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Crystallization process of a biomaterial, the lithium disilicate, obtained from rice husk silica

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Abstract. In this work, the crystallization process of lithium disilicate glass-ceramic was investigated with SiO₂ from rice husk silica replacing the high-purity SiO₂ starting powder from commercial source. 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. To compare the SiO₂ sources, the influence of the one from rice husk on crystallization process was measured using different granulometry, analyzing microstructure and the kinetic behavior. Investigations were carried out by means of differential thermal analysis (DTA), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Amorphous glasses were obtained after melting at 1550⁰C. The position of lithium disilicate glass-ceramic crystallization peaks (Tp) are between 550 to 660⁰C to different granulometry (<63mm, 63mm < x < 250mm and 1mm < x < 2mm) and DTA heat rates (5; 10; 15; and 20⁰C/min) in both glasses, and the relevant formed crystalline phase after DTA analysis (verified for XRD) was Li₂Si₂O₅. SEM images showed the increase of glass substitution for crystalline phase to both glass-ceramics from different silica sources.

1. Introduction

The use of alternative sources of raw materials for manufacturing of glass-ceramics has been subject of different studies [1,2]. By definition glass-ceramics are obtained by a process of controlled crystallization of suitable glass system (common glasses are amorphous, in other words, have no ordered interatomic structure). The material is first formed as a glass using the same procedure as conventional glasses, giving the desired shape, and controllably cooling to room temperature for reheating later or, instead, directly leading to the temperature at which crystal nucleation occurs at a characteristic rate [3]. These crystallization processes provide superior resistance to the glass can be produced with uniform and very small grain size and with no porosity [4]. The materials use in certain applications is made possible due to their characteristic properties: low values of thermal expansion, high levels of translucency, and in some cases high transparency, chemical stability and relatively high values of mechanical strength.

Glass-ceramics based on lithium disilicate glass ceramics were first developed by Stookey [5, 6], taking as an initial basis for the development of materials on this system some compositions derived from the stoichiometric composition of phyllosilicates Li₂Si₂O₅ crystals. The glass formation and crystallization of phases in the binary system SiO₂-LiO₂ have been subject of many studies in recent years [7, 8, 9], with special attention to the stoichiometric composition of 33.33 mol% LiO₂ and 66.67% mol SiO₂. The nucleation of glasses based on lithium disilicate with exactly stoichiometric composition was studied in detail by several authors [9, 10, 11, 12]. They determined that the mechanism of embryo crystals near the melting temperature of glasses with stoichiometric composition was pointed out as the potential mechanism of nucleation of the crystalline phase. In addition to studies that determined the major mechanisms of nucleation of SiO₂-LiO₂-phase in the glass-ceramic system in the 80s and 90s, great attention was paid to microstructural analysis and improvement in chemical durability [13]. Considerable improvements were obtained by using Al₂O₃ and K₂O to stoichiometric glasses aiming to boost the use of ceramic as a biomaterial in medicine and especially as restorative material in dental



prostheses systems [14, 15]. The aim of this study is to evaluate the properties of glasses based on lithium silicate obtained from two sources of silica: commercial high purity and rice husk.

2. Experimental Procedure

Commercial high-purity SiO₂ (Fluka-Germany) and rice husk SiO₂ powders (purity higher than 99%) with commercial Li₂CO₃ were used to produce the lithium disilicate in stoichiometric composition, 66%.mol SiO₂:33%.mol Li₂O. The mixtures (from commercial silica – GCS, and rice husk silica - GRS) were taken to the furnace to melt them in a platinum melting pot, with 10°C/min of rate, 1.550°C of step and for 1 hour. The melted mixtures were poured into a bronze mould, and the obtained bars were annealed at 500°C for 3 hours, then the glasses were slowly cooled until room temperature.

After that, the DTA was carried out and with the results was possible to set some temperatures to perform heat treatments (610 and 840°C) with 10°C/min for 10 minutes of landing. Different heating rates and granulometry were used in this analysis.

X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were carried out seeking analyse microstructural properties. All the exothermic peaks were analysed to find the important temperatures and tendency with changing variables at the DTAs measurements.

3. Results and Discussion

Amorphous and transparent glasses were obtained after melting. These glasses, presented T_g near to 480°C and crystallization peak at 660°C, in both compositions, and Li₂Si₂O₅ as crystalline phases after heat-treatment. Figure 1 presents XRD patterns of GCS and GRS glasses before and after DTA analysis, showing crystallization of the Li₂SiO₃ and Li₂Si₂O₅ phases for both silica sources.

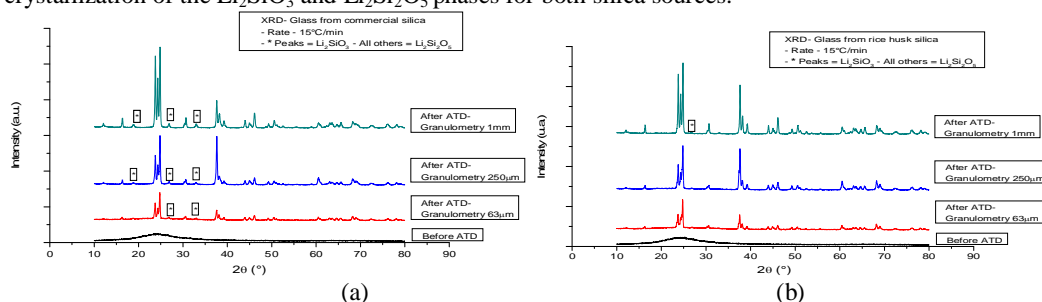


Fig. 1 XRD patterns of GCS (a) and GRS (b) before and after DTA.

