

## CRYSTALLIZATION OF A SiO<sub>2</sub>-CaO-Na<sub>2</sub>O GLASS FROM SUGARCANE BAGASSE ASH

M. Romero<sup>1</sup>, J.Ma. Rincón<sup>1</sup> and S.R. Teixeira<sup>2</sup>

<sup>1</sup> Group of Vitreous and Ceramic Materials. Department of Building Construction Systems. Eduardo Torroja Institute for Construction Sciences (CSIC). C/ Serrano Galvache, 4. 28033 Madrid, Spain.

<sup>2</sup> Universidade Estadual Paulista - UNESP, Brasil

### Abstract

This work reports the feasibility results of recycling sugar cane bagasse ash (SCBA) to produce glass-ceramic. The major component of this solid residue is SiO<sub>2</sub> (>89%). A 100g batch composition containing ash, CaO and Na<sub>2</sub>O was melted and afterward, poured into water to produce a glass frit. The crystallization kinetic study by non-isothermal method was performed on powder samples (<63µm) at five different heating rates. Wollastonite is the major phase in crystallization at T>970°C, and below this temperature there is a predominance of rankinite. The crystallization activation energies calculated by the Kissinger and Ligero methods are equivalent: 374 ± 10 kJ/mol and 378 ± 13 kJ/mol. The growth morphology parameters have equal values n = m = 1.5 indicating that bulk nucleation is the dominant mechanism in this crystallization process where there is a three-dimensional growth of crystals with polyhedron-like morphology controlled by diffusion from a constant number of nuclei. However, DTA curves on both monolithic and powder glass samples suggest that crystallization of the powder glass sample occurs through a surface mechanism. The divergence in both results suggests that the early stage of surface crystallization occurs through a three-dimensional growth of crystals, which will then transform to one-dimensional growth.

**Keywords:** sugarcane bagasse ash, waste, glass, glass-ceramic, wollastonite, crystallisation

### INTRODUCTION

Brazil is the world's largest producer of alcohol and sugar from sugarcane. In view of the strong national demand and the great interest shown by industrialized countries for ethyl alcohol, there is a current race in Brazil for the implementation of a substantial number of factories for the production of

sugar and alcohol. The estimated 2007/2008 sugarcane harvest is 528 Mt to produce sugar (49.47%) and alcohol (50.53%). The sugarcane stalks are crushed to extract their juice and the fibrous residue remaining is named bagasse. Currently, sugarcane bagasse is burned in boilers to produce steam, which is utilized in the factory processes and also to power turbines for the production of electrical energy, which supplies the factory energy needs with the excess being commercialized in the region. The volume of ash that will be produced in this harvest is approximately 3.2 Mt (1000 kg cane → 250 kg bagasse → 6 kg ash).

There is worldwide consensus that there is a need to recycle and reutilize waste residues for an efficient utilization of natural resources. A wide variety of industrial residues have been used in the production of glass-ceramics [1-3]. Published works have shown the potential of transforming silicate-based residues into glass-ceramic products of great utility. The general process involves the vitrification of a silicate (residue), or mixture of various residues, followed by a crystallization process to form the glass-ceramic.

The most significant glass-ceramic for building applications is manufactured under the brand name Neoparies [4], which is produced on a large scale as a building material especially for interior and exterior walls. A basic composition in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO system (wollastonite) must first be melted to produce a melt which is poured into water to produce a frit. After molding, the glass grains are sintered to a dense monolithic glass by heat treatment and the glass-ceramic is obtained according to the mechanism of controlled surface crystallization.

In the present study, we use sugarcane bagasse ash as silica raw material to obtain a

glass-ceramic with wollastonite as main crystalline phase.

## EXPERIMENTAL

The bottom ash used in this work was collected in a sugar/alcohol factory from Presidente Prudente, Brazil. Prior to its use, the ash was hand crushed, sieved (18 mesh, 1 mm) and grounded (400 rpm, 10 min) using a planetary steel ball mill (RETSCH, model PM100). CaCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> of reagent grade were used as source of CaO and Na<sub>2</sub>O, respectively.

