# IONIC EXCHANGED LZSA GLASS POWDERS TO PRODUCE LOW POROSITY GLASS-CERAMICS FOR CERAMIC FLOOR TILES

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## 1. INTRODUCTION

The ceramic sector is continually seeking to develop new materials to obtain products with better performance. Among the developed ceramic materials in the last 40 years, glass-ceramics have assumed very important positions since they display the properties of glasses and crystalline solids [1-3]. Traditionally glass-ceramics are obtained from the melting of oxides and the forming of the viscous liquid [1-2]. This process is similar to that used for the fabrication of glasses, though the resulting material contains crystals and residual glassy phase.[3] In the last 20 years, glass-ceramic materials have been produced by powder technology. In this case, the glass-ceramic starting glass powder is compacted in the desired shape and dimensions and, in a later step, the obtained compact is subjected to a heat-treatment which involves sintering and crystallization and, hence, the consolidation and the definition of properties [3]. In fact, the properties of glass-ceramic materials depend, fundamentally, on the intrinsic properties of the crystalline and glassy phases that form and their amounts, dimensions and morphology and also, in this case, on residual porosity. Residual porosity can be an important limitation in certain applications. The reduction or elimination of porosity leads to higher material densification, which can be obtained by adequate sintering and crystallization heat-treatments and also by an adjustment or modification of the characteristics and properties of the glass-ceramic starting glass powder. Chemical treatments used to reduce heterogeneities can be an alternative in order to modify the particle surfaces of glass powders and thus to retard the nucleation and crystallization processes enlarging the sintering interval to higher temperatures. Some examples of surface treatments, which improve the glass powder sinterability are etching by NaOH solutions, chemical coating and ionic exchange [4-5]. The ionic exchange is used to obtain high-density glass-ceramics and consists in the substitution of a small ion in the amorphous glass network by a larger ion from a mixture of alkali salts. Sintered glass-ceramics resulting from chemically treated glass powders could show higher densities with respect to the untreated ones. In this context, this work has as objectives the production and characterization of a glass powder belonging to the LZSA ($Li_2O$-$ZrO_2$-$SiO_2$-$Al_2O_3$) glass-ceramic system [6-7] modified by ionic exchange in sodium salts to obtain high density glass-ceramics materials with optimized properties and high performance for ceramic floor tile applications. In this case, unglazed and glazed ceramic floor tiles with higher staining resistance could be obtained.

## 2. EXPERIMENTAL PROCEDURES

A LZSA glass-ceramic frit ($19Li_2O.8ZrO_2.64SiO_2.9Al_2O_3$-molar basis) obtained by melting (1500°C/7h) industrial raw materials ($ZrSiO_4$, $Li_2CO_3$, quartz and natural

spodumene) was wet milled in laboratory alumina ball mill so that a powder with a main particle size of approximately 15 μm was obtained, determined by laser scattering analysis (CILAS 1064 L). Subsequently, mixtures containing (proportion: 1:2) LZSA glass powders and alkaline salts (70 wt% $NaNO_3$ and 30 wt% $NaSO_4$) were prepared and heat-treated (electric furnace) at 450°C in the 2-10 h time range at a heating rate of 10°C.min$^{-1}$ for ionic exchange. After heat-treatments, powders were washed with deionized water and 0.1 mol.L$^{-1}$ HCl solution. Moreover, electric conductivity was measured in order to obtain electric conductivity similar to the deionized water. Chemical compositions of heat-treated (ionic exchanged powders) and non-heat-treated LZSA glass powders were determined by X-ray fluorescence spectroscopy (Philips, PW 2400) and by atomic absorption (UNICAM, Solar 969) for the lithium determination.

Thermal linear shrinkage ($\Delta L/L_o$) of compacted (50 MPa) samples were measured by using an optical dilatometer (Expert System Solutions, MISURA ODHT) at 10°C.min$^{-1}$ in air. The crystallization temperature of the glass powders was measured using differential thermal analysis, DTA (Netzsch, STA EP 409) in air at a heating rate of 10°C.min$^{-1}$ using powdered specimens of about 60 mg in an alumina sample holder with an empty alumina crucible as reference material. The obtained compacted samples, after drying at 110 ± 5°C were isothermally sintered in an electric furnace at 10°C.min$^{-1}$ in air at 800-850°C for 30 min. After sintering, samples were air-quenched to room temperature.