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

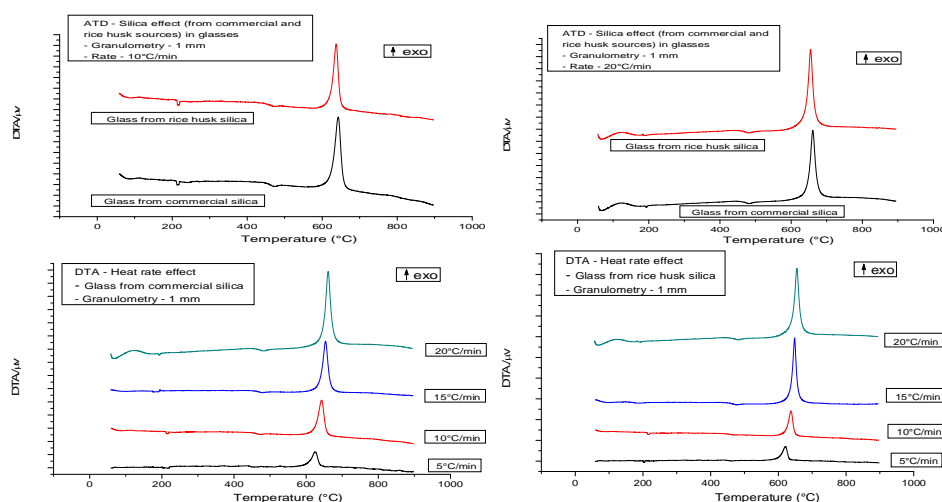


Fig.2 DTAs of different conditions: Silica effect for the same granulometry (1mm) using heat rates of 10 (a) and 20°C/min (b); Heat rate effect setting the granulometry (1mm) to the silica sources GCS (c) and GRS (d).

The Figures 2 (a) and (b) are comparing the silica sources (commercial and rice husk). It is possible to note that the difference in peaks compartment 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 (GCS and GRS). 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 temperatures [16-18].

Figure 3 shows the micrograph of GCS and GRS after different heat treatment at 610°C and 840°C, using 10 minutes of step, and 10C°/min of heat rate.

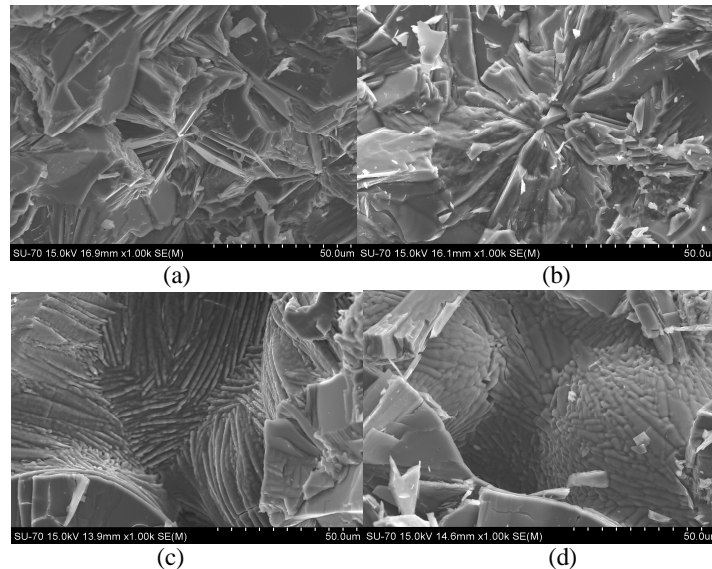


Fig. 3. SEM Micrographs of heat treated samples for 10 min of step and 10°C/min of rate at 610°C (a and b), and 840°C (c and d) to GCS (a and c) and GRS silica sources (b and d).

It may be noted in the micrographs of Figure 3 that there is no significant differences between S (3a and 3b) and SA (3c and 3d). 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 propagate [19-21].

Figure 4 presents a comparative analysis peak temperature crystallization of the both GCS and GRS glasses, for different heat rate, in different particle sizes.

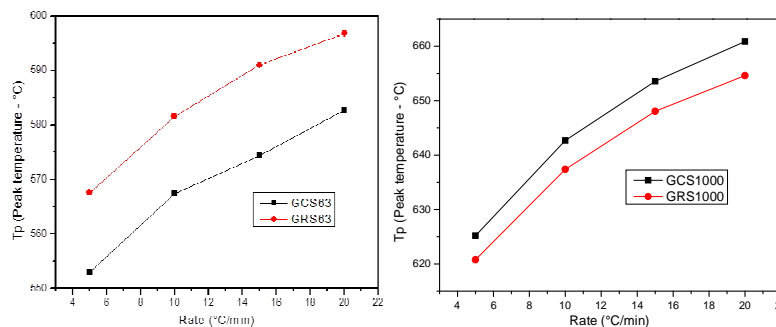


Fig. 4 Rate versus peak temperature to both silica sources, S and SA, to granulometry 63mm (a) and 1 mm (b).

In accordance of Figure 4 it possible to observe that, to the major granulometry (b), the difference between the silica sources is less significant than the difference found to the minor granulometry (a). It can indicate that to minor granulometries, and their respective larger contact surface, are influenced for the number of different oxides found in rice husk silica, which retards the crystallization reaction (crystallization peak temperature).

4. Conclusions

In relation to the use of different sources of silica (commercial and from rice husk), the results indicate the possibility of replacement without significant effects on microstructural and thermal behavior of materials;

- Temperature ranges, contained in the peak of differential thermal analysis, followed the same tendency for both materials;
- The behavior of the materials in the variations, particle size and heating rate, was also quite similar;
- The morphologies contained in micrographs from scanning electron microscopy showed quite similar glasses comparing both. The morphology change, from needles to rods, also can be noted;

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