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Bulk and sintered glass-ceramics by recycling municipal incinerator bottom ash

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Abstract

Glass-ceramics were produced using an Italian municipal incinerator bottom ash and glass cullet coming from a community glass recycling program. The capability of three different mixtures to be vitrified and subsequently devitrified by both bulk and sintering process was investigated by means of differential thermal analysis, X-ray diffraction, hot stage microscopy, firing shrinkage, water absorption and bulk density measurements, as well as scanning electron microscopy observations. High ash contents favour the growth of crystallised fraction volume and the formation of crystals of the pyroxene group, and anorthite in addition to wollastonite. Since the nucleation mechanism starts from the surface and sintering occurs before crystallisation, all the compositions humidified with a water solution are easily sinterable in dense materials at the relatively low temperature of about 850°C, in such way as to render the process economically advantageous © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Glass ceramics; Incinerator waste; Recycling; Sintering; X-ray methods

1. Introduction

For those countries where the population density is high, the production of municipal wastes is generating social and economical problems. In Italy, each inhabitant produced in 1997 about 462 kg of rubbish, for a total of 26.6 million tons of municipal waste, with an increase of 2.5% with respect to the previous year.[1] The most common disposal methods are the laying in dump and the incineration. The first is the most simple and practical method, but it is dangerous for both the soils and the atmosphere because of those substances prone to putrescence, producing biogases and favouring the greenhouse effect. On the other hand, incineration reduces the waste volume by approximately 90%, exploits the calorific power of the wastes to produce energy (vapour, electricity), but this process gives rise to considerable amounts of solid residues (bottom and boiler ashes, filter fly ashes). By considering the mass balance of an incinerator process, it appears evident that the solid residues of major size represent the most important problem as far as the ash produced amount is concerned. In particular, when burning 1000 kg of municipal waste the obtained products are around 300 kg of bottom ash (special waste laid in dump) and 30 kg of fly ash (hazardous waste that must be inertized before the laying in dump). Because national regulations are reinforcing environmental protection measures, there is a great interest in finding alternative technological options capable, at the same time, to convert a by-product into a new marketable material. The vitrification and the promotion of controlled crystallisation by forming a glass-ceramic [2–9] appears a promising solution because it is able to convert, at a relatively low cost, complex chemical compositions into useful materials with good technological properties. This is a peculiar characteristic of glass-ceramics, high-quality products whose production, from an energy-intensive process (melting temperatures >1300°C), can be fully justified because of their optimised properties. Glass-ceramics can be made both by a traditional glass-forming technique starting from the melted glass, followed by a nucleation/crystallisation heat treatment, and by glass powders sintering through heating to high temperatures. The latter technique is especially used where unusual product shapes, that cannot be obtained by the normal

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means of glass shaping are required, and presents an advantage in that it is not necessary to take into account the glass workability characteristics and it is possible to choose easily devitrifiable compositions. Furthermore, since sintering is the result of atomic motion stimulated by high temperature and diffusive processes are generally dominant and favoured by the presence of liquid phase (this increases the sintering rate), this methodology is exploitable for materials developing a glassy phase, i.e. glass-ceramics rather than ceramics. Liquid-phase sintering is an attractive option for many of the high performance materials because of the rapid processing cycle, high finally density, and excellent final properties.[10] Previous works on recycling of fly ashes from Spanish and German urban incinerators has been carried out recently .[11,12]

In this work, we investigated the possibility to obtain bulk or sintered glass-ceramics starting from Italian municipal incinerator bottom ash mixed with glass cullet in order to establish the best conditions to obtain a product with a high density and crystallinity degree.

2. Experimental procedure

Bottom ash from the Reggio Emilia municipal incinerator (Italy) and glass cullet from a community glass recycling programme were used. From the average chemical composition of the raw materials shown in Table 1 (as for bottom ash the data listed are the result of 10 analyses conducted by inductively coupled plasma, ICP-Varian Liberty 200), it appears evident that the relatively high SiO_2 content of the bottom ash indicates the suitability for this waste to be employed in the development of vitreous products, while glass cullet can help the formation of an amorphous material with lower viscosity thanks to the Na_2O content and the contribution of a pre-formed glass network.