A 100g batch composition containing 49.1g of ash, 45.8g of CaO and 5g of Na<sub>2</sub>O was mixed and homogenized. The batch was heated at 10°C/min and melted in an alumina crucible at 1450°C for one hour. Afterward, the melt was poured into water to produce a glass frit. The chemical composition of the bottom ash and frit was determined by XRF analysis. To determine the crystallization behaviour of the glass, both a powder (<63μm) and a monolithic glass sample were analyzed by thermal analysis (DTA/TG – SETARAM Labsys) from room temperature to 1400°C at a heating rate of 50°C/min. The DTA scans were conducted in flowing air, platinum crucibles and calcined Al<sub>2</sub>O<sub>3</sub> as reference. The kinetic study by non- isothermal method was performed on powder samples (<63μm) from 20 to 1300°C and heating rates of 5, 10, 20, 30, 40 and 50°C/min.

To study the development of the crystalline phases, powder samples (<63μm) were crystallized at different temperatures for 15 min. After this time, each sample was taken out the oven and cooled to room temperature. Phase identification was carried out by X-ray diffraction (XRD, Philips X'PERT MPD) using CuKα radiation and operating at 50 kV and 30 mA.

For many transformations in the solid state, the crystallized fraction at time t, with the velocity of crystallization constant, is expressed by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation as follows:

$$x(t) = 1 - \exp[-(kt)^n] \quad (1)$$

where n is the Avrami exponent, which describes the mechanism of crystallization and provides qualitative information on the nature of the processes of nucleation and growth of the crystals. Taking the

logarithm of the crystallization rate (dx/dt), an expression is obtained that establishes a linear relationship between the logarithm and the inverse absolute temperature [5],

$$\ln\left(\frac{dx}{dt}\right) = \ln[k_o \cdot f(x)] - \frac{E}{R \cdot T} \quad (2)$$

where, E is the activation energy, R is the ideal gas constant and T is the isothermal temperature in Kelvin. In the crystallized fraction interval, it is seen that ln[k<sub>o</sub>f(x)] = constant. This condition permits the calculation of the Avrami exponent, n.

The Kissinger method [6] is another kinetic approach used to analyze DTA data:

$$\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E}{R \cdot T_c} + \text{constant} \quad (3)$$

where T<sub>p</sub> is the peak crystallization temperature and φ is the DTA heating rate. A modified form of this equation was proposed by Matusita and co-workers [7]:

$$\ln\left(\frac{\phi^n}{T_p^2}\right) = -\frac{m \cdot E}{R \cdot T_c} + \text{constant} \quad (4)$$

where m is a numerical factor depending on the dimensionality of crystal growth

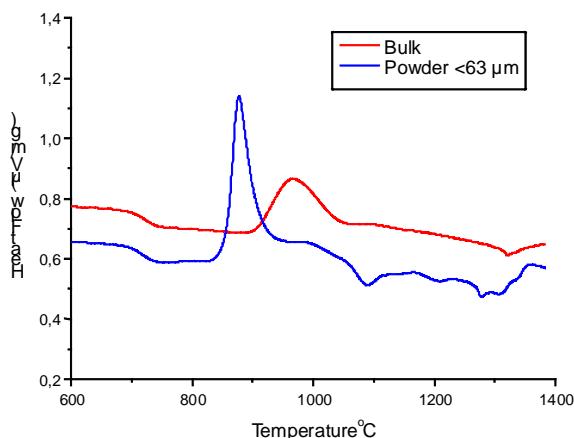
## RESULTS AND DISCUSSION

Table 1 shows the chemical analyses by XRF of the sugarcane bagasse ash and derived glass frit. The major component of the ash is SiO<sub>2</sub>, and among the minor components K<sub>2</sub>O show the highest concentration. This composition differs from that reported in a previous study [8] due to differences in the type of sugarcane and, principally, in the soils where it was harvested. The Al<sub>2</sub>O<sub>3</sub> amount in the glass is incompatible with the ash composition, indicating a contamination from the alumina crucible. Other chemical elements, such as nucleating agents, are presents in low amounts. X-ray diffraction of the ash showed that quartz is the major phase.

**Table 1.** Chemical composition (wt. %) of sugarcane bagasse ash and derived glass frit

	Ash	Frit
SiO <sub>2</sub>	89.61	42.38
Al <sub>2</sub> O <sub>3</sub>	1.62	3.10
Fe <sub>2</sub> O <sub>3</sub>	1.33	0.93
Na <sub>2</sub> O	-----	4.72
K <sub>2</sub> O	3.54	0.84
CaO	1.01	47.03
MgO	0.98	0.43
TiO <sub>2</sub>	0.29	0.11
P <sub>2</sub> O <sub>5</sub>	1.37	0.20
Cr <sub>2</sub> O <sub>3</sub>	0.08	0.13

