ceramic samples pressed to 35MPa and 45MPa and sintered at 1175°C and 1185°C, table 2.

| Condition | 1h, 35MPa, 1185°C | 1h, 45MPa, 1185°C | 2h, 35MPa, 1175°C | 2h, 35MPa, 1175°C |
|---|---|---|---|---|
| $CET_{(25-325)}$ ($10^{-6}°C^{-1}$) | 1.37 | 1.33 | 1.29 | 1.23 |

*Table 2. $CET_{(25-325)}$ for different conditions of processing of the studied glass-ceramics.*

Comparing the values of $CET_{(25-325)}$ among the glass-ceramics processed under different conditions, there is a reduction of the coefficient of thermal expansion (CET) as the particle size reduces and the compaction pressure increases, table 2. With the reduction of particle size and the increasing of compaction pressure there is a reduction of the porosity by glass particle packing increasing during pressing, which consequently increases the rate of crystallization during sintering, thus reducing the value of $CET_{(25 -325)}$.

The mechanical behaviour of the glass-ceramic was evaluated by the determination of the bending resistance in three points. Table 3 presents the averages of the modulus of resistance to bending for each glass-ceramic obtained under different conditions of processing.

| Condition | 1h, 35MPa, 1185°C | 1h, 45MPa, 1185°C | 2h, 35MPa, 1175°C | 2h, 35MPa, 1175°C |
|---|---|---|---|---|
| Modulus of resistance to bending (MPa) | 80±3 | 70±10 | 71±8 | 79±2 |

*Table 3. Modulus of resistance to bending for different conditions of processing of the studied glass-ceramic.*

With respect to the measured values of the bending resistance modulus, there is no expressive variation of the module for the studied conditions of milling, compaction and sintering on the LSA glass-ceramic system, since they have presented very similar values. The results show the need to determine the mechanical behaviour using the Weibull distribution for this system.

The micrographs presented in figure 3 show the crystals formed on the surface of the glass-ceramic (typically surface crystallization) after chemical etching (HF 5 vol%, 60s). According to the micrographs, it appears that the glass precursor ground during 1h have larger crystals compared to the glass ground during 2h. As the crystallization occurs on the surface of the particles, the glass-ceramics with larger particles have formed larger crystals, while the 2h ground glass-ceramics were formed by smaller crystals.

