Lithium Disilicate Glass-Ceramic Obtained by the Silica Extracted from Rice Husk

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Abstract. In this work lithium disilicate glass-ceramic and glasses based on the Li_2O-SiO_2 system have been investigated by replacing the high-purity SiO_2 starting powder by silica obtained from rice husk. Glasses were developed at the stoichiometric composition of 66%.molSiO_2:33%.molLiO_2 using SiO_2 obtained by thermochemical treatment of rice husk. The influence of rice husk-SiO_2 on phase formation, microstructure, hardness and fracture toughness was determined and discussed. Investigations were carried out by means of differential thermal analysis, X-ray fluorescence, X-ray diffractometry and scanning electron microscopy. Amorphous and transparent glasses were obtained after melting. The glasses presented T_g near to 480 ^{0}C, crystallization peak at 660 ^{0}C in both glasses from different silica sources and $Li_2Si_2O_5$ as the crystalline phase after heat treatment. The hardness (HV_{300gF}) presented average values near to 430 HV for both high-purity and rice husk silica powders. Fracture toughness measurements present results near to 1.7 MP am$^{1/2}$ for both compositions.

Introduction

Full exploitation of materials, including the use of agricultural and industrial waste in production processes, either as feedstock or as energy source, is a growing and developing alternative because of the serious environmental and economic problems that arose with industrialization.

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 process 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 $Li_2Si_2O_5$ crystals. The glass formation and crystallization of phases in the binary system SiO_2-LiO_2 have been subject of many studies in recent years [7, 8, 9], with special attention to the stoichiometric composition of 33.33 mol% LiO_2 and 66.67% mol SiO_2. 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 SiO_2-LiO_2-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 Al_2O_3 and K_2O 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]. It is worth noting that major advances in chemical durability have also been reached by the development of glass-ceramic in non stoichiometric composition.

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 the silica obtained from rice husk.

Experimental Procedure

Powder mixtures based on stoichiometric composition of $66SiO_2$:$33LiO_2$ (in mol%), using both silicas, commercial and extracted from rice husk, were melted and the glasses were obtained. The effect of the SiO_2 substitution on phase formation, microstructure, mechanical properties and chemical property were investigated by means of differential thermal analysis; X-ray diffractometry, X-ray fluorescence composition analysis, Vickers hardness and scanning electron microscopy.

Figure 1 shows the processing route used in this work.

