Thermal approach to evaluate the sintering–crystallization ability in a nepheline–forsterite-based glass-ceramics

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Abstract

A glass in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--Na}_2\text{O}$ system was formulated using a non-conventional silica source and other pure raw materials. The thermal stability and crystallization mechanism have been studied by means of differential scanning calorimetry (DSC). Besides, the glass ability to sintering–crystallization has been examined by optical dilatometry, a non-contact technique allowing the acquisition of dilatometric data in the viscoelastic temperature region. The experimental data were confirmed with theoretical equations. X-ray diffraction and field emission scanning electron microscopy were used to verify the crystallization study and electron scanning microscopy to examine the fired sample microstructures. The prevalent crystallization mechanism has been evaluated from different parameters derived from characteristic temperatures of non-isothermal DSC curves, namely the working range (ΔT_{TS}), reduced glass transition temperature (T_{gr}), and the dissimilarity in crystallization temperature (ΔT_{p}) between fine ($<63\text{ }\mu\text{m}$) and coarse (fragment) glass samples.

Keywords

Glass-ceramics; Nepheline; Forsterite; Sintering–crystallization; Optical dilatometry (ODL); Differential scanning calorimetry (DSC)

Introduction

Glass-ceramics are polycrystalline materials produced through controlled devitrification of parent glasses. These materials, which are comprised of an amorphous phase and one or more crystalline phases, are produced by controlled crystallization of a parent glass in contrast to ungoverned crystallization, which is usually undesirable in glass manufacturing. The earliest glass-ceramics were produced by a conventional glass route that involves the manufacture of a glass that is subsequently crystallized, usually by a heat treatment in two stages: formation of submicroscopic

nuclei (nucleation), and their growth into macroscopic crystals (crystal growth) [1]. The sintering method was proven to be a technically viable route for the manufacture of glass-ceramics. This process usually involves the milling of a glass frit into fine particles which subsequently are shaped by conventional forming techniques and afterwards heat-treated to provide sintering and crystallization of the glass particles. A sintering process is normally used when the parent glass exhibits a strong tendency for surface crystallization or when complex shapes are required [2].

Usually, the raw materials used in the production of glass-ceramics are naturally occurring minerals commonly used in the glass industry, such as clay, quartz sand, dolomite, limestone, feldspar, calcite, and natural diopside mineral. [3–6]. However, they can also be prepared from cheaper raw materials such as wastes because the glassceramic process has been established as a suitable way to valorize mining and industrial wastes [7–9].

Rice is the second largest cereal produced worldwide, and Italy is the first European producer (1.43 million ton year⁻¹, 2013) [10]. Burning the rice husk as a fuel substitute in kilns (brick making and other clayed products) or in the rice mills to produce steam (parboiling process) generates rice husk ash (RHA) as a waste. This residual ash is composed mainly of amorphous silica (85–90 mass%) and could be a sustainable and interesting alternative silica resource to obtain glass-ceramics.

In recent years, several studies were conducted in the ceramic sector to valorize RHA. In particular, the use of this ash was investigated as a secondary raw material in the manufacture of Whiteware products [11], pigments [12, 13], glazes [14, 15], brick compositions [16], and glass-ceramic materials in the SiO₂–Na₂O–CaO [17] and SiO₂–Al₂O₃–Li₂O [18] systems, as well as in cordieritebased glass-ceramics [19].

In recent papers [20, 21], the authors demonstrated the feasibility of producing an original glass in the SiO₂–Al₂O₃–MgO–Na₂O-based system from a rice husk ash mixture that incorporates B₂O₃ and Na₂O for facilitating the melting process.

In the present work, a thermal approach using differential scanning calorimetry (DSC) supported by a theoretical analysis and non-contact optical dilatometry is discussed, in order to establish the preferential crystallization mechanism and better explain the sintering behaviour of a powdered glass produced from RHA.

