

Lithium Disilicate Bioceramic Obtained from Alternative Silica Source, the Rice Husk

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Abstract. The crystallization process of lithium disilicate glass-ceramic with SiO₂ from rice husk silica replacing the high-purity SiO₂ starting powder has been investigated in this work. Glasses were developed at the stoichiometric composition of 66%.molSiO₂:33%.molLiO₂ using commercial SiO₂ and the one obtained by thermochemical treatment of rice husk. The influence of rice husk-SiO₂ on crystallization process to different granulometry, microstructure and kinetic behavior was determined and discussed. Investigations were carried out by means of differential thermal analysis (DTA), X-ray fluorescence (XRF), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Amorphous and transparent glasses were obtained after melting. The lithium disilicate glass-ceramic crystallization peaks (Tp) are between 550 to 660°C to different granulometry (<63µm, 63µm < x < 250µm and 1mm < x < 2mm) and DTA heat rates (5; 10; 15; and 20°C/min) in both glasses from different silica sources, and the formed phase was Li₂Si₂O₅ as the crystalline phase after DTA thermal analysis as XRD confirmation. Improve in mechanical properties were estimated by morphological analysis of the microstructure modification in increasing the heat treatments temperature by SEM. The increase of glass substitution for crystalline phase was also observed with SEM images to both glass-ceramics from different silica sources.

Introduction

Nowadays, the most part of ceramic raw materials for dental function in Brazil is imported. Among these materials is contained infrastructure ones developed with oxide ceramics like alumina (Al₂O₃) and zirconia (ZrO₂) and feldspathic porcelain or glass-ceramic based on leucite and/or lithium disilicate.

To prosthesis applications, these ceramic are made in block form to use in CAD/CAM system. Lithium disilicate has great highlight for having good esthetical, mechanical and chemical properties, besides, also allows precision machining in CAD/CAM system.

The samples granulometry variation, and different heat rates in differential thermal analysis (DTA) provides different responses in the kinetic of the crystallization process. What imply in modification of glass to glass-ceramic transition compartment. The transitions peaks tend to dislocate ourselves to major temperatures with grain size or/and heat rate increases¹⁻². Besides the oxide complexities, in others words the number of different elements, visualized in XRF for raw silica can also affect the peak position. The heat treatments can provide an idea of the type of crystallization that is happening.

This work aims to study the effect of these three variables, granulometry, heat rate and silica source substitution in crystallization process of lithium disilicate glass and their possible intermediate phases. The rice husk is an abundant industrial waste in Brazil, for this reason the substitution of commercial silica by rice husk silica seem to be an interesting alternative to these biomaterial productions.

Materials and Methods

Figure 1 show the fluxogram used in this work.

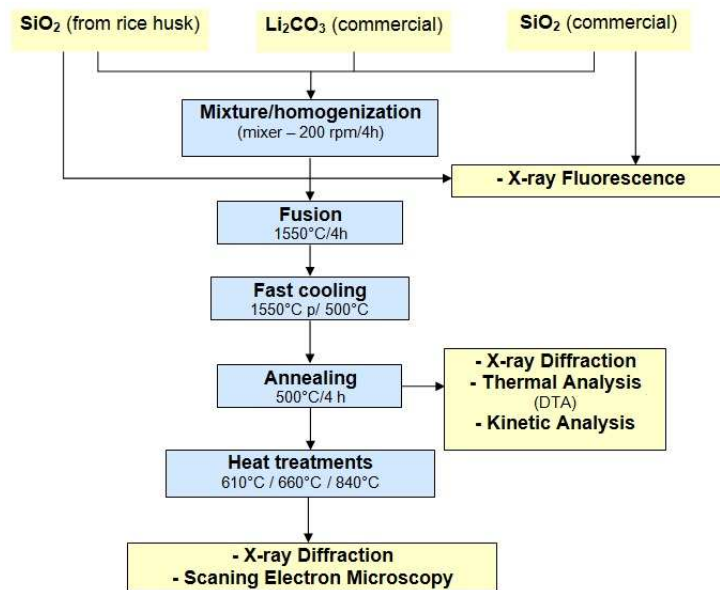


Figure 1 – Fluxogram with the steps performed in this work.