The theoretical density ($\rho_t$) of the sintered samples was measured by using a pycnometer and the apparent density ($\rho_{ap}$) was measured by the Archimedes principle with water immersion at 20°C. Taking in account the apparent density and theoretical density measurements, the relative density ($\rho_r$) and porosity were calculated. After sintering, samples were transversally cut, ground and polished with 1 μm alumina paste. 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 Kα) powder diffractometer (XRD). After heat-treatments, samples, in appropriate formats, were subjected to surface abrasion wear (NBR 13818/97 – Part D) and staining (NBR 13818/97 – Part G and ISO 10545-14/95) measurements.

## 3. RESULTS AND DISCUSSION

Table 1 shows the results related to the chemical composition of heat-treated (ionic exchanged powders) at 450°C for 30, 60, 120, 360, and 480 min and non-heat-treated LZSA glass powders. It can be seen from table 1 that the ionic exchange effectively occurred in all the heat-treated LZSA glass powders, in particular for samples heat-treated at 450ºC for 120 min (small lithium ions were replaced by large sodium ions).

| Consti-tutive oxides | Non-heat-treated powder (wt%) | Heat-treated powders (wt%) at 450ºC | | | | |
|---|---|---|---|---|---|---|
| | | 30 min | 60 min | 120 min | 360 min | 480 min |
| $SiO_2$ | 60.04 ± 2.6 | 55.82 ± 0.0 | 56.23 ± 0.7 | 56.62 ± 1.3 | 56.61 ± 1.5 | 56.24 ± 0.5 |
| $Al_2O_3$ | 15.05 ± 0.5 | 13.81 ± 0.0 | 13.94 ± 0.2 | 14.14 ± 0.3 | 14.13 ± 0.4 | 14.03 ± 0.2 |
| CaO | 0.58 ± 0.6 | 0.49 ± 0.0 | 0.52 ± 0.0 | 0.48 ± 0.0 | 0.47 ± 0.0 | 0.47 ± 0.0 |
| $Fe_2O_3$ | 0.20 ± 0.0 | 0.19 ± 0.0 | 0.18 ± 0,0 | 0.19 ± 0.0 | 0.19 ± 0.0 | 0.19 ± 0.0 |
| $K_2O$ | 0.51 ± 0.0 | 0.71 ± 0.1 | 0.75 ± 0.3 | 0.51 ± 0.0 | 0.52 ± 0.1 | 0.51 ± 0.0 |
| MgO | 0.17 ± 0.1 | 0.12 ± 0.0 | 0.15 ± 0.0 | 0.22 ± 0.0 | 0.18 ± 0.0 | 0.19 ± 0.0 |
| MnO | 0.06 ± 0.0 | 0.05 ± 0.0 | 0.05 ± 0.0 | 0.05 ± 0.0 | 0.05 ± 0.0 | 0.06 ± 0.0 |
| **$Na_2O$** | **1.01 ± 0.0** | **10.87 ± 0.0** | **10.82 ± 0.1** | **11.71 ± 0.6** | **11.51 ± 0.6** | **11.46 ± 0.2** |
| $P_2O_5$ | 0.07 ± 0.0 | 0.07 ± 0.0 | 0.06 ± 0.0 | 0.06 ± 0.0 | 0.06 ± 0.0 | 0.06 ± 0.0 |
| $TiO_2$ | 0.03 ± 0.1 | - | - | - | - | 0.03 ± 0.0 |
| $B_2O_3$ | - | - | - | - | - | - |
| **$Li_2O$** | **8.52 ± 0.0** | **3.07 ± 0.1** | **3.02 ± 0.0** | **2.81 ± 0.1** | **2.96 ± 0.0** | **2.92 ± 0.0** |
| BaO | 0.50 ± 0.2 | 0.67 ± 0.1 | 0.46 ± 0.1 | 0.41 ± 0.2 | 0.43 ± 0.2 | 0.34 ± 0.1 |
| ZnO | 0.92 ± 0.0 | 0.65 ± 0.0 | 0.72 ± 0.1 | 0.75 ± 0.1 | 0.78 ± 0.1 | 0.78 ± 0.0 |
| $ZrO_2$ | 14.19 ± 0.4 | 13.40 ± 0.1 | 13.33 ± 0.2 | 13.39 ± 0.5 | 13.53 ± 0.3 | 13.0 ± 0.2 |