While traditional mechanical dilatometers can measure the thermal expansion of a sample only while it is rigid enough to remain undeformed by the pressure of the rod, the non-contact method allows following the entire sintering–crystallization process without interfering with it. Since the measurements are taken without any contact between the measurement system and the sample, this technique makes possible the study of incoherent or viscous materials, widening the investigation

field into the temperature range above the glass transition temperature [22], and allows to take measurements with the same resolution over the full size of the specimen, i.e. the measurement will never go out of scale. This feature enables to follow perfectly even a viscous flow sintering process, yielding the true sintering curve in real time [23].

Experimental procedure

To obtain a RHA glass frit in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--Na}_2\text{O}$ based system, a mixture composed of rice husk ash from a plant producing semi-parboiled rice (Garibaldi 1889, Colussi S.p.A., Milan, Italy) as a silica source and pure raw materials such as Al_2O_3 , MgO , B_2O_3 , and Na_2CO_3 (the B_2O_3 and Na_2O were added to the ash to facilitate the melting process, while Al_2O_3 and MgO were used to favour the forsterite crystallization) was formulated. The as-received RHA contained about 9 mass% of unburned organic carbon. Therefore, prior to its use, it was thermally treated at 500 °C and sieved to a particle size <250 μm . The batch components (46.52 % ash, 13.84 % Al_2O_3 , 13.16 % MgO , 22.17 % Na_2CO_3 , and 4.33 % B_2O_3) were mixed for 30 min in a blender (TURBULA) to produce a homogeneous mixture. The frit was obtained by melting the raw material mixtures at 1450 °C for 120 min in an electric furnace and subsequently quenching the melt into cool water.

The chemical compositions of the RHA and the obtained glass were determined by X-ray fluorescence (XRF; Thermo Scientific model ARLADVANT'XP) and inductively coupled plasma (ICP; Varian model Liberty 200), respectively.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques are normally used to know the main parameters required for understanding glass crystallization behaviour [24–28]. To investigate the effect of particle size on the crystallization ability, the frit was separated by sieving in five fractions with different particle size ranges, namely <63 μm ; 63–100 μm ; 100–160 μm ; 160–250 μm ; and 250–400 μm . DSC analyses (SETARAM model Labsys) were performed on both fine (different particle size fractions) and coarse (~3 x 3 x 4 mm fragment) samples. The samples were heated from 25 to 1450 °C at a heating rate of 30 °C min⁻¹. The DSC scans were conducted in flowing air, platinum crucibles, and calcined Al_2O_3 as reference material. The characteristic temperatures were determined from the non-isothermal DSC analyses, and the experimental errors in their values are approximately $\pm 2\text{--}3$ °C.

The dilatometric tests were performed using the optical dilatometer Misura ODLT (ODL; Expert System Solution model Misura ODLT). The sample was placed horizontally into the furnace and lighted by two beams of blue light with a wavelength of 478 nm, which enabled an optical resolution of 0.5 $\mu\text{m pixel}^{-1}$. During the test, two digital cameras captured the images of the last few hundred microns of each tip, providing an absolute measurement. The sintering curve was collected

on samples of parallelepiped shape prepared from fine glass particles ($<63\ \mu\text{m}$). The glass powder was mixed with a 5 mass% PVA solution and uniaxially pressed with a hydraulic press at 40 MPa to obtain $50 \times 5 \times 5\ \text{mm}^3$ parallelepipeds; subsequently, the binder was removed with a permanence of 30 min at $250\ ^\circ\text{C}$ into an electric furnace. The tests on the powdered samples were carried out with a heating rate of $10\ ^\circ\text{C}\ \text{min}^{-1}$ up to different maximum temperatures ($750\text{--}1000\ ^\circ\text{C}$) with a holding time of 40 min.