Commercial high-purity SiO_2 and rice husk SiO_2 powders with commercial Li_2CO_3 were used to produce the lithium disilicate in stoichiometric composition, $66\%.\text{molSiO}_2:33\%.\text{molLiO}_2$, in this work. Starting silica powders were characterized by X-ray fluorescence (XRF).

The mixtures (from commercial and rice husk silica) were taken to the furnace to melt them in a platinum melting pot, with $10^\circ\text{C}/\text{min}$ of rate, 1.550°C of step and for 1 hour. The melted mixture was poured into a bronze mold, and the obtained bars were annealed at 500°C for 3 hours, then the glasses were slowly cooled until room temperature.

Differential thermal analysis (DTA) were held varying the heat rates (5, 10, 15 e $20^\circ\text{C}/\text{min}$) and granulometries ($< 63\mu\text{m}$, $63\mu\text{m} < x < 250\mu\text{m}$ and $1\text{mm} < x < 2\text{mm}$) to both glass from different silica sources (commercial and rice husk silica), and with the results was possible to set some temperatures to perform heat treatments (610 , 660 e 840°C – rate $10^\circ\text{C}/\text{min}$ and 10 min of landing).

All the exothermic peaks were analysed to find the important temperatures and tendency with changing variables at the DTAs measurements.

For determination of crystallization fractions the software OriginPro8.1[®] from OriginLab was used. The total and partial areas were determined to find these fractions from each chosen temperature.

In order to verify the presence of intermediate phases in the system, like lithium metasilicate, high temperature X-ray diffraction (HTXRD) was performed.

The analysis were plotted in comparative curves that drawn a wide vision and a better understanding about the substitution of commercial silica by rice husk silica and their respective crystallization processes.

Results and Discussions

Figure 2 shows the DTA comportment related with variables granulometry, heat rate and silica source.