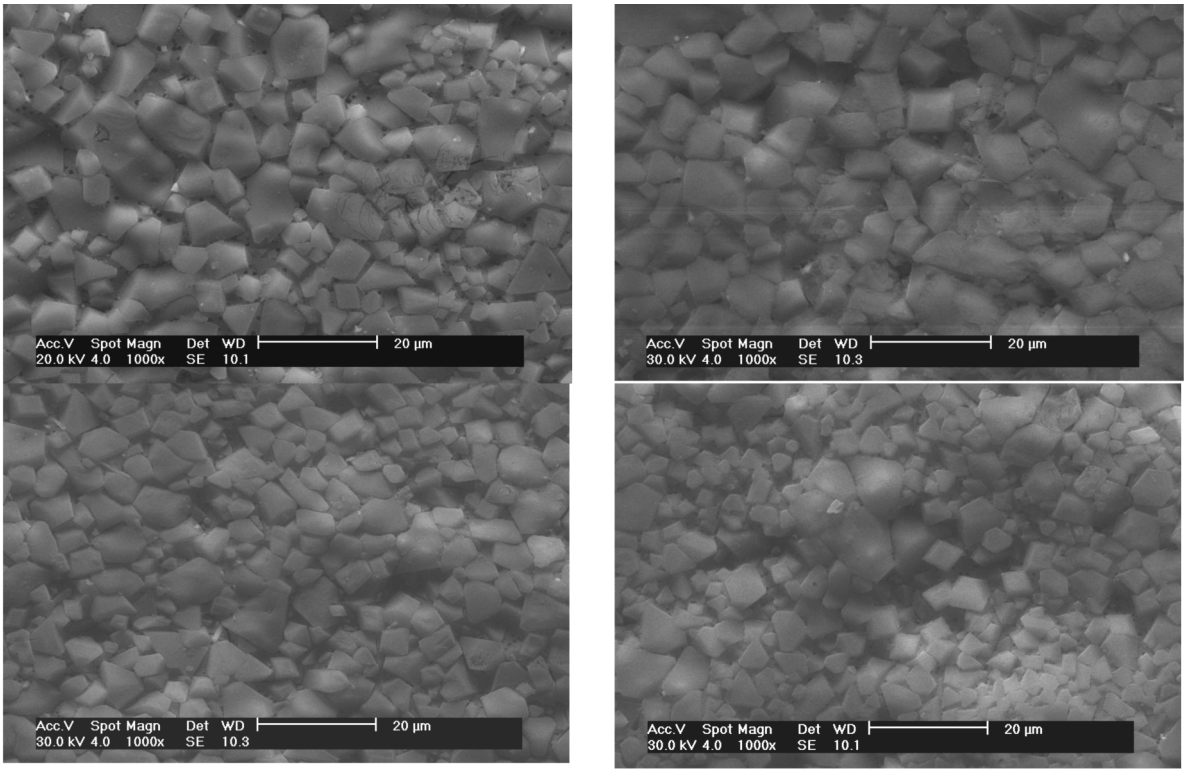


*Figure 3. Micrographs of the surface of the glass-ceramics (SEM, 5 vol% HF, 60s): 1h, 35MPa, 1185°C; 1h, 45MPa, 1185°C; 2h, 35MPa, 1175°C; 2h, 45MPa, 1175°C.*

Regarding the differences in compaction of the glass-ceramics, it can be seen in figure 4 that the 1h ground glass sintered at 1185°C, when subjected to a compaction pressure of 45MPa presents a more closed microstructure, with some crystals near each other when compared to the glass compressed at 35MPa and milled and sintered in the same condition (1 hour and 1185°C). The same situation can be checked for the glass milled for 2 hours and sintered at 1175°C when compressed to 45MPa in comparison to its counterpart compressed to 35MPa, Figure 4. The micrographs presented in figures 3 and 4 also showed a uniform crystal size distribution, an extremely important feature regarding the final properties of the glass-ceramics.