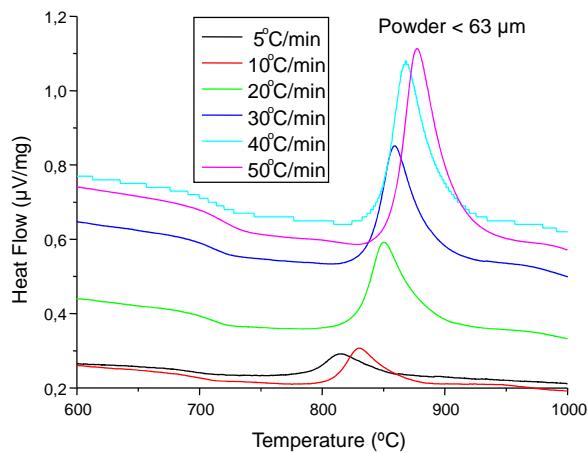
DTA results for powder (< 63 μm) and monolithic sample are shown in Figure 2. The decrease in particle size leads to both a shift of the maximum of the exothermic peak to a lower temperature and an increase in the crystallization peak height. Considering that crystallization peak height is proportional to the number of nuclei formed in the glass, the difference in the results to both samples (Fig. 2) implies that surface crystallization plays a major role in the crystallization of the glass sample. X-ray diffraction of the powder frit after thermal treatment at 970°C/15 min showed that wollastonite (CaO·SiO<sub>2</sub>) is the major crystalline phase in the glass-ceramic.



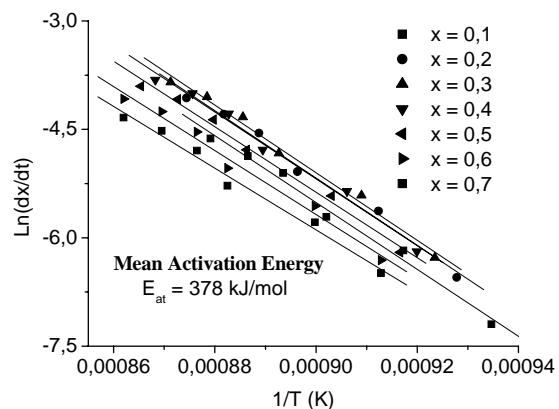
**Figure 1.** DTA curves of the glass powder and monolithic sample (50°C/min).

Figure 2 depicts part of the DTA curves recorded for powder samples (< 63 μm) at six different heating rates from room temperature to 1300°C. From curves showed in Fig.2, the kinetic parameters were calculated using the Ligero method [5] in which the crystallized fraction interval at which the model is constant was taken into account (Eq. 2). Figure 3 shows the plot of  $\ln(dx/dt)$  with the inverse absolute temperature (1/T) at the same value of

crystallized fraction (x) for the different heating rates. It is seen that this plot is linear ( $r > 0.99$ ) in the range  $x = 0.10$  to  $0.70$  giving an average activation energy of  $378 \pm 13$  kJ/mol for glass crystallization. The Avrami parameter, n, was obtained by selecting many pairs of  $x_1$  and  $x_2$  that satisfy the condition  $\ln[k_0 \cdot f(x_1)] = \ln[k_0 \cdot f(x_2)]$ . The average parameter value using this method is 1.50.



**Figure 2.** DTA curves for the glass powder at different heating rates (5, 10, 20, 30, 40 and 50°C/min)



**Figure 3.** Mean activation energy by Ligero method (x ranging from 0.1 to 0.7).

The activation energy calculated from the slope of the plot of  $\ln[\phi/T_p^2]$  versus  $1/T_p$ , using the Kissinger method [6] (Eq. 3), is  $374 \pm 10$  kJ/mol, which is in good agreement with that estimated by the Ligero. Using the Matusita equation, n from Ligero equation and activation energies (Ea) from Ligero and Kissinger methods, the numerical factor m obtained was 1.51 (for Ligero Ea) and 1.53 (for Kissinger Ea). Both parameters (n and m) have values close to 1.5, which is an indication of a three-dimensional growth of crystalline phases with

polyhedron-like morphology. These results also indicate that bulk nucleation is the dominant mechanism and that crystal growth is controlled by diffusion from a constant number of nuclei. It is important to point out that kinetic results are in disagreement with the previous results taken from DTA curves (Fig.1), which indicate that crystallization of the powder glass sample occurs through a surface mechanism. Taken together, these results suggest that the early stage of surface crystallization occurs through a three-dimensional growth of crystals, which will then transform to one-dimensional growth. This result has been confirmed by scanning electron microscopy (SEM). Thus, Figure 4 shows the microstructure observed by SEM on a glass sample sintered at 1050°C for 1 hour. It is clearly observed a crystallization shell consisted of spherulitic crystals (three-dimensional), which induce the development of linear fiber-like crystals aggregations.