**Table 1.** *Chemical composition of heat-treated (at 450°C for 30-480 min) and non-heat-treated LZSA glass powders.*

Table 2 show results related to the chemical composition of heat-treated (ionic exchanged powders) at 450°C for 30, 60, 120, 360, and 480 min and non-heat-treated LZSA glass powders but on a molar basis for the main oxides present. From table 2 data it can be seen that in fact the lithium ions were replaced and so compensated by the sodium ions so that the initial stoichiometry formula [19($Li_2O$+$Na_2O$)**.**8$ZrO_2$**.**64$SiO_2$**.**9$Al_2O_3$] with partial lithium substitution was approximately maintained.

| Constitutive oxides | Non-heat-treated powder (mol%) | Head-treated powders (mol%) at 450ºC | | | | |
|---|---|---|---|---|---|---|
| | | 30 min | 60 min | 120 min | 360 min | 480 min |
| $SiO_2$ | 64.0 | 63.1 | 63.3 | 63.1 | 63.0 | 63.0 |
| $Al_2O_3$ | 9.3 | 9.2 | 9.3 | 9.3 | 9.3 | 9.3 |
| $Na_2O$ | 1.0 | 11.9 | 11.8 | 12.7 | 12.4 | 12.5 |
| $Li_2O$ | 18.0 | 7.0 | 6.8 | 6.3 | 6.6 | 6.6 |
| $ZrO_2$ | 7.3 | 7.4 | 7.3 | 7.3 | 7.3 | 7.1 |

*Table 2. Molar percentage of the main oxides present in the heat-treated (at 450°C for 30-480 min) and non-heat-treated LZSA glass powders.*

The sinterability of heat-treated powders was strongly affected: that is, densification, represented by the thermal linear shrinkage (figure 1), was much higher for heat-treated than for non-heat-treated (0 h) glass powder compacts.

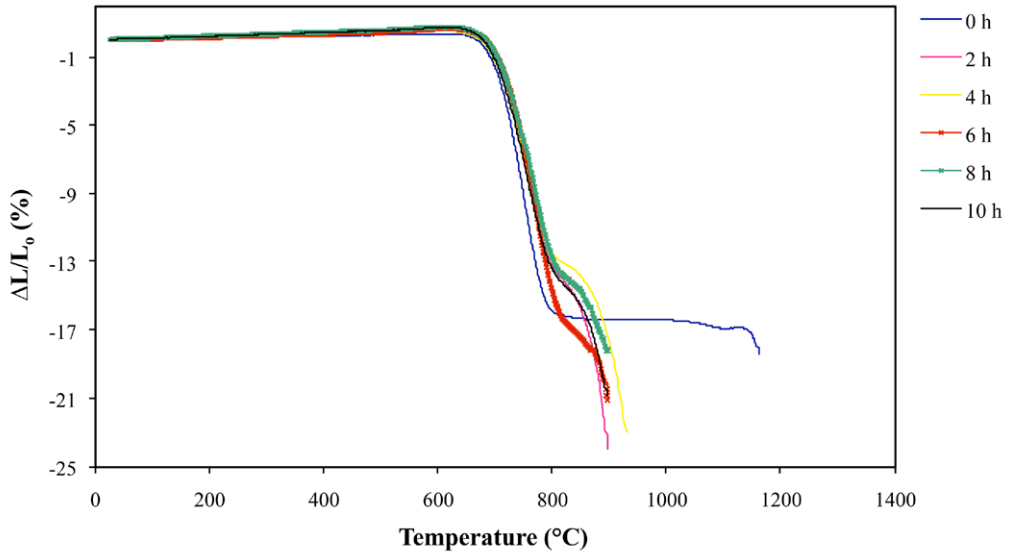


*Figure 1. Thermal linear shrinkage of compacts obtained from glass powders heat-treated at 450°C in sodium salts and non-heat-treated in sodium salts (0 h).*

