

# Sintered glass-ceramics from incinerator fly ashes. Part II. The influence of the particle size and heat-treatment on the properties

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## Abstract

A composition obtained by mixing MSW ashes with sand and glass cullet was melted at 1500 °C and quenched in water. The obtained frit was sieved and separated in different fractions: L (large, 2–5 mm), I (intermediate, 1–2 mm) and S (small, <1 mm). The sintering of the glass particles, carried out in an alumina mould, occurred in the 700–950 °C range. The curve of the crystal growth rate as a function of the temperature was obtained by means of 1 h heat-treatment in the 850–1050 °C range. The crystal growth started at 850 °C and the maximum rate, 0.013 mm/min, occurred at 1020 °C. The ferrobustamite crystal phase was evaluated by XRD analysis and observed by optical microscopy. The mechanical, thermal and chemical properties of the L, I and S glass-ceramics were measured and discussed. They resulted to be influenced by the grain size of the glass particles and by the percentage of crystal phase.

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## 1. Introduction

The sinter-crystallisation of glass frit is a process based on a combined sintering of the glass particles and crystal phase formation induced by the thermal treatment. Glass-ceramics acquire exceptional properties and, after grinding and polishing, their appearance might imitate the structure of natural stones.<sup>1–5</sup>

If the parent glass shows a high crystallisation rate, the sintering process may be inhibited by the crystalline phase, mainly formed on the grain surface; a porous material is obtained with poor mechanical and chemical properties.<sup>6</sup> In the first part of this study<sup>7</sup> it was highlighted that, in glasses containing high percentages of municipal solid waste ashes (MSWA), the sintering was inhibited due to the formation of large amounts of gehlenite ( $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ). Non-porous glass-ceramics were obtained if less than 15 wt.% crystal phase was formed before sintering; i.e. at a high heating rate

(20–30 °C/min) and at a holding step near the liquidus temperature. At a low heating rate (2 °C/min), surface and bulk crystallisation takes place with up to 50% crystal phase formation so that a consistent porosity is attained by the sintered glass-ceramics.

In the present work, a new composition (G-60) containing 60% of MSWA, glass cullet and sand is investigated. Compared to G-70 glass (70% MSWA) discussed in the first part,<sup>7</sup> in order to decrease the crystallisation rate and improve the chemical durability, the new composition contains lower percentages of  $\text{Al}_2\text{O}_3$  and CaO and higher percentages of  $\text{SiO}_2$ . The mechanical, thermal and chemical properties of the glass-ceramic were measured and discussed as function of the thermal treatment regime, the size of the glass frit and the percentage of crystal phase formed.

## 2. Experimental

A glass made of 60 parts dried incinerator fly ashes (MSWA), 25 parts of glass cullet, 25 parts of quartz sand and 4 parts of  $\text{H}_3\text{BO}_3$  was prepared. The composition, labelled G-60, is reported in Table 1, together

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Table 1  
Chemical compositions of the used wastes and G-60 glass (wt.%)

	MSWA	Glass cullet	G-60
SiO <sub>2</sub>	24.42	72.53	57.92
TiO <sub>2</sub>	1.91	0.18	1.10
Al <sub>2</sub> O <sub>3</sub>	11.52	0.53	6.93
Cr <sub>2</sub> O <sub>3</sub>	0.10	–	0.06
Fe <sub>2</sub> O <sub>3</sub>	2.35	0.12	1.65
CaO	30.0	8.72	20.08
MgO	4.21	3.94	3.53
BaO	0.14	–	0.11
ZnO	1.42	–	0.79
PbO	0.14	–	0.07
CuO	0.05	–	0.03
CdO	0.015	–	0.01
NiO	0.01	–	0.01
Na <sub>2</sub> O	2.12	13.54	5.24
K <sub>2</sub> O	0.62	0.23	0.39
SO <sub>3</sub>	2.31	–	–
P <sub>2</sub> O <sub>5</sub>	1.48	–	–
L.O.I	17.12	–	–

with the composition of the utilised MSWA and glass cullet.