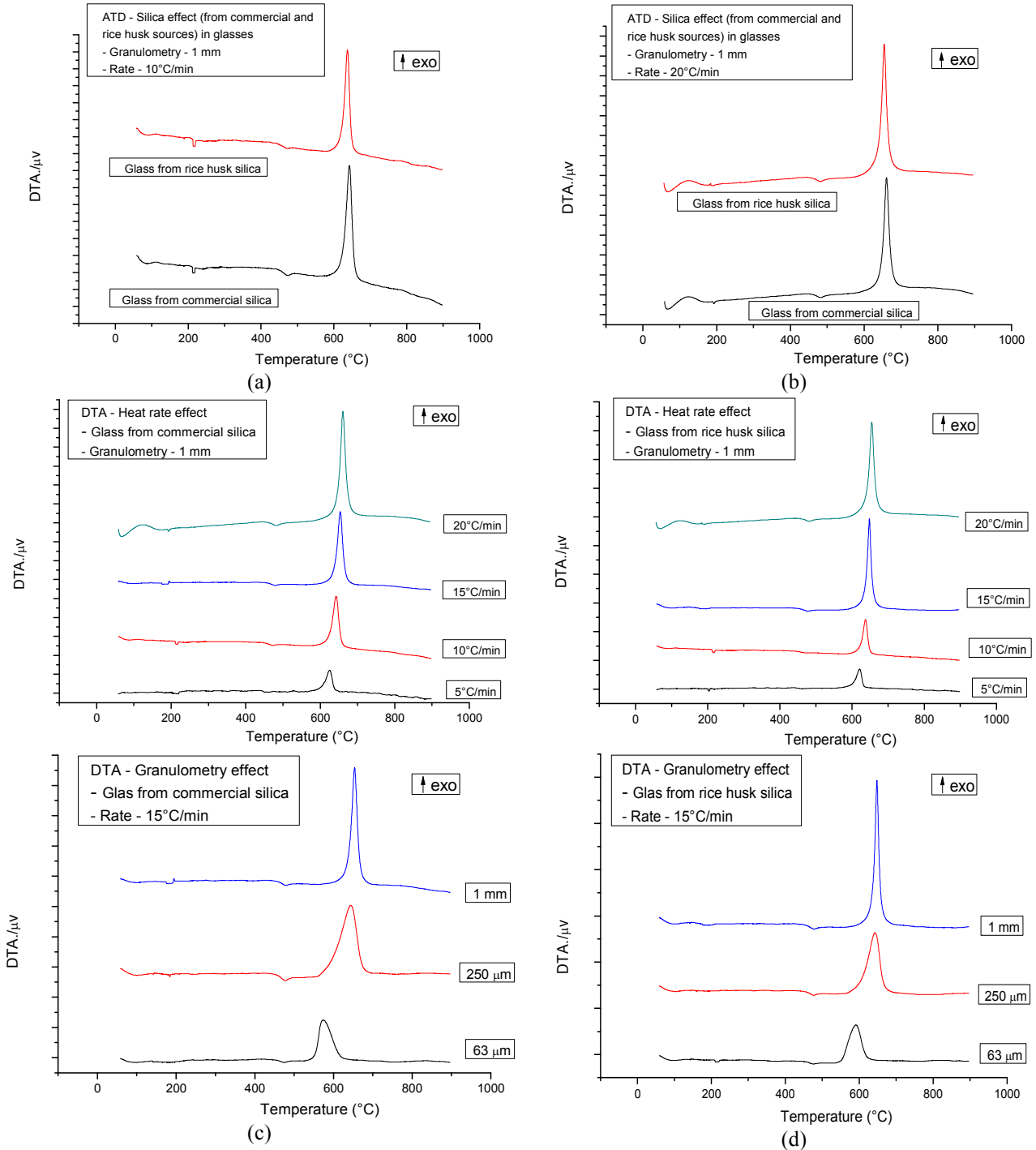


Figure 2 - DTAs to different variable conditions. Silica effect for the same granulometry (1mm) using heat rates of 10°C/min (a) and 20°C/min (b). Heat rate effect setting the granulometry (1mm) to the silica sources S (c) and SA (d). Granulometry effect for the same heat rate (15°C/min) in the silica sources S (e) and SA (f).

The Figures 2 (a) and (b) are comparing the silica sources (commercial and rice husk). Is possible to note that the difference in peaks comportment is very similar, the silica sources not provides significant differences on crystallization process.

The modification at the peaks is related with the increase of heat rate DTA temperatures in Figures 2 (c) and (d). The peaks are dislocated to major temperatures and tend to be higher and narrower with the heat rate temperature increase than the ones with lower rates. An increasing heat rate temperature, the peaks are dislocated to major temperatures and tends to be higher and narrower than the ones with lower rates. These effects can be seen for both materials (S and SA).

The dislocation to major temperatures occurs because increasing the heat rate the time for the occurrence reaction becomes less, since there is no time for the reaction to occur at lower temperatures²⁻⁴.

The tendency that appears in Figures 2 (e) and (f) are very similar to those that occur in the case of heat rate variation, the peaks are also dislocated to major temperatures, but here increasing the particle size. The effect that the particle surface cause on thermal equilibrium can explain this phenomena. Larger surfaces, and therefore smaller particle sizes, approaching the reaction of an equilibrium situation².

Figure 3 shows the crystalline fraction as a function of temperature obtained from exothermic DTA peak of S and SA samples for different rates, and fixing the granulometry (63 μm).

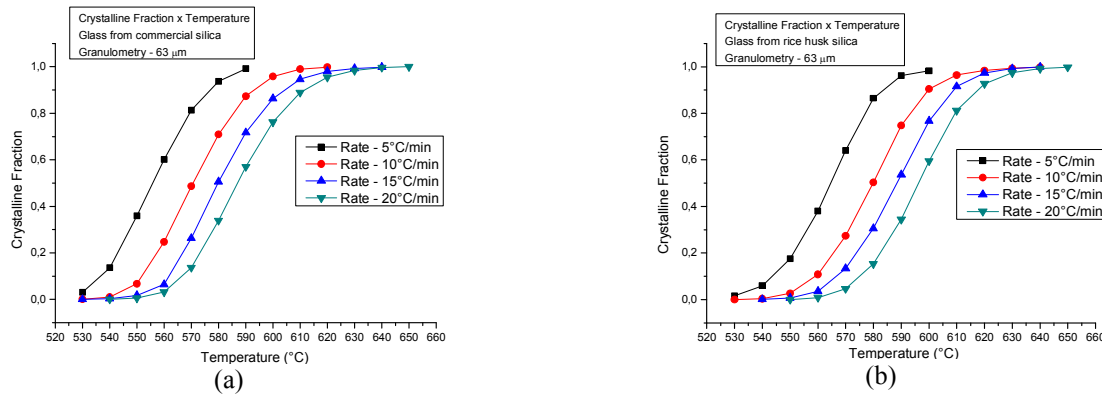


Figure 3 - Crystalline fraction versus temperature at different rates, setting the granulometry (63mm) in the S (a) and SA (b) samples.