Densification started at about 600ºC for all conditions, in close agreement with the glass transition temperature (~600ºC) determined by DTA, attaining maxima at 756ºC for the non treated powder and at 758, 750, 781, 776, 758ºC for 30-480 min, respectively for heated-treated powders, when the shrinkage rate tends to zero. This behaviour is related, initially, to the crystallization mainly of zircon and β-spodumene crystalline phases according to XRD analysis and, at higher temperatures, to a higher viscous liquid-phase volume formation caused by a higher volume fraction occupied by sodium ions. In fact, SEM micrographs (figure 2) of heat-treated and non-heat-treated glass powder compacts, sintered at 800 and 850°C for 30 min, respectively show that samples heat-treated with alkaline salts (at 450°C for 360 min) are denser than the non-heat-treated samples, as was also verified by the relative density calculations: that is, 85% for non treated samples and 91 to 96% for all the samples treated with sodium salts.

Preliminary staining testes using chromium and iron oxides on abraded surfaces, after 12,000 revolutions in the abrasion test equipment, revealed no staining points on samples treated with alkaline salts, indicating that is possible to obtain unglazed or glazed ceramic floor tiles with optimized porosity for a specific application.

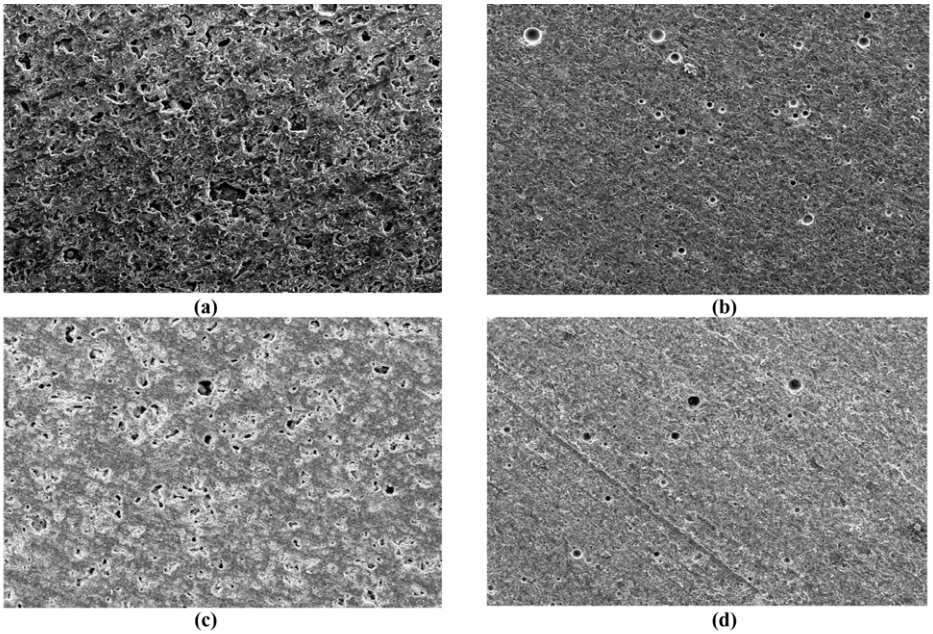


*Figure 2. SEM micrographs of sintered samples: (a) and (c) non treated LZSA glass-ceramics sintered at 800ºC and 850ºC for 30 min, respectively; (b) and (d) treated (in alkaline salts) LZSA glass-ceramics at 450°C for 6 h (360 min) and sintered at 800ºC and 850ºC for 30 min, respectively. Magnification: 100 X.*

## 4. CONCLUSIONS

Glass powders of the LZSA glass-ceramic system were successfully obtained by ionic exchange in sodium salts at 450ºC in the 2-10 h time range. Lithium ions were effectively replaced by sodium ions so that after about 30 min in the alkaline salts, the sodium content in the glass powders was approximately 10 wt%. Compacts obtained from heat-treated and non-heat-treated powders and sintered at 800 and 850ºC for 30 min, respectively show relative densities up to about 96%. Preliminary staining tests (using chromium and iron oxides) on abraded surfaces (after 12,000 revolutions in the abrasion test equipment) containing LZSA glass-ceramics obtained from heat-treated glass powders did not show any staining points. This last result is very encouraging, since it indicates that is possible to obtain unglazed and glazed ceramic floor tiles with relatively low porosity for a given application.

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