The melting of G-60 glass was carried out in a gas furnace utilising 1 litre Al<sub>2</sub>O<sub>3</sub> crucibles. The batch was heat-treated at 1500 °C for 4 h and then the melt was fritted (quenched in water). The frit was broken, sieved and separated in different fractions. In the present work three fractions were used: from 2 to 5 mm, labelled as L (large); from 1 to 2 mm, labelled as I (intermediate); and < 1 mm, labelled as S (small), respectively. A part of the melt was quenched in a steel mould, annealed and cut in specimens with a 3×3×2 cm<sup>3</sup> size. These samples were heat-treated for 1 h at different temperatures in the 850–1150 °C range, annealed, cut, polished and observed using optical microscopy. The result was used to plot the curve of the crystal growth rate as function of the temperature. Crystallisation was investigated by DTA technique, (Netzsch STA 409 apparatus), using 100 mg bulk and powder glass samples at a heating rate of 10 °C/min. The crystalline phase formed was deter-

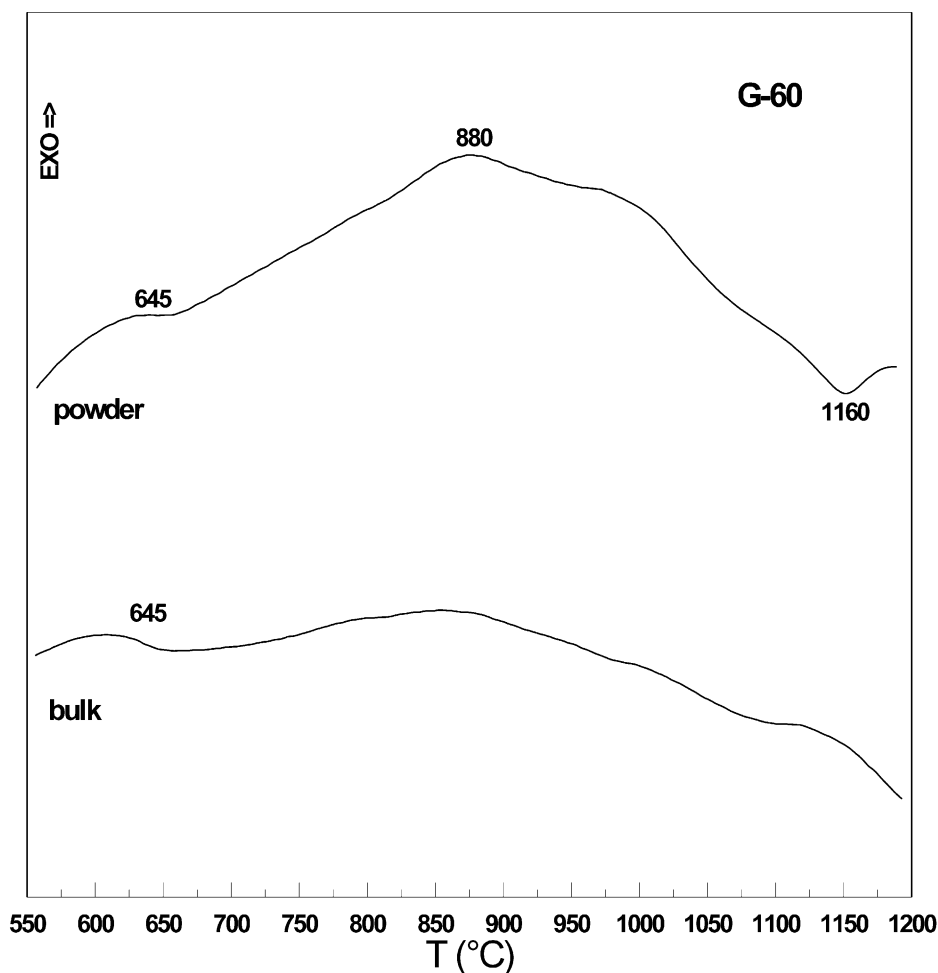


Fig. 1. DTA traces of G-60 bulk and powder glass samples.

mined by XRD technique (Philips PW1830 apparatus and  $\text{CuK}_\alpha$  radiation). The percentages of crystal phase in the glass-ceramics were obtained by comparing the area of amorphous and crystalline phases in the XRD spectrum.<sup>8,9</sup>

Frit, placed in  $\text{Al}_2\text{O}_3$  moulds, was heat-treated at different temperatures in the 700–1000 °C range for 10–20 min and the degree of sintering was observed by optical microscopy. The sinter-crystallised samples were obtained after heating the glass fractions L, I and S at 10°/min to the temperature of maximum crystal growth (1020 °C), 1 h holding and cooling at 5 °C/min. The samples were polished and the crystal growth and texture observed by optical microscopy. The L samples were also obtained at heating and cooling rates of 15 °C/min and with a holding step of 20 min at 1020 °C.

