

Crystallization Process of Lithium Disilicate Glass-Ceramic Obtained from Rice Husk Silica Source

Felipe Antunes Santos^{1,2}, Erika Davim³, Maria Helena Figueira Vaz Fernandes³,
Claudinei dos Santos^{1,4}, Daltro Garcia Pinatti¹ and Dolores Ribeiro Ricci Lazar²

Affiliation 1: EEL – USP
DEMAR (Materials Department)
School of Engineering Lorena of University of São Paulo
Lorena, São Paulo, Brazil

Affiliation 2: IPEN
CCTM (Centre of Materials Science and Technology)
Institute of Nuclear and Energy Research
São Paulo, Brazil

Affiliation 1: UA
DCV (Glass and Ceramic Department)
University of Aveiro
Aveiro, Portugal

Affiliation 4: UNIFOA
Materials Master Degree
University Centre of Volta Redonda
Volta Redonda, Rio de Janeiro, Brazil

felipeantunes@usp.br

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 SiO₂ obtained by thermochemical treatment of rice husk. The influence of rice husk-SiO₂ on crystallization process to different particle sizes, 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 particle sizes (63 micrometers, 250 micrometers and 1 millimeter) 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. The Tp is dislocated to higher temperatures in accordance with increasing of particles sizes and/or DTA-heat rates. The increase of glass substitution for crystalline phase was observed with SEM images to both glass-ceramics from different silica sources. The preliminary results show that there are no significant differences between lithium disilicate from both silica sources, therefore it seems to be a promising technique for this biomaterial.

Keywords: Lithium disilicate, bioceramic, glass-ceramic, crystallization, rice husk silica.

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 increases^{1,2}.

This work aims to study the effect of granulometry and heat rate variations, and silica source substitution in crystallization process of lithium disilicate glass. Being the rice husk an abundant industrial waste in Brazil, the substitution of commercial silica for rice husk silica seem to be an interesting alternative to these biomaterial production.

Experimental

The Fig. 1 shows the flowchart used at the present work.

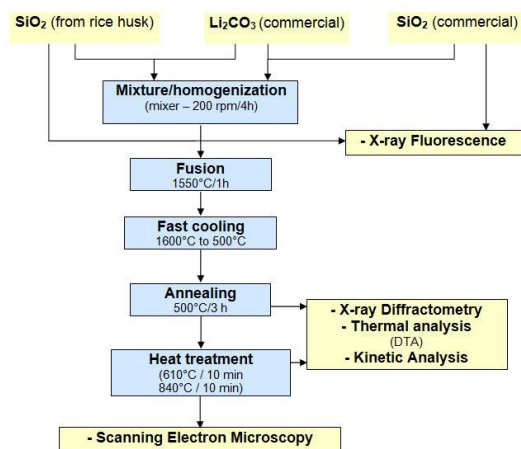


Fig. 1 Fluxogram of the stages of this work.

In this work the high purity silica from commercial source (Fluka) and from rice husk (98% and 99% purity by X-ray fluorescence (XRF), respectively) were mixed with lithium carbonate at the stoichiometric composition of 66%.molSiO₂:33%.molLi₂O.

The mixtures (from commercial and rice husk silica) 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 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.

After that, the ATD 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.

To DTA were used different granulometry of material (< 63µm, 63µm < x < 250µm and 1mm < x < 2mm) and different rates (5, 10, 15 and 20°C/min) for both glasses from different silica sources to verify the influences of those variations.

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.

Results and Discussion

The effect of granulometry can be estimated using Fig. 2 by XRD analysis. The diffractograms were obtained using samples before and after (setting the variable heat rate in 15°C/min) DTA of the glasses obtained from both silica sources,

commercial (S) and rice husk silica (SA), Figs. 2a) and 2b), respectively.

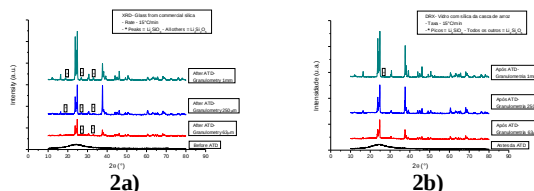


Fig. 2 X-ray diffractogram of S (a) and SA (b) before and after DTA.