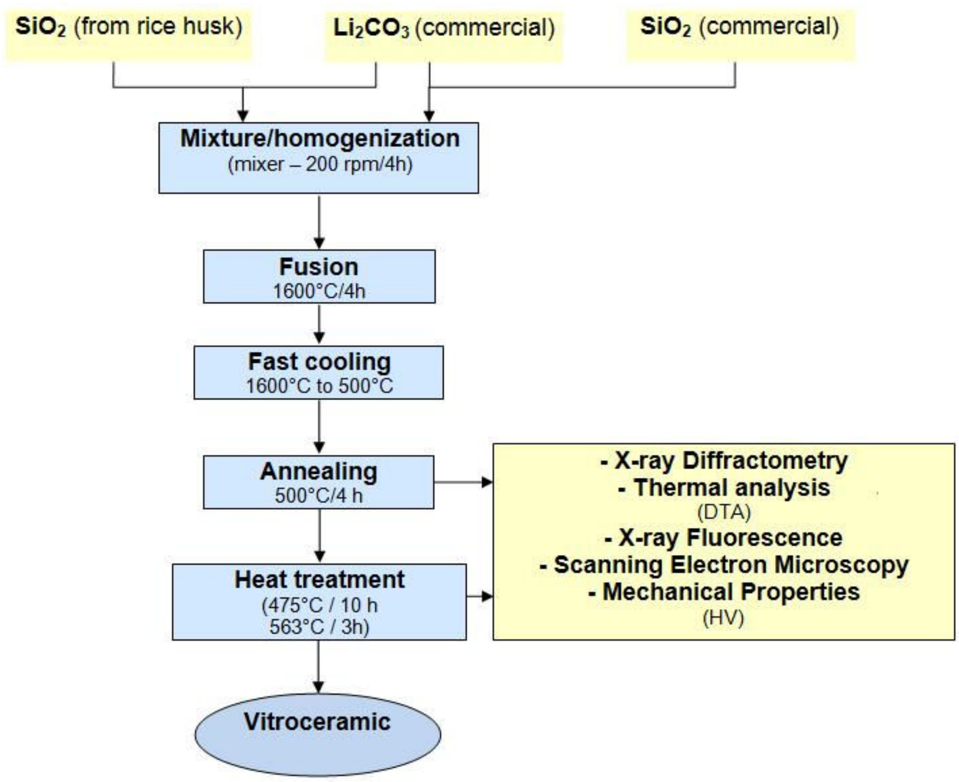


Figure 1 – Processing route used in this work.

Melted samples with subsequent annealing were characterized. After that the samples were submitted to the crystallization heat treatment, which has the following conditions of temperature:

475°C for 10 h for nucleation and then 563°C for 3 h for grain growth [16, 17]. The crystallized samples were mechanical characterized for Vickers Hardness (HV) and fracture toughness (K_{IC}) using Vickers indentation method.

Results and Discussion

Table 1 shows X-ray fluorescence results for commercial silica and rice husk silica.

Tabela 1 – XRF results of commercial and rice husk-sílica starting powders

Element / Compound	Rice husk silica (wt %)	Commercial silica (wt %)
SiO_2	99	98
CaO	0,4	< 0,05
SO_3	0,3	-
Fe_2O_3	0,2	0,07
MgO	0,1	0,09
K_2O	0,1	0,5
P_2O_5	-	0,09
MnO	< 0,05	-
Al_2O_3	< 0,05	0,7
NiO	< 0,05	-
CuO	< 0,05	-
SrO	< 0,05	< 0,05
ZrO_2	< 0,05	< 0,05

According to the XRF analysis it was possible to check that both powders have a good purity, with a few oxide impurities. Probably because the higher oxide iron concentration in the rice husk silica, the glass obtained from this silica before heat treatment had a light green color. Figure 2 shows the XRD patterns of the powder mixtures, fused samples and heat-treated samples developed with commercial- and rice husk- silica.

Comparatively, Fig. 2a and Fig 2b indicate that the mixture with rice husk-silica present an tendency to amorphization caused probably by the processing route to obtain the rice husk-silica. On the other hand, this behavior is not important because the powder mixture will be melted. Comparing XRD patterns of the glasses, Fig 2c and Fig.2d, no crystalline peaks are present in both compositions, indicating total amorphous glass-matrix of the samples. Heat treated samples, Fig. 2e and Fig. 2f, indicate high crystallization degree in both samples, with lithium disilicate peaks, which proves that the heat treatment procedure was suitable.