The sigmoidal form that the curve follows it has been pointed out and is in accordance with the literature⁴⁻⁶. This curves allows once more that increasing the heat rates, the crystallization temperatures are dislocated to major values. Furthermore it is possible to note that the temperature range is the same for both materials obtained from different silica sources, S (3a) and SA (3b).

Figure 4 show the HTXRD used to verify the possible intermediate phases in the system.

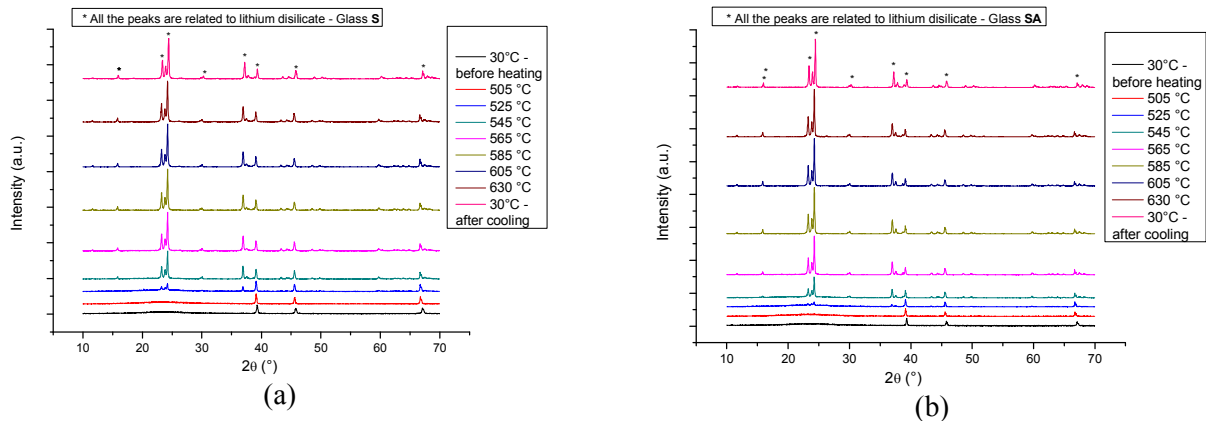


Figure 4 –HTXRD startig from room temperature (30°C) to 630°C and returning to room temperature at the end, to both materials, S (a) and SA (b).

Is not possible to see intermediate phases, there are no significant peak of a different phase beside lithium disilicate during the heating process.

Figure 5 shows the micrograph of S and SA after three different heat treatment, 610°C, 660°C and 840°C, using 10 minutes of step, and 10C°/min of heat rate.