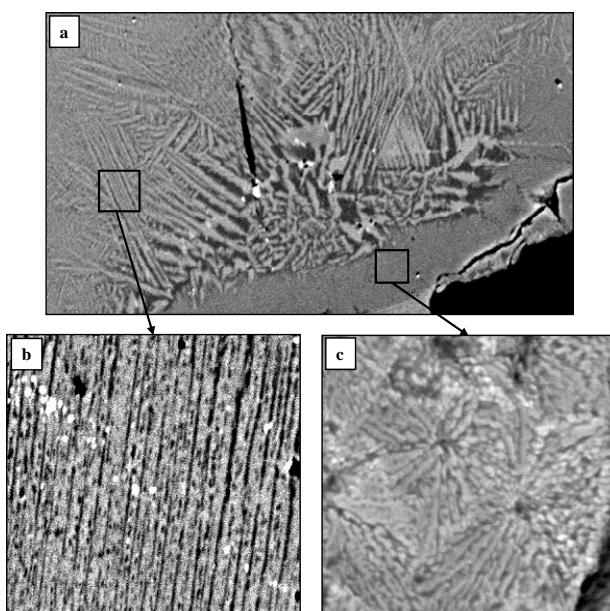


Figure 4. SEM observation on a glass sample sintered at 1050°C for 1 hour.

## CONCLUSIONS

The results obtained in this investigation show that it is possible to use sugarcane bagasse ash to produce useful glass-ceramic products with wollastonite as major crystalline phase at T>970°.

The crystallization activation energies calculated by the Kissinger and Ligero methods are equivalent:  $374 \pm 10$  kJ/mol and  $378 \pm 13$  kJ/mol. DTA curves suggest that surface crystallization plays a major role in the crystallization of the glass sample. However, growth morphology parameters have equal values  $n=m=1.5$ , indicating that bulk crystallization is the

dominant mechanism in this crystallization process where there is a three-dimensional growth of crystals with polyhedron-like morphology controlled by diffusion from a constant number of nuclei. Taken together, these results suggest that the initial stage of surface crystallization occurs through a three dimensional growth of crystals.

## REFERENCES

- [1] M. Romero, R. D. Rawlings, and J. Ma. Rincón, "Development of a new glass-ceramic by means of controlled vitrification and crystallization of inorganic wastes from urban incineration", *J. Eur. Ceram. Soc.*, 19, 2049-2058 (1999).
- [2] M. Romero, and J. Ma. Rincón, "El proceso de vitrificación/cristalización controlada aplicado al reciclado de residuos industriales inorgánicos", *Boletín de la Sociedad Española de Cerámica y Vidrio*, 39, 155-163 (2000).
- [3] R. D. Rawlings, J. P. Wu, and A. R. Boccaccini, "Glass-Ceramics: Their Production from Wastes - A Review", *J. Mater. Sci.*, 41, 733-761 (2006).
- [4] <http://www.neg.co.jp/arch/neoparies.html>
- [5] R. A. Ligero, J. Vázquez, P. Villares, and R. Jiménez-Garay, "A study of the crystallization kinetics of some Cu-As-Te glasses". *J. Mater. Sci.*, 26, 211–215 (1991).
- [6] H. E. Kissinger, "Variation of peak temperature with heating rate in differential thermal analysis", *J. Res. Natl Bur. Stnd.*, 57, 217-221 (1956).
- [7] K. Matusita, and S. Sakka, "Kinetic-study on crystallization of glass by differential thermal-analysis: Criterion on application of Kissinger plot", *J. Non-Cryst. Sol.*, 38-39, 741–746 (1980).
- [8] S. R. Teixeira, A. E. Souza, G. T. A. Santos, A. F. V. Peña, and A. G. Miguel, "Sugar cane bagasse ash (SCBA) as a potential quartz replacement in red ceramic", *J. Am. Ceram. Soc.*, 91, 1883-1887 (2008).

## Acknowledgements

S.R.Teixeira is greatly indebted to FAPESP (04368-4/08), to UNESP/PROPE-SANTANDER post-doc program for the scholarship and to ICCET/CSIC for the laboratories and materials accessibility.