After dilatometric tests, the same samples were subjected to microstructural analysis by scanning electron microscopy (SEM; XL40, Philips Research Laboratories) equipped with an energy-dispersive spectroscopy (EDS) equipment (EDAX, Philips Research Laboratories). SEM specimens were polished using alumina pastes after grinding with silicon carbide paper and water. Besides, in order to better observe the crystalline phase formation on the compact treated at $700\ ^\circ\text{C}$ for 40 min was performed a field emission scanning electron microscopy analysis (FESEM; JEOL model JSM 6500F) using an accelerate voltage of 20 kV. FESEM specimen was polished using alumina pastes after grinding with silicon carbide paper and water and then etched for 10 s in a 5 vol% HF solution, washed ultrasonically with distilled water and ethylic alcohol, dried, and subsequently coated with Au–Pd in a Balzers SCD050 sputter.

The evaluation of the amorphous nature of glass after melting and the crystalline phases devitrified after thermal treatments was performed by X-ray diffraction (XRD; Phillips model PW3710) with Ni-filtered Cu K α radiation operating at 35 mA and 35 kV. For the qualitative mineralogical study, data were recorded in the $3^\circ\text{--}75^\circ\ 2\theta$ range (step size 0.02° and 6 s counting time for each step). The identification of crystalline phases was made under comparison with data ICPS files. Moreover, the quantitative study was performed by combined Rietveld–RIR (reference intensity ratio) method from X-ray diffractogram recorded in the $5^\circ\text{--}140^\circ\ 2\theta$ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld–RIR refinements, using GSAS software and EXPGUI as graphical interface [29, 30], were rescaled on the basis of the absolute mass of corundum originally added to the mixtures as an internal standard.

Results and discussion

The chemical composition of the used RHA (after pretreatment at $500\ ^\circ\text{C}$) and the glass obtained (Table 1) confirmed that the major component of the ash is SiO_2 ($\sim 91\ \text{mass}\%$), while other oxides such as alkalines and alkaline earths (Na_2O , K_2O , CaO , MgO) are present in percentages lower than 1.5 mass% [20]. Chromophore oxides, such as Fe_2O_3 and TiO_2 , that can influence the colour developed in a ceramic matrix, are present only as traces. Rietveld–RIR analysis undergone on the

RHA sample showed that it is mainly constituted by amorphous silica (77.2 mass%) and low-cristobalite (17.2 mass%) and tridymite (5.6 mass%) as crystalline phases. The final amount of amorphous or crystalline silica contained in the ash depends on the combustion conditions (time, temperature, etc.). In order to obtain high amount of silica into the ash, a long combustion process is desirable (normally the content is >60 %). Our results agree with those of previous studies that demonstrated as the RHA obtained at around 1000 °C contains a certain amount of cristobalite and tridymite [31, 32]. These results allowed focusing the research towards the use of this residue as silica source for glass-ceramics. The SiO₂–Al₂O₃–MgO–Na₂O system was chosen in order to obtain glass-ceramics with properties suitable to be used as wall tiles. Regarding the RHA glass, as expected, SiO₂, Al₂O₃, Na₂O, and MgO are the main components in its composition [20].

Table 1 Chemical composition of RHA and RHA glass

Oxide	RHA/mass%	RHA glass/mass%
SiO ₂	90.75	44.18
P ₂ O ₅	3.62	0.48
SO ₃	1.62	–
K ₂ O	1.56	1.86
CaO	1.20	0.68
MgO	0.84	12.24
Fe ₂ O ₃	0.16	0.06
MnO	0.16	–
Al ₂ O ₃	0.06	18.22
TiO ₂	0.03	–
ZnO	0.01	–
Na ₂ O	–	17.06
B ₂ O ₃	–	5.21