Three different mixtures containing different proportions of bottom ash and glass cullet were prepared. The following ash contents were considered: 10, 50 and 100 wt%, and the chemical analysis of the corresponding obtained glasses is reported in Table 2. The good agreement between the formulated and the experimental data, evident from the same table, confirms the absence of reactivity between the melting batch and the crucible.

Table 1
Average chemical analysis (wt%) of the main components in the used raw materials

Oxide	Municipal bottom ash	Glass cullet
SiO_2	45.13	70.3
Al_2O_3	9.73	2.18
CaO	18.78	9.30
MgO	2.20	2.13
Na_2O	4.64	13.32
K_2O	1.29	1.19
Fe_2O_3	3.84	0.293
TiO_2	0.93	0.068

Table 2
Formulated and ICP average chemical composition (wt%) of the prepared glasses

Composition Oxide	S1 (10% ash)	S5 (50% ash)	S10 (100% ash)
SiO_2	69.48/67.33	62.28/65.14	52.14/53.56
Al_2O_3	3.01/3.08	6.42/7.05	11.25/12.62
CaO	10.50/11.97	15.15/13.86	21.71/20.31
MgO	2.19/2.51	2.34/2.37	2.54/2.81
Na_2O	12.77/12.57	9.69/7.69	5.36/4.22
K_2O	1.23/1.56	1.34/1.28	1.49/0.96
Fe_2O_3[a]	0.66/0.80	2.24/2.10	4.44/4.45
TiO_2	0.16/0.18	0.54/0.51	1.07/1.05

[a] Fe total (Fe_2O_3 + FeO) is expressed as Fe_2O_3.

The three binary batches were obtained by dry-mixing the grounded raw materials, packing them in refractory crucibles and placing them into a high-temperature electric furnace reaching a maximum temperature of about 1500°C (thermal cycles of 5 h). Since the objective was to produce bulk and sintered glass-ceramics, two batches were made for each composition. In the first case the amorphous material was rapidly extracted from the furnace, cooled down to room temperature in a graphite mould in air, annealed at a temperature between 580 and 660°C (chosen for each composition at about 10°C degree over the DTA glass transition temperature) for 1 h, then cut by a diamond saw blade in identical pieces suitable for thermomechanical characterization and devitrification studies. In the second case, for what concerns batch that would eventually be used for sintering studies, the glasses quenched in water were dry-milled in an agate ball mill for 4 h to obtain an average particle size < 38 μm. The grounded powder was subsequently humidified at 6 wt% with distilled

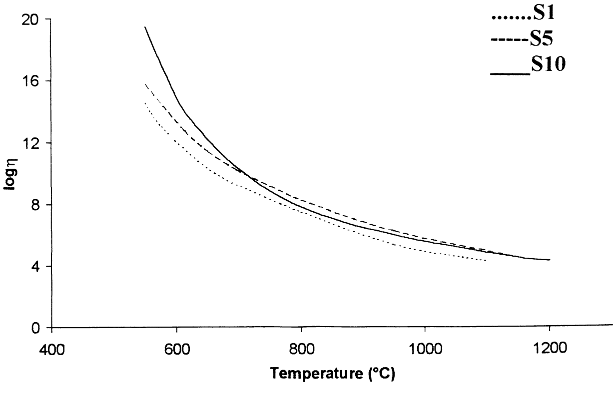

Fig. 1. Relative viscosity variation with temperature of S1, S5 and S10 glasses.

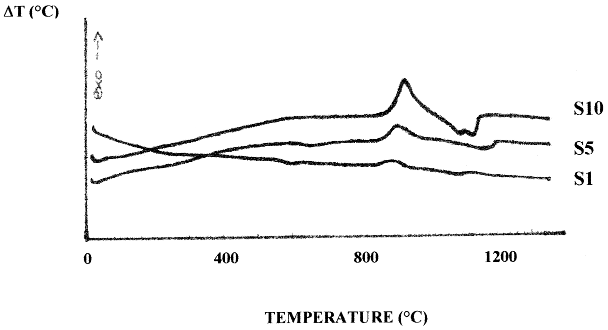

Fig. 2. DTA curves of the glasses prepared.