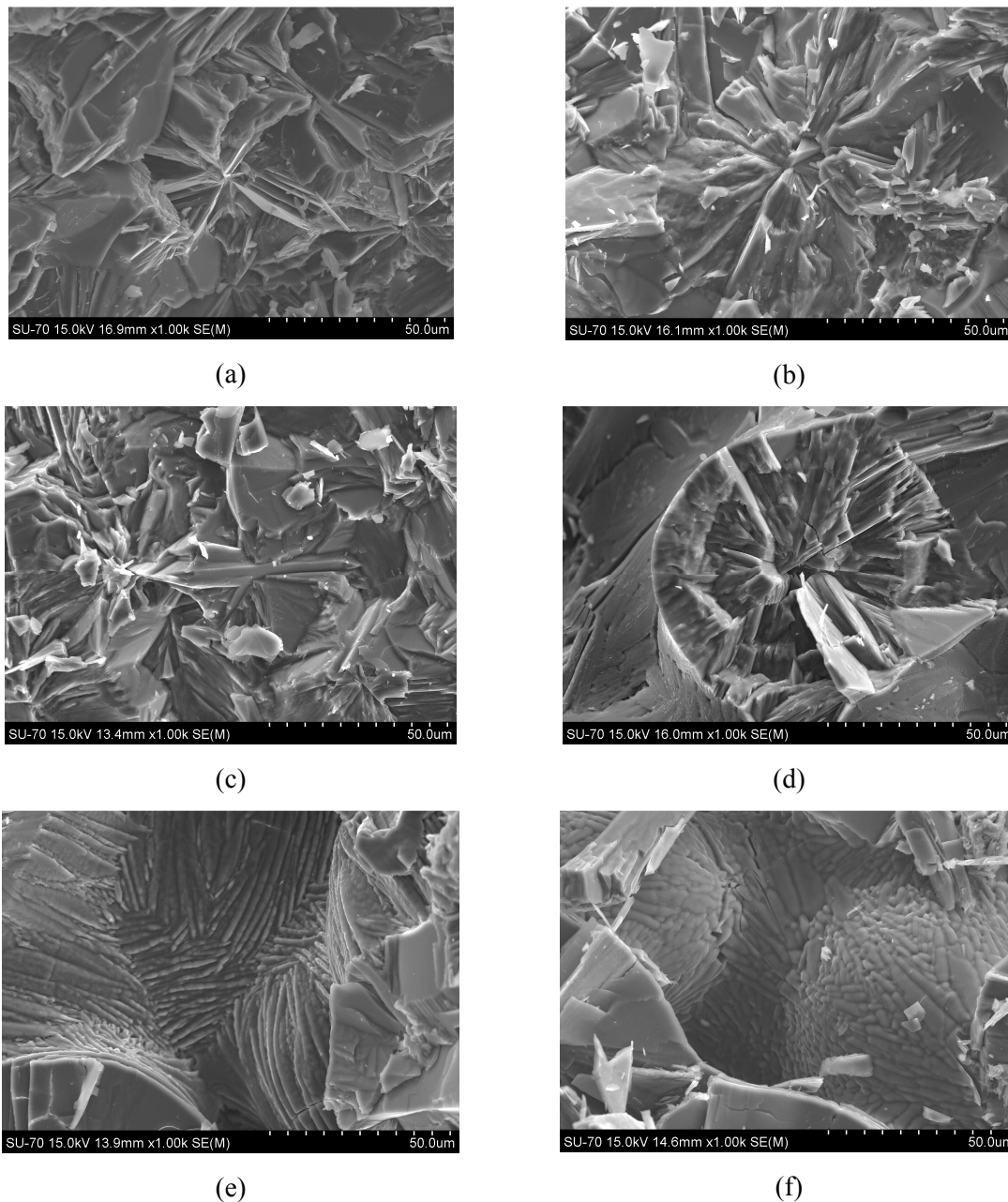


Figure 5 – Micrographs of glass obtained with commercial silica (a), (c) e (e); and with rice huska silica (b), (d) e (f) with respective heat treatments of 610°C, 660°C e 840°C using 10 minutes of landing and 10°C/min of heat rate.

It may be noted in the micrographs of Figure 5 that there is no significant differences between S (5a and 5b) and SA (5c and 5d). It also may be noted the grain morphology changing increasing heat treatments temperature.

The morphology modification from rod-shape to needle-shape according to the increase of heat treatments temperatures could mean an improvement in fracture toughness, since the cracks will be more difficult to propagate⁷⁻⁹.

Conclusions

The differences in contributions of the silica sources were very similar. Increasing the heat rate temperatures and/or the granulometry the crystallization peaks in the glass are dislocated to major temperatures.

The curve of crystallization fraction shows that the range of temperatures to occur the crystallization process is the same to both materials (S and SA).

Through the HTXRD is possible to note that are no intermediate phase in a lithium disilicate route to the glass S and SA.

Morphology found at micrographs in accordance with increased heat treatment temperatures was similar to S and SA glass. The modification from rod-shape to needle-shape can provide better compartment in fracture toughness.

At the present moment the substitution of commercial silica for rice husk silica seem to be a possible technique to produce lithium disilicate, that can be applied as a dental material.

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