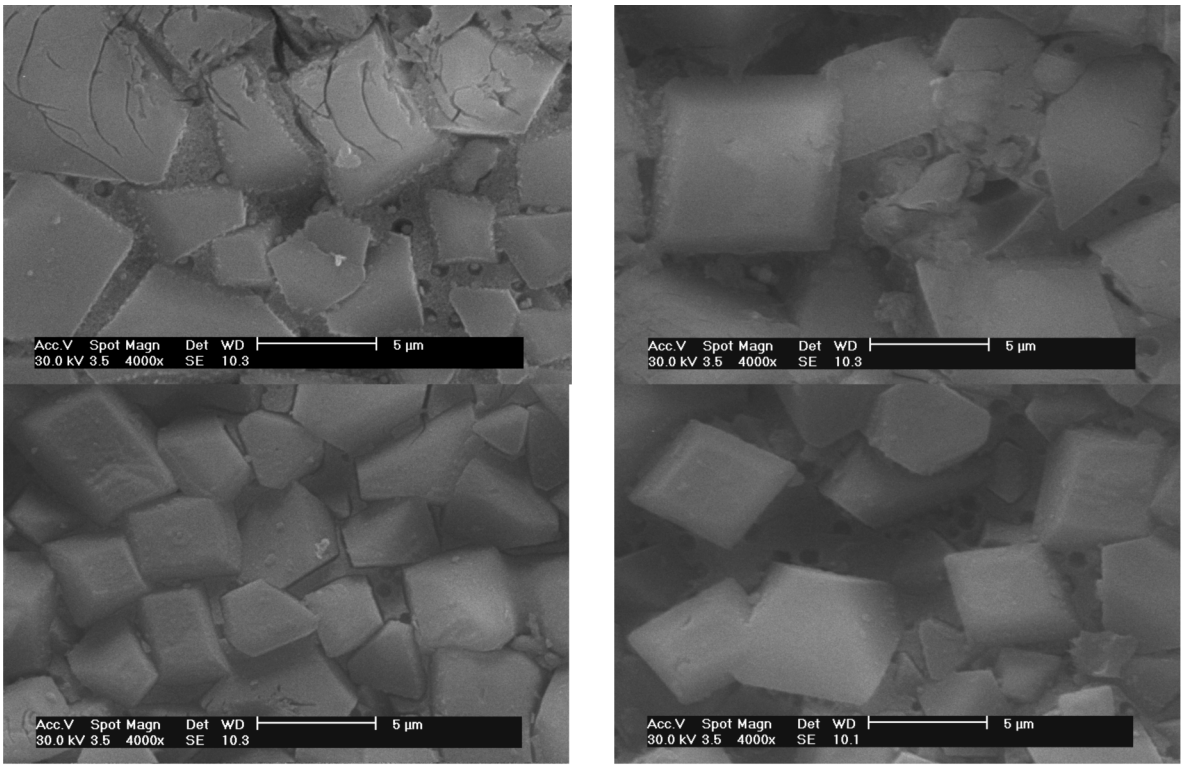


*Figure 4. Micrographs of the surface of the glass-ceramics (SEM, 5 vol% HF, 60s): 1h, 45MPa, 1185°C; 1h, 35MPa, 1185°C; 2h, 45MPa, 1175°C; 2h, 35MPa, 1175°C.*

The obtained glass-ceramics showed a high density of closed pores, as shown in the sample cross section micrograph, figure 5. However, these pores are shown with a rounded shape and a uniform distribution, which tends to avoid the stress concentrators.

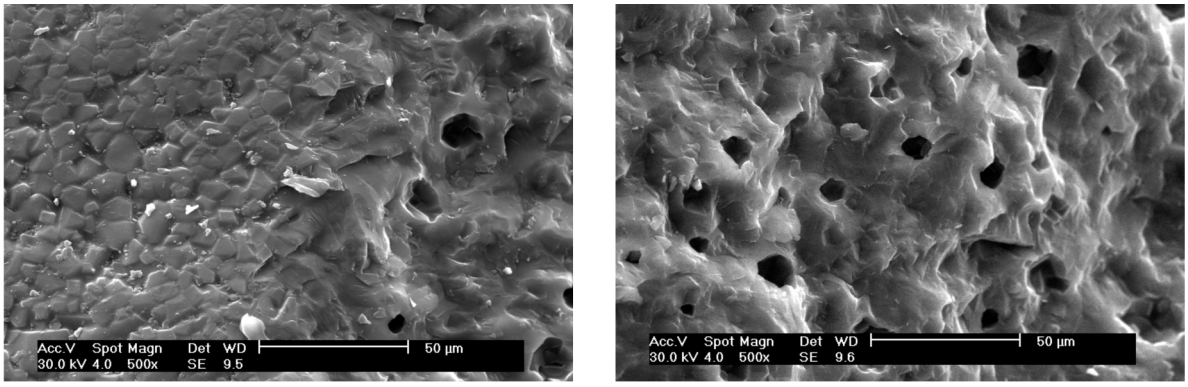


*Figure 5. Micrographs of the cross section of the 1h ground glass-ceramic, compressed to 45MPa and sintered at 1185°C.*

Finally, the X-ray diffraction analysis shows that the heat treatment process, sintering with crystallization in a single stage, has favoured the formation of the desired crystalline phase, and in all processing conditions there is the presence of the spodumene phase, figure 6.