water and at 1 wt% with a 5 wt% polyvinil alcohol (PVA) water solution to verify the effect connected to the binder used. Cylindrical specimens (1.3×0.5 cm) were prepared by cold uniaxial pressing (20 MPa) and subsequent drying in an electric oven at 110°C for 2 h. Finally, the samples were subjected to the following firing tests to determine the correct experimental conditions which provide flat and highly sintered samples:

a. for samples prepared by using distilled water and in PVA solution:

$$20^\circ\mathrm{C} \underset{10^\circ\mathrm{C/min}}{\rightarrow} T_{\max} \overset{20\ \mathrm{min}}{\rightarrow} T_{\max}$$

$$\rightarrow \text{natural cooling to room temperature}$$

b. for samples prepared by using PVA solution:

$$20^\circ\mathrm{C} \underset{10^\circ\mathrm{C/min}}{\rightarrow} 400^\circ\mathrm{C} \underset{5^\circ\mathrm{C/min}}{\rightarrow} 600^\circ\mathrm{C} \underset{10^\circ\mathrm{C/min}}{\rightarrow} T_{\max} \overset{20\ \mathrm{min}}{\rightarrow} T_{\max}$$

$$\rightarrow \text{natural cooling to room temperature}$$

Six maximum temperatures for all the three compositions (750–800–850–900–950–1000°C), $T_{\max}$, were chosen around the crystallization peak as detected by DTA measurements.

As far as the experimental characterization of the obtained materials is concerned, the transformation temperatures were determined on the glassy powders (< 38 μm in size) by a Netzsch DSC 404 from 20 to 1400°C at the heating rate of 10°C/min and on bar-shaped specimens of 4×0.5×0.5 cm heated from 20°C to the softening point at the same heating rate of the DTA by a dilatometer Netzsch 402 EP. The mineralogical analysis was performed on both bulk glass-ceramics obtained by heating identical pieces of 1×1×0.5 cm with different devitrification thermal treatments (characteristic for each composition) and on sintered samples. Patterns were collected using a powder diffractometer (Philips PW 3710) with Ni-filtered CuK_α radiation on powders of approx. 30 μm particle size in the 2θ = 5–60° range. Optical heating microscopy (Misura 2.0 Microscope) was used on pressed glassy powders by recording the images of the profile of the compact at regular temperature intervals of 10°C from sintering to melting. On the sintered samples linear shrinkage, water absorption and density in water by the Archimedes method were determined. Finally, both on bulk and sintered glass-ceramics, microstructural and porosity observations were performed by scanning electron microscopy (SEM) (Philips XL 40) on the polished surface of samples coated with a thin Au/Pd film.

3. Results and discussion

All the formulated compositions resulted completely amorphous after quenching, pointing out the vitrification capability of the municipal bottom ash (S10 composition) with different viscosity, depending on the