The glass stability of RHA glass was evaluated by DSC tests on both fine (<63 µm) and coarse (bulk) samples. The curves in Fig. 1 put out a different behaviour towards the crystallization process. Both samples experiment the endothermic jump associated with glass transition temperatura (T_g) at around 600 °C, but afterwards the termal behaviour of the samples differs with the particle size. Thus, the curve recorded on bulk glass sample does not exhibit noticeable exothermic effects, indicating that a subsequent heat treatment at higher temperatures does not result in the development of nuclei in the internal volumen of the glass sample. Conversely, the powder glass simple highlights two exothermic effects at 745 and 900 °C, respectively. This

behaviour indicates that the devitrification process of RHA glass will primarily occur through a surface crystallization mechanism. Normally, nepheline glass-ceramics are produced by controlled heat treatments in two steps (nucleation and crystal growth) from bulk glasses whose composition includes nucleating agents as TiO_2 [33, 34]. If this surface crystallization mechanism will be confirmed, glass-ceramics at lower temperatures and without the use of nucleating agent could be obtained through a sintering route. From a theoretical point of view, the prevalence of a surface

Fig. 1 DSC curves of fine and coarse RHA glass samples at a heating rate of $30\text{ }^{\circ}\text{C min}^{-1}$

crystallization mechanism in the devitrification of RHA glass was evaluated by means of different parameters estimated from the characteristic temperatures in DSC curves, namely the glass transition temperature (T_g); onset and peak crystallization temperatures (T_x and T_p , respectively); and melting temperature (T_m), which is the temperature at the minimum of the endothermic peak. In order to evaluate the particle size fraction more adequate for obtaining glass-ceramic materials from RHA glass by a sintering–crystallization process, DSC on different particle size fractions separated from ground RHA glass were recorded. In Table 2 were collected the values of the characteristic temperatures for the different particle size fractions of RHA glass, and the calculated ΔT_{TS} for the both crystallization peaks (calculated by Eq. 2) and T_{gr} (calculated by Eq. 3). From the data reported, it is possible to note the maximum peak shifts to higher temperatures when the particle size increases, indicating that the crystallization kinetics of RHA glass is highly dependent to the glass particle size as above hypothesized.

Table 2 Characteristic temperature values (T_x , T_p , T_m) for the different particle size fractions of RHA glass, the calculated DTTS for both crystallization peaks and the calculated T_{gr}

Fraction	T_{x1}	T_{p1}	T_{x2}	T_{p2}	T_m	ΔT_{TS} (1st peak)	ΔT_{TS} (2nd peak)	T_{gr}
<63 μm	680	745	795	900	1137	80	195	0.634
63–100 μm	682	774	866	955	1187	82	266	0.611
100–160 μm	714	798	872	983	1193	114	272	0.610
160–250 μm	715	812	885	1009	1207	115	285	0.604
250–400 μm	720	800	898	1027	1222	120	298	0.598

The Thakur and Thiagarajan method [35] was employed by determining the crystallization temperature difference (ΔT_p) between fine and coarse RHA glass sample powders, as follows:

$$\Delta T_p = T_{p(\text{fine})} - T_{p(\text{coarse})}. \quad (1)$$

If glass devitrification occurs through surface crystallization, a strong dependence on glass particle size would be expected, with ΔT_p yielding negative values in Eq. 1. By considering the RHA glass fractions with the finest (<63 μm) and coarsest (250–400 μm) particle size, both crystallization peaks lead to $\Delta T_p < 0$, i.e. -55 and -127 °C for peak 1 and peak 2, respectively. The negative values of ΔT_p confirm the dominance of surface crystallization mechanism in RHA glass.

An evaluation of the thermal stability of the glass was also achieved by measuring its working range (ΔT_{TS}), which is the temperature interval between T_g and the onset of crystallization (T_x)

$$\Delta T_{TS} = T_x - T_g. \quad (2)$$

The smaller is this interval of temperature, the lower is the thermal stability of the glass and consequently, it exhibits a greater tendency to crystallize. The data calculated are reported in Table 2. Considering both crystallization peaks, ΔT_{TS} increases as a function of the particle size for RHA glass. Therefore, for finest particle size powder samples, the glass shows lower thermal stability (high tendency to crystallize) than coarse samples, and glass stability increases with the increase in glass particle size. This result is in agreement with a surface crystallization mechanism.