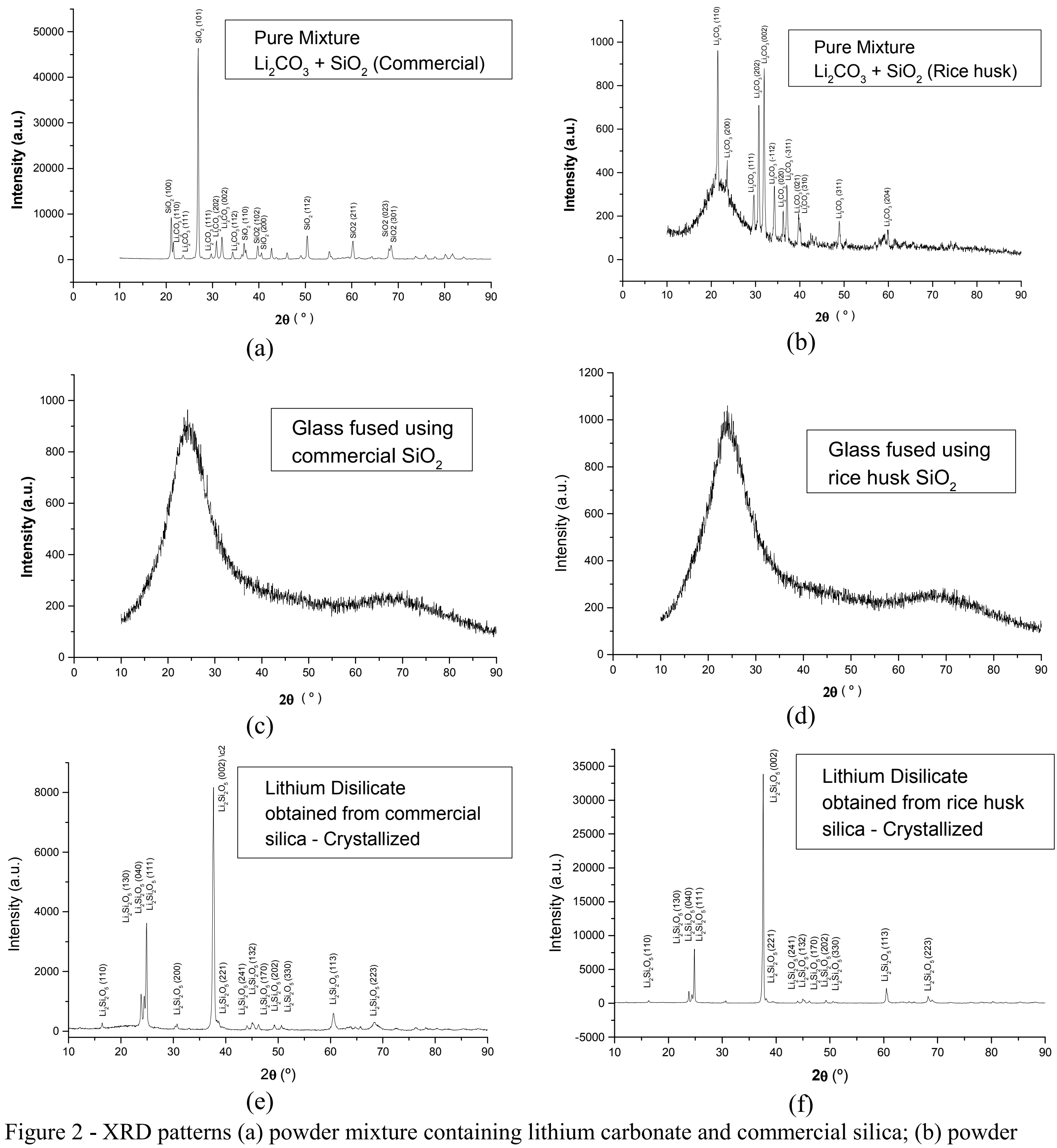
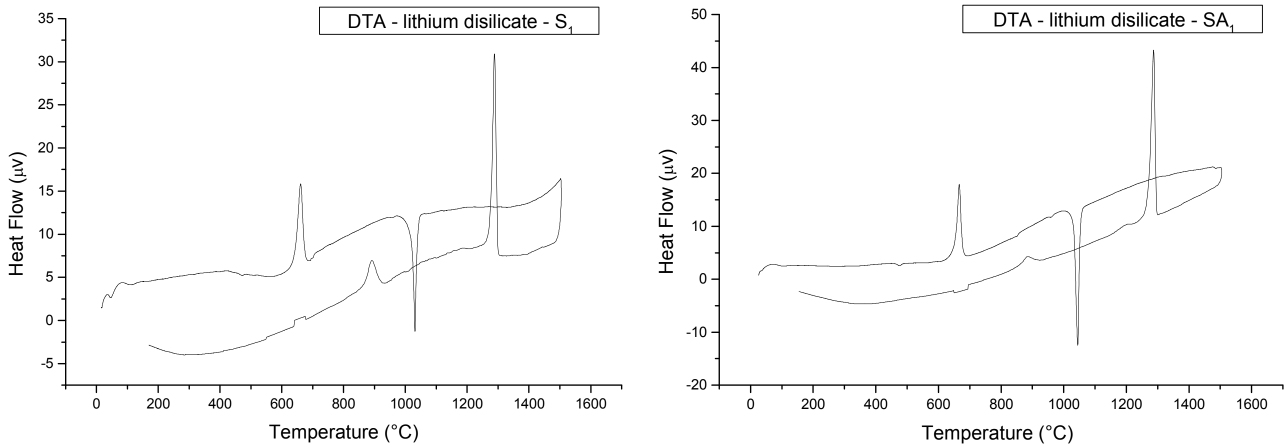