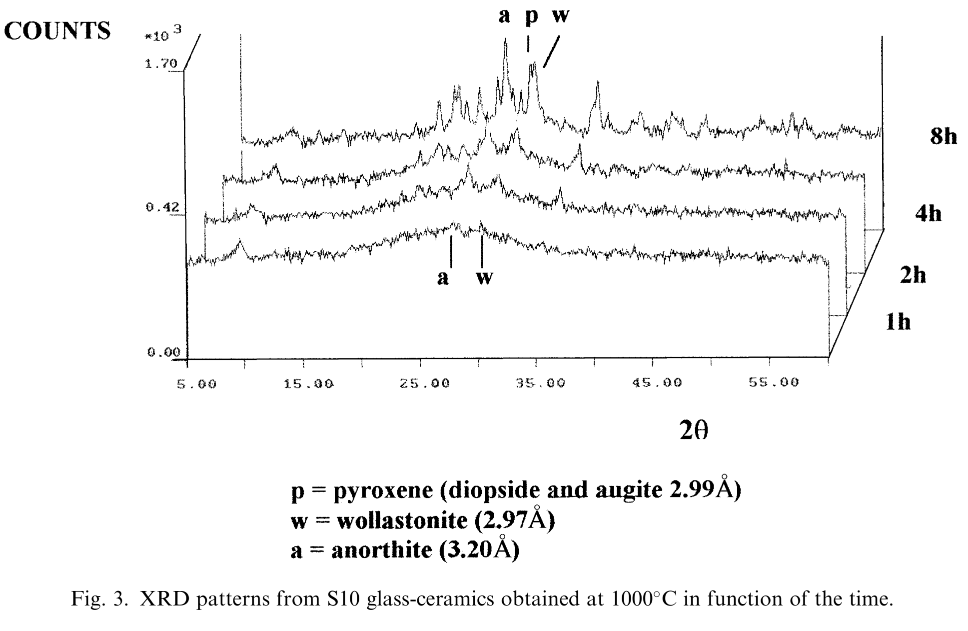

Fig. 3. XRD patterns from S10 glass-ceramics obtained at 1000°C in function of the time.

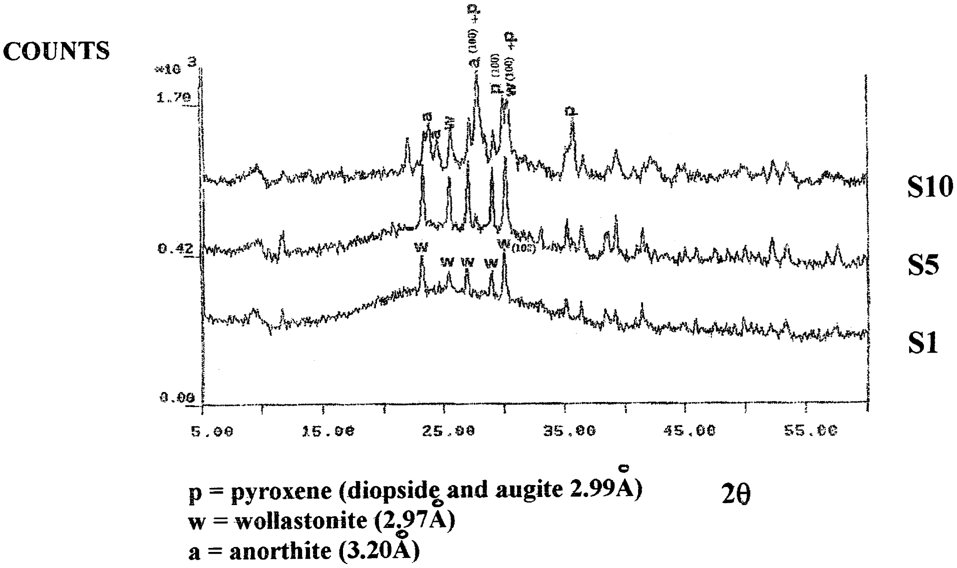

Fig. 4. Comparison between the XRD patterns recorded on the glassy compositions studied obtained at 1000°C for 8 h.

composition. The curves of Fig. 1, obtained by evaluationing dilatometric and optical heating microscopy data, show that the higher Al_2O_3 content of the S5 composition with respect to the S1 results in an increase in viscosity. The S10 formulation shows the typical trend of glasses with a high alkaline-earth rather than alkaline oxide content. This causes an increase and a decrease in viscosity at lower and higher temperature, respectively.

A first idea of the crystallisation tendency was inferred from the DTA experiments. By comparing the thermograms of Fig. 2 it appears evident that the exothermic crystallisation peak in the 840–960°C range becomes sharper and sharper by increasing the bottom ash amount. Glass transition interval and crystallization temperature increase with increasing the CaO, Al_2O_3 and Fe_2O_3 content with respect to the alkaline oxides.