Finally, another important parameter used to determine the crystallization mechanism was studied: the reduced glass transition temperature (T_{gr}) [36]:

$$T_{gr} = T_g / T_m. \quad (3)$$

On the basis of Zanotto findings [37, 38], glasses with T_{gr} values higher than 0.58–0.60 display only surface crystallization, whereas glasses with T_{gr} values lower than 0.58–0.60 exhibit volume crystallization. From the data calculated reported in Table 2, RHA glass shows a prevalent surface crystallization mechanism for particles size $<160\ \mu\text{m}$, although for the other size classes, the T_{gr} values are higher than 0.58.

To verify the preferential crystallization mechanism, compacts of RHA glass powder ($<63\ \mu\text{m}$) were subjected to thermal treatment at $700\ ^\circ\text{C}$ for 40 min in order to induce crystal growth. Figure 2 shows a low-magnification FESEM image. It is clear that at early stages, the devitrification process occur throughout a mechanism of controlled surface crystallization in which crystals develop along the edge of the former glass particles, while internal nucleation is not initiated.

Therefore, the devitrification study reveals that the sintering–crystallization method is the most suitable route for preparing glass-ceramic materials from RHA glass. The sintering behaviour of glass powder ($<63\ \mu\text{m}$) compacts was evaluated in the range $20\text{--}1200\ ^\circ\text{C}$ by optical non-contact dilatometry. The choice of a non-contact method allows following the entire sintering–crystallization process without interfering with it. The measurements are absolute, because they are not affected by the sample holder or by a push rod, as in traditional dilatometers [22].

Fig. 2 FESEM secondary electron image of RHA glass ($<63\mu\text{m}$) of polished surface compacts heat-treated at $700\ ^\circ\text{C}$ for 40 min and etched with 5 vol% HF solution

Figure 3 shows the behaviour of linear shrinkage of RHA glass powder ($<63\ \mu\text{m}$) versus temperature overlapped with its DSC curve recorded at the same heating rate ($10\ ^\circ\text{C min}^{-1}$). The

test was conducted using a continuous heating ramp up to 1300 °C in order to identify the sintering and bloating attitude of the glass sample.

Fig. 3 Non-isothermal dilatometric and DSC curves for RHA glass powder simple (<63 μm ; heating rate: 10 °C min^{-1})

The non-isothermal dilatometric sintering curve shows that the sintering begins after T_g (≈ 600 °C), and the maximum linear shrinkage ($\Delta L/L_0$) is about 8 % at 760 °C. During the sintering process, the dimensions of the sample decrease, but the specimen does not change its shape; the maximum sintering rate calculated as the first derivative of the sintering curve is at 723 °C. Above this temperature, the densification is inhibited by the crystallization of the new phases, as denoted by the corresponding exothermic peaks in the DSC curve. For temperatures higher than 1000 °C, a bloating phenomenon is present, and the deformation of the sample starts. At the same time, in the DSC curve, it is possible to note an endothermic event associated with the formation of liquid phases.

In order to understand the sintering–crystallization mechanism, further dilatometric measures were taken up to different temperatures (750, 800, 850, 900, and 1000 °C) with 40 min of holding time. The use of a non-contact dilatometer is an advantage in glass or materials that begins to soften during the measure with respect to the traditional ones [22].

On the basis of experimental data regarding closed and open porosity, apparent and absolute density, and water absorption, it is possible to affirm that the experimental density values are close

to nepheline density (2.60 g cm^{-3}) and in agreement with Rietveld analysis that underlines that nepheline is the main crystalline phase. Regarding apparent density, the increase in the sintered material densities by increasing the sintering temperature up to 900°C is in accordance with the viscous sintering theory, which correlates the temperature dependence of the sintering process to the temperature dependence of the glassy phase viscosity. Figure 4 underlines that 900°C is the maximum firing temperature for obtaining glass-ceramic materials from RHA parent glass, since firing above 900°C results in overfiring.