Is possible to see that at increasing particle size, the intensity of the crystalline peaks also increase, what can indicate a volumetric type crystallization. The phase formed for both materials after DTA were mostly lithium disilicate, with some lithium metasilicate peaks appearing for larger particle sizes.

The Fig. 3 shows the DTA comportment related with variables granulometry, heat rate and silica source.

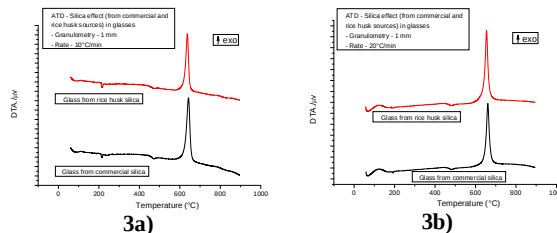
When the effect of silica source is compared in Figs. 3a) and 3b), is possible to note that the difference in peaks comportment is very similar, the silica sources not provides significant contribution on crystallization process.

The Figs. 3c) and 3d) shows a modification at the peaks related with the increase of heat rate DTA temperatures. 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 Figs. 3e) and 3f) are very similar to those that occur in the case of heat rate variation. The peaks are dislocated to major temperatures increasing the particle size.

This phenomena can be explained by the effect that the particle surface cause on thermal equilibrium. Larger surfaces, and therefore smaller particle sizes, approaching the reaction of an equilibrium situation².



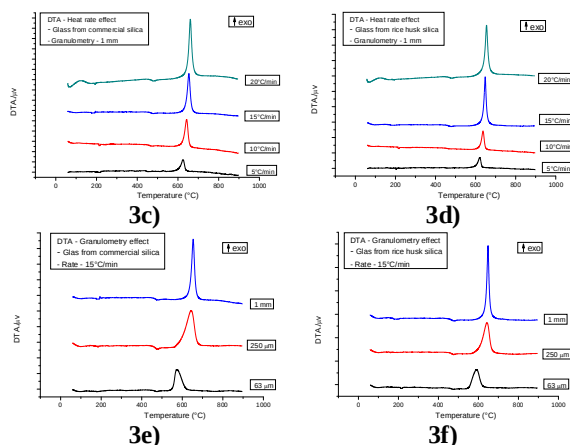


Fig.3 DTAs to different variable conditions. Silica effect for the same granulometry (1mm) using heat rates of 10°C/min (a) and 20°C/min (b). Heat rate effect setting the granulometry (1mm) to the silica sources S (c) and SA (d). Granulometry effect for the same heat rate (15°C/min) in the silica sources S (e) and SA (f).

Fig. 4 present the micrographs of S and SA after two different heat treatment, 610°C and 840°C, using 10 minutes of step, and 10C°/min of heat rate.

It may be noted in the micrographs of Fig. 4 that there is no significant differences between S (Figs. 4a and 4b) and SA (Figs. 4c and 4d). It may be noted too, that increasing heat treatments temperature the grain morphology is changed.

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 propagate⁵⁻⁷.

Fig. 5 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).

The curve follows the sigmoidal form as it has been pointed out in the literature⁸⁻¹⁰. One more time it is possible to see 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 (Fig. 5a) and SA (Fig. 5b)

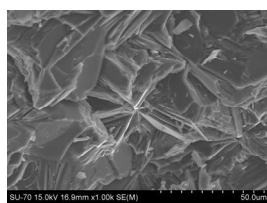


Fig. 4a

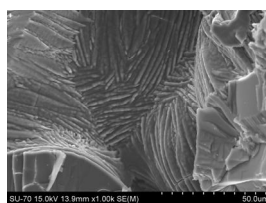


Fig. 4b

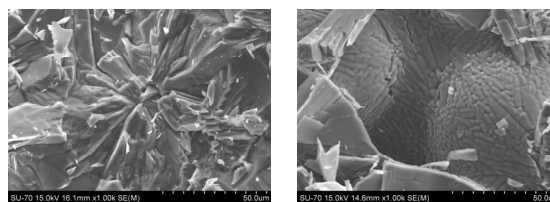


Fig. 4 Micrographs heat treated for 10 min of step and 10°C/min of rate at 610°C to S and SA (a and c respectively), and 840°C (b and d respectively).