The XRD analysis of the bulk treated samples revealed different tendency towards crystallization as a function of both the thermal treatment and the composition, as shown in the following figures. In the same composition, thermal treatments at a particular temperature but for different times point out the different steps of crystallisation (Fig. 3). Furthermore, for the same thermal treatment (both for what concerns temperature and time) the crystallized fraction volume increases by increasing the amount of bottom ash (Fig. 4), that is the CaO and Fe_2O_3 content. The crystalline phases present in the glass-ceramics correspond to wollastonite ($CaSiO_3$) in each one of the three systems together with crystals of the pyroxene group [diopside/augite, Ca(Mg, Fe, Al)(Si, Al)$_2$O$_6$] starting from S5

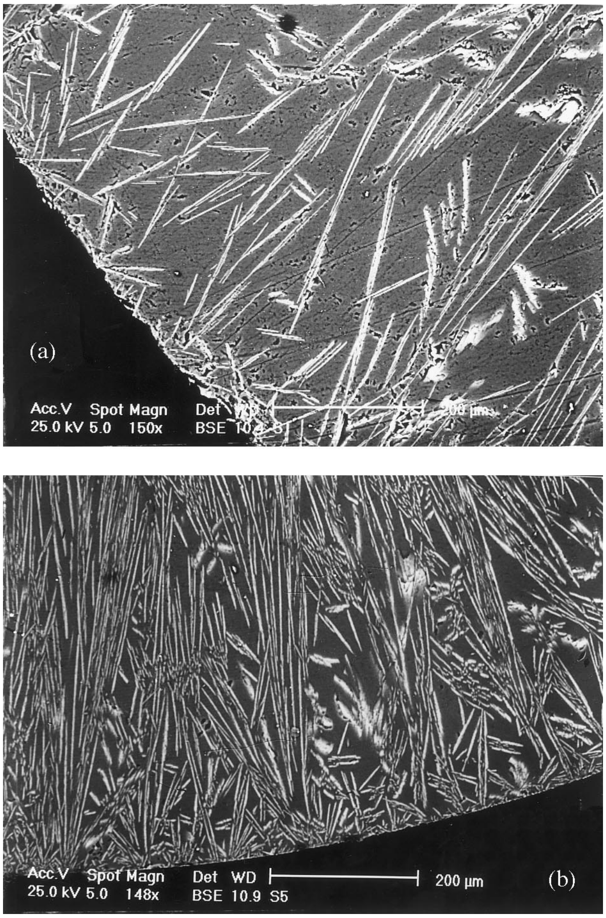

Fig. 5. SEM micrograph (60x) of (a) S1 and (b) S5 glass-ceramics heat-treated at 1000°C/8 h showing surface devitrification mechanism.

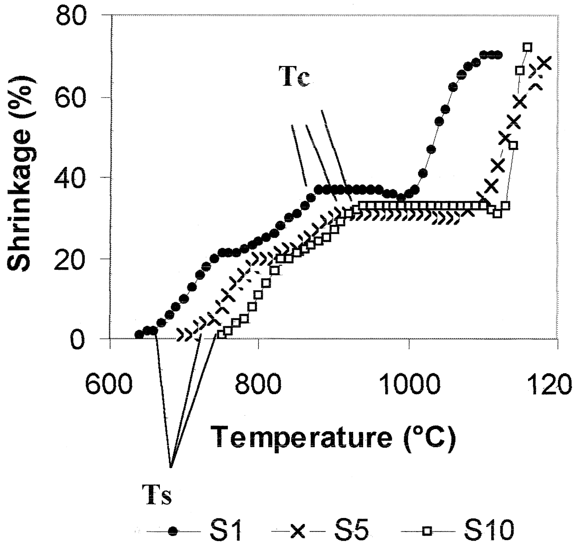

Fig. 6. Profile of the linear shrinkage of the S1, S5 and S10 compositions.

especially for long thermal treatments and anorthite with some sodium substitution [$(Ca,Na)(Si,Al)_4O_8$] in the S10.

These XRD data were confirmed by SEM analysis that showed a surface crystallization mechanism with the formation of acicular and dendritic crystals of wollastonite and pyroxene, respectively, homogeneously dispersed into the glassy matrix and in increasing amount passing from the S1 to the S10 composition (Fig. 5).