These results are in agreement with SEM observations carried out on sections of RHA glass compact fired at 850 , 900 , 1000°C (Fig. 5a–c). It is possible to note as closed porosity increases when the firing temperature increases. Total and open porosity values decrease until 900°C , indicating a densification process. On the other hand, the sample treated at 1000°C shows a lower apparent density value. Besides, closed porosity strongly increases with the temperature reaching 22% . The bloating phenomenon, in the form of a high concentration of coarse pores, takes place by retention of gas within the mass when a considerable quantity of glassy phase ($50 \text{ mass\%}$ by Rietveld data) of adequate viscosity is present.

Fig. 4 Sintering curves of compacts prepared from RHA glass powder ($<63 \mu\text{m}$) heat-treated up to different temperatures with a holding time of 40 min

Fig. 5 SEM micrographs of glass-ceramics prepared after firing RHA glass compacts at **a** 850 °C, 40 min; **b** 900 °C, 40 min; **c** 1000 °C, 40 min

The evolution of the phase composition of resulting glassceramics, treated at different temperatures with holding time 40 min, was studied by XRD analysis, and the results are summarized in Fig. 6. The XRD pattern at 700 °C indicates an amorphous material; yet this technique is not enough sensible to identify the neo formation crystalline phase, evidenced by FESEM, but the increase in temperature leads to the development of glass-ceramics composed of nepheline (NaAlSiO_4) and forsterite (Mg_2SiO_4) in varying proportions. The nepheline formation is evident at 750 °C; the intensity of nepheline phase varies slightly up to 900 °C and decreases at 1000 °C, while forsterite from 800 °C reached an almost constant intensity.

The Rietveld–RIR analysis performed confirmed that the maximum amount of nepheline (45.5 mass%) arises in the glass-ceramics prepared at 750 °C, and heat treatments at higher temperatures result in a slight decrease in the nepheline content with increasing temperature. The growth of forsterite begins at 750 °C and reaches its máximo development at 800 °C (~11 mass%); treatments at higher temperatures not lead to further development of forsterite, and its content remains almost constant in the 800–1000 °C temperature interval. The amount of crystalline phases

(nepheline + forsterite) in the glass-ceramics obtained at 800 °C is 54.7 mass%. Since the amount of nepheline progressively decreases from 750 (45.5 mass%) to 1000 °C (40 mass%), it is possible to hypothesize that nepheline phase melts and, therefore, the glassy phase increases. The Rietveld–

Fig. 6 XRD patterns of RHA glass after thermal treatments for 40 min at different temperatures [nepheline (circle); forsterite (square)]

RIR analysis showed that glassy phase increases from 45 mass% at 800 °C to 48 mass% at 1000 °C confirming the bloating phenomenon [21].

The experimental T_g and T softening values determined by a non-contact dilatometry of a bulk annealed sample are in agreement with DSC data. In fact, the dilatometric transition temperature T_g (dil) (591 °C) was determined from the $\Delta L/L_0$ curve as the point of intersection of the tangents below and above the slope change and T softening (dil) (731 °C) was identified as a maximum value of the peak [39]. It is known that in glass-ceramics, the coefficient of thermal expansion (CTE) could be associated with the expansion characteristics of the crystalline phases, and its value depends on the type and amount of both crystalline phase and residual glass phase contents. In our case, the CTE value determined ($9.89 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) permits to confirm the presence of nepheline, which CTE value is around $10.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ from the literature data [40].

Conclusions

A glass in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--Na}_2\text{O}$ based system was evaluated using DSC and optical non-contact dilatometry to establish both the preferential crystallization mechanism and the sintering behaviour. The results showed that the devitrification process occurs throughout a mechanism of controlled surface crystallization, and the experimental data were confirmed by application of theoretical equations.

The glass-ceramics obtained crystallize in nepheline and forsterite phases at 800 °C reaching a maximum amount of crystallinity (54.7 mass%) determined by Rietveld-R.I.R analysis. The optimization of sintering process studied by optical dilatometry permitted to consider between 800 and 900 °C the temperature interval most suitable to obtain nepheline–forsterite glass-ceramics with low porosity using powdered compact samples.

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