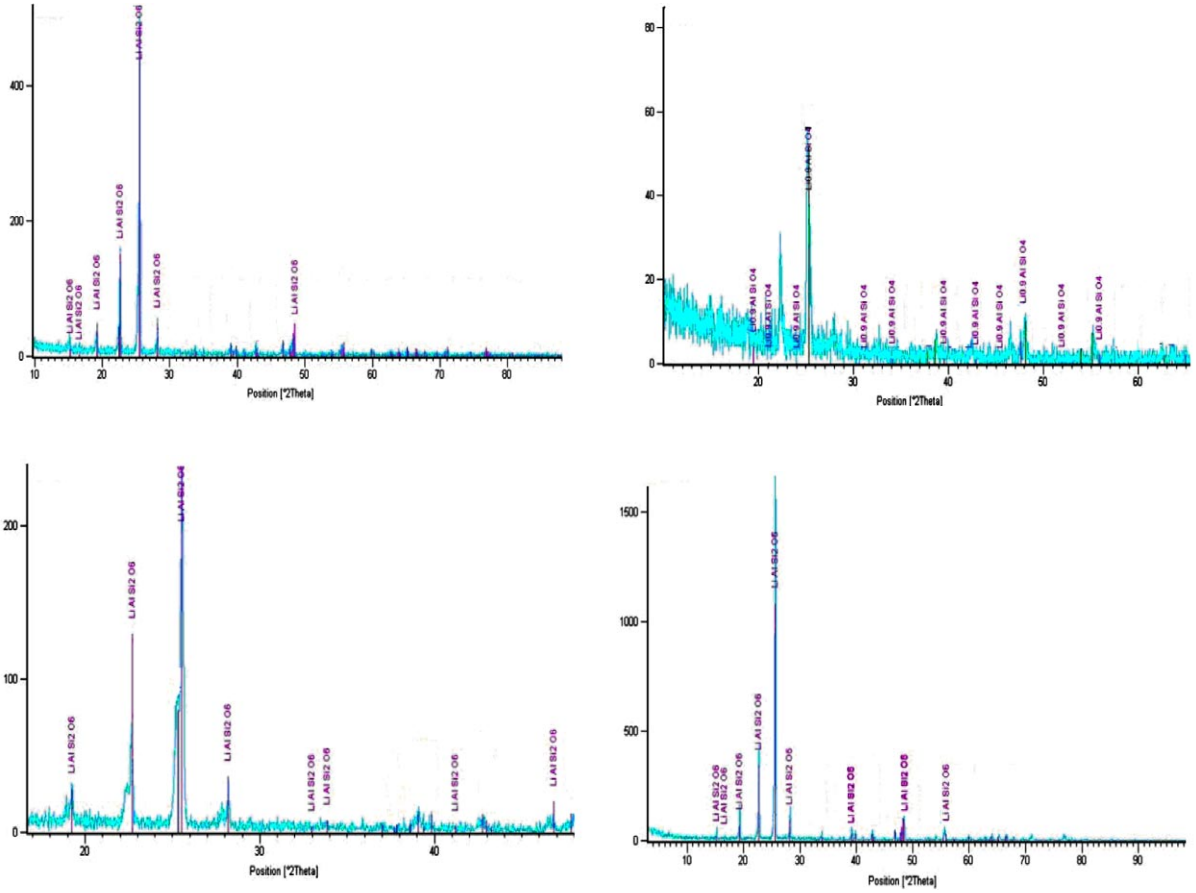


*Figure 6. Diffractograms of the glass-ceramics: 1h, 35MPa, 1185°C; 1h, 45MPa, 1185°C; 2h, 35MPa, 1175°C; 2h, 45MPa, 1175°C.*

## 4. CONCLUSION

Glass-ceramic materials can be processed using conventional techniques commonly used in ceramic tiles, such as glass melting, milling, pressing and sintering. The temperature of maximum shrinkage was influenced by the grinding and pressing processes; there is a reduction in the maximum shrinkage temperature with increasing compaction pressure and reduction in particle size.

Regarding the mechanical behaviour of the studied glass-ceramics system, the resistance to bending modulus showed satisfactory values, 80MPa on average. All glass-ceramics had presented a coefficient of thermal expansion compatible with the LSA system. However, the smaller the particle size and greater the compaction pressure, the lower the coefficient of thermal expansion.

Based on the microstructural analysis of the glass-ceramics for the processing conditions studied, crystal formation during sintering and the influence of grinding on the final size of the formed crystals were verified, the crystals being smaller as the particle size of the precursor glass was reduced.

Finally, the heat treatment applied to the LSA glass-ceramic studied was appropriate for the simultaneous crystallization and sintering. The major glass-ceramic phase crystallized from the sintering of powder compacts obtained from ground ceramic frits has been identified as spodumene.

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