Table 3
Porosity values of the series of the glasses studied treated at 950°C as a function of the humidification conditions

Composition	Porosity$_{H_2O}$%	Porosity$_{PVA}$%	ΔP
S1	8	9	1
S5	14	26	12
S10	9	30	21

The results obtained by hot stage microscopy are very interesting. The profile of the linear shrinkage of the three compositions in Fig. 6 is characteristic of a semicristalline material, where the plateau between 900 and 1100°C corresponds to the devitrification process during which shrinkage mantains a constant value, and at higher temperatures the sample does not mantain its shape any more. The length of the plateau increases from S1 to S10 and the sintering, T_s, and crystallisation, T_c, temperatures shift towards higher values. Furthermore, the fact that sintering occurs before crystallisation is of a significant importance from a technological point of view, for example to obtain monolithic glass-ceramic materials by powder sintering.

To study sintering, density, linear shrinkage and water absorption are monitored because these parameters are related to the sintered bodies properties. Among all the glasses examined in the thermal range considered (750–1000°C), the S10 composition is the most stable, i.e. the most adequate for producing a good final material by sintering, because S5 swells between 950 and 1000°C (rapid increase of the porosity with a corresponding expansion of the sample) while S1 softens

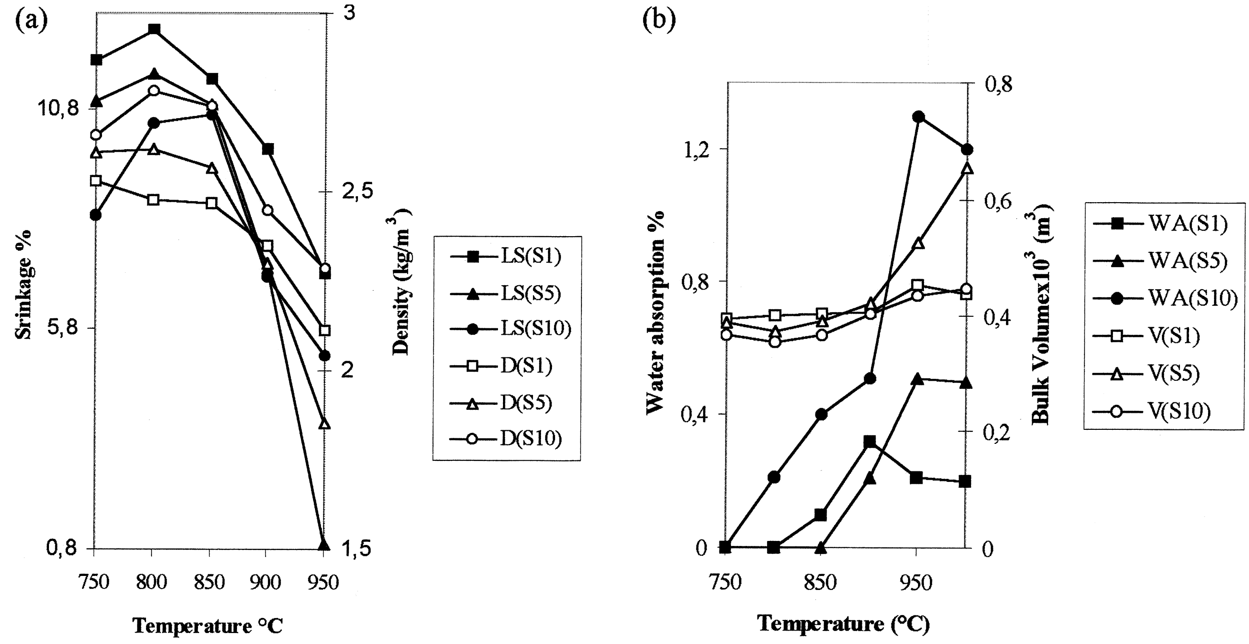

Fig. 7. Trend of (a) linear shrinkage (LS) and bulk density (D), (b) water absorption (WA) and bulk volume (V) of the sintered materials studied as a function of the temperature.