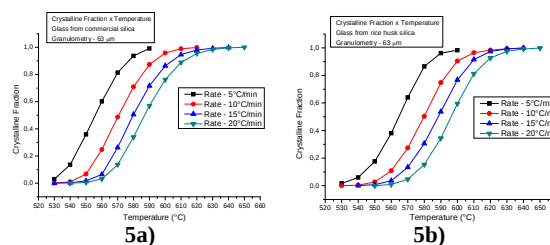


Fig. 5 Crystalline fraction versus temperature at different rates, setting the granulometry (63mm) in the S (a) and SA (b) samples.

Conclusions

The influence of different sources of silica in the material, commercial and rice husk sources, were very similar. The temperatures range and the peaks dislocations in ATD also followed the same tendency for both materials.

Those peaks dislocations had a very similar variation using different heat rates and granulometry for S and SA samples.

The morphology extracted of micrographs changes at the same manner for S and SA as increasing heat treatment temperatures.

At the present moment the substitution of commercial silica for rice husk silica seem to be a quite promising technique to produce lithium disilicate as a biomaterial.

Acknowledgement

The authors acknowledge the CNPq, FAPESP, CAPES, University of São Paulo (USP), Institute of Nuclear and Energy Research (IPEN) and University of Aveiro (UA) by their respective supports, in the laboratory structure and financial ways.

References

1. A.L. Oliveira, J.M. Oliveira, R.N. Correia, R.N.; M.H.V. Fernandes, J.R. Frade, Crystallization of Whitlockite from a Glass in the System CaO-P₂O₅-SiO₂-MgO. *J. Am. Ceram. Soc.* **vol 81** (1998), 3270-3276.

2. S.J. Kim, Y.H. Rim, Y.S. Yang, Kinetics of non-isothermal crystallization process in various sized $\text{Li}_2\text{B}_4\text{O}_7$ glasses. *Solid State Comm.* **vol 131** (2004), 129-133.
3. A. Arora, A. Goel, E.R. Shaaban, K. Singh, O.P. Pandey, J.M.F. Ferreira, Crystallization kinetics of $\text{BaO-ZnO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glass. *Phys. B* **vol 403** (2008), 1738-1746.
4. Z.Z. Yuan, X.D. Chen, B.X. Wang, Y.J. Wang, Kinetics study on non-isothermal crystallization of the metallic $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glass. *J. Alloys Compd.* **vol 407** (2006), 163–169.
5. P. Goharian, A. Nemati, M. Shabanian, A. Afshar, Properties, crystallization mechanism and microstructure of lithium disilicate glass–ceramic. *J. of Non-Cryst. Solids* **vol 356** (2010), 208–214.
6. G. Wen, X. Zheng, L. Song, Effects of P_2O_5 and sintering temperature on microstructure and mechanical properties of lithium disilicate glass-ceramics. *Acta Mat.* **vol 55** (2007), 3583–3591.
7. A. Arvind, A. Sarkar, V.K. Shrikhande, A.K. Tyagi, G.P. Kothiyal, The effect of TiO_2 addition on the crystallization and phase formation in lithium aluminum silicate (LAS) glasses nucleated by P_2O_5 . *J. Phys. Chem. Sol.* **vol 69** (2008), 2622-2627.
8. Z.Z. Yuan, X.D. Chen, B.X. Wang, Y.J. Wang, Kinetics study on non-isothermal crystallization of the metallic $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glass. *J. Alloys Compd* **vol 407** (2006), 163–169.
9. C. Popescu, Integral method to analyze the kinetics of heterogeneous reactions under non-isothermal conditions A variant on the Ozawa-Flynn-Wall method. *Therm. Acta* **vol 285** (1996), 309-323.
10. S.H. Al-Heniti, Kinetic study of non-isothermal crystallization in $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ metallic glass. *J. Alloys Compd* **vol 484** (2009), 177-184.