Figure 2 - XRD patterns (a) powder mixture containing lithium carbonate and commercial silica; (b) powder mixture containing lithium carbonate and rice husk silica; (c) Glass obtained from commercial silica; (d) glass obtained from rice husk silica; (e) Lithium disilicate glass-ceramic obtained from commercial silica; (f) Lithium disilicate glass-ceramic obtained from rice husk silica.

Figure 3 shows the thermal behavior of Li-Si-O-glass through differential thermal analysis (DTA), for both glasses (obtained with commercial silica - S_1 and with rice husk silica SA_1).



(a) (b)

Figure 3 – Differential thermal analysis (DTA) of lithium disilicate obtained from: (a) commercial silica (S_1); (b) rice husk silica (SA_1).

Thermal analysis allows to verify some important transformations in materials. The thermal variation of the sample during the test provides approximate information as glassy transformation temperature (T_G) and approximate crystallization temperature, which are important to optimize heat treatment parameters. It can be observed that for both Li-Si-O glasses the thermal variations appear in similar positions.

Table 2 shows the mechanical behavior of the Li-Si-O glasses and lithium disilicate glass-ceramics obtained from both silica-matrixes.

Table 2 – Mechanical properties of the glasses and glass-ceramics

Composition	**Vickers Hardness (HV_{300gf})**		**Fracture Toughness ($MPa.m^{1/2}$)**	
	Before heat-treatment (glass)	After heat treatment (glass –ceramic)	Before heat-treatment (glass)	After heat treatment (glass –ceramic)
Li_2O-SiO_2 (Commercial silica)	425 ± 8	430 ± 5	0.75 ± 0.08	1.81 ± 0.15
Li_2O-SiO_2 (Rice husk silica)	435 ± 7	437 ±5	0.81 ± 0.13	1.84 ± 0.12

A significant improvement of the fracture toughness (near to 100%) has been observed in samples after heat treatment. Independently on the starting powder the crystallization heat treatment presented an important contribution for toughness increase. It is related to the crystallization of the $Li_2Si_2O_5$ phase, which leads to the organization in the atomic-scale structure with grains formation and activation of the toughening mechanisms. Hardness is not significantly influenced for heat treatment. Furthermore, the different silica powders are not influenced the results.

The results confirm that mechanical properties of heat-treated samples are superior than the samples before heat treatment. Heat treatment conditions were mainly chosen within bibliographic references information. BRAUN, 2008, held different treatment conditions, involving nucleation and grain growth temperature levels. One of the bests conditions to guarantee the maximum of phase crystallization was 475°C for 10 h for nucleation followed by 563°C for 3 h for grain growth, which were used in this work. The most important data collected by the mechanical characterization of the present work were the comparison of glass-ceramics obtained from different sources. The results were very similar, with HV and K_{IC} values of glass-ceramic obtained from rice husk silica about 1,6% better than the glass ceramic obtained from commercial silica.

Conclusions

Li_2O-SiO_2-based glasses and glass-ceramics were prepared with rice-husk silica as starting powder and compared with commercial high-purity silica. Thermal behavior and crystalline phases presented for both glasses and glass-ceramics were are similar. Hardness and fracture toughness of the glasses presented results of 430 HV and 0.8 $MPam^{1/2}$, respectively. After heat treatment, $Li_2Si_2O_5$ was the unique crystalline phase present in both compositions. Furthermore, improvement of 100% in fracture toughness was observed for devitrification of the structure. These partial results are totally positive with respect to the replacement of commercial silica by rice husk silica. It is then possible to reduce environment impacts caused by inappropriate disposal of rice husk at the same time that glass-ceramic materials are obtained with similar mechanical properties as the ones preparared with commercial silica powder.

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