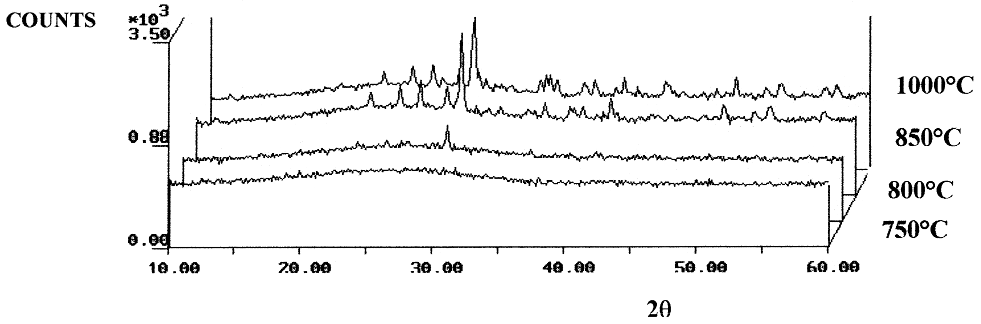

Fig. 8. XRD patterns of S5 sintered glass-ceramic as a function of the temperature.

around 1000°C (decrease of the porosity since the 90 wt% of glass cullet present causes the formation of amorphous liquid phase). As for the humidification conditions, no difference was found between the samples prepared with PVA but subjected to the two different firing cycles. On the contrary, the humidification with water only reduces the porosity formation as shown in Table 3 where data were obtained by images elaboration of SEM micrographs. Other observations can be drawn from the same table: (a) porosity becomes higher and higher with increasing the bottom ash content because the formation of crystalline phases at the expense of the amorphous phase increases and for this reason the porosity difference between the samples humidified with PVA and H_2O also increases; (b) the apparent anomaly for the S5 sample without organic binder is due to the swelling of the sample at this temperature.

Since the trend of the studied properties in the sintered materials is similar both in water and in PVA solution, and the only effect of the organic reagent is to magnify the variation (Δlinear shrinkage PVA > Δlinear shrinkage H_2O; $\Delta\rho$PVA > $\Delta\rho H_2O$) because of degassing reactions, from now on only the results for samples humidified with H_2O are reported. A quantitative determination of the sintering degree was expressed by considering linear shrinkage, bulk density, water absorption and bulk volume (data obtained by the ratio of the weight of the sample in water and the water density) for each composition as a function of temperature. From Fig. 7, it appears evident that the maximum densification of the waste-containing material is achieved in the 800–850°C range because the highest shrinkage and density, and the lowest volume and water absorption values, respectively, correspond to this temperature range. This is due to the amorphous material viscous flow (bulk transport mechanism) that causes the coalescence of the particles and both the rate and the intensity of this effect depend on the material viscosity and the liquid volume formed.[10] Furthermore, because the maximum densification range of temperature (800–850°C) is near to the DTA onset of the crystallisation peak and from the XRD data of the sintered samples it was observed that, for each composition, the maximum crystallisation degree is achieved at about 850°C while at 800°C the amorphous phase is the prevalent one (Fig. 8), it is possible to think that the sintering process at this temperature is for the most part completed.

As regards the mineralogical analysis, it was observed that there are no differences in the crystalline phases identification between the glass-ceramics obtained by the two preparation techniques, except for the S10 sintered sample, in which the anorthitic phase did not appear because it needs longer thermal treatments. However, the sintering favours the devitrification process because all the samples show the maximum crystallization degree possible for each composition already at about 850°C, while for the corresponding bulk glass-ceramics thermal treatments at least at 1000°C are necessary in order to obtain the same devitrification degree.

4. Conclusions

The investigated municipal incinerator bottom ash has a good vitrification and devitrification capability, also without using other kinds of materials capable to help these processes. This is of a significant importance for the disposal and the valorisation of the municipal bottom ash, which is not a dangerous waste to be inertised, but whose volume is higher than that of dangerous special municipal fly ash and costantly growing. Therefore, its employment in small percentages is less interesting for the technological and economical point of view. All the compositions investigated are devitrifiable by both bulk and sintering, with a reduction of the time and temperature of the thermal treatment for the last technique, and develop the same crystalline phases typical of the conventional glass-ceramic products (wollastonite, diopside/augite) by a surface nucleation mechanism. For this last reason, all the compositions are easily sinterable in dense products at a relatively low temperature (about 850°C). Moreover, the employment of no organic binder represents a further economical advantage.

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