The mechanical, thermal and chemical properties of the L, I and S glass-ceramics were measured. The density of the parent glass and glass-ceramics was evaluated by He displacement Pycnometer (AccyPyc 1330). The compressive strength was determined by using 10/10/10 mm<sup>3</sup> samples and compression rate of 0.5 mm/min. The bending strength was determined by a three point bending test with 40 mm outer span and a speed of 0.1 mm/min (SINTEC D/10). The Young modulus was determined by means of the non-destructive resonance frequency technique (Grindosonic). In all these experiments, a series of five samples were used. The Vickers

hardness (at 10 kg loading) was estimated by using a WOLPERT apparatus. The thermal expansion coefficient was evaluated in the 20–300 °C temperature interval by a Differential Dilatometer (Netzsch 402 ED) at 5 °C/min. The chemical durability (as wt.% loss) was estimated in 0.01 N HCl and 0.01 N NaOH, respectively.<sup>10</sup> In these experiments 2 g grained samples with sizes from 0.4 to 0.5 mm were placed in contact with 70 ml solution for 1 h at 95 °C.

### 3. Results and discussion

#### 3.1. Sinter-crystallisation

The DTA traces of G-60 powder and bulk glass samples are shown in Fig. 1. The  $T_g$  temperature at 645 °C is well-distinguished in both samples while the crystallisation exo-effect and the melting endo-effect are evident only in the powder sample where the crystallisation peak occurs at 880 °C and the melting at 1160 °C, respectively. The DTA trace indicates that the crystallisation process is not very intensive and takes place mainly on the grain surface. The curve of the crystal growth rate as function of the temperature is shown in Fig. 2. The crystallisation starts at relatively low temperatures, 850–900 °C with a dense formation of needle-like crystals, growing perpendicularly from the surface. The maximum rate occurs in the 1000–1050 °C interval with a maximum of 0.013 mm/min at 1020 °C, i.e. 140 °C below the liquidus temperature. Fig. 3 shows the optical microscopy picture of polished section, thermal treated by 1 h at 1015 °C.

The sintering started at 700 °C but a non-porous sample with a smooth surface was attained at 950 °C. At this temperature, however, the crystal growth rate is very slow, 0.0023 mm/min, and, in order to obtain a crystal length of 1 mm about 7 h are required. By a 10 °C/min heating rate and 1 h step at 1020 °C a crystal length of about 0.95 mm is obtained; i.e. this heat-

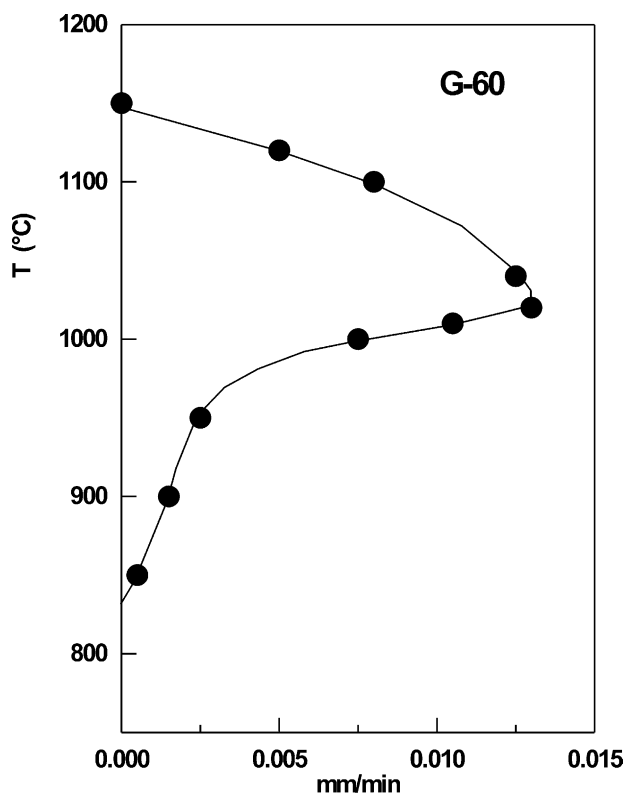


Fig. 2. Curve of crystal growth rate as a function of temperature.

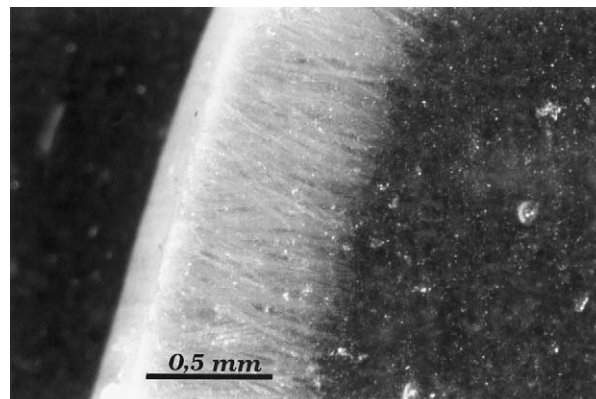


Fig. 3. Image of crystal growth after 1 h at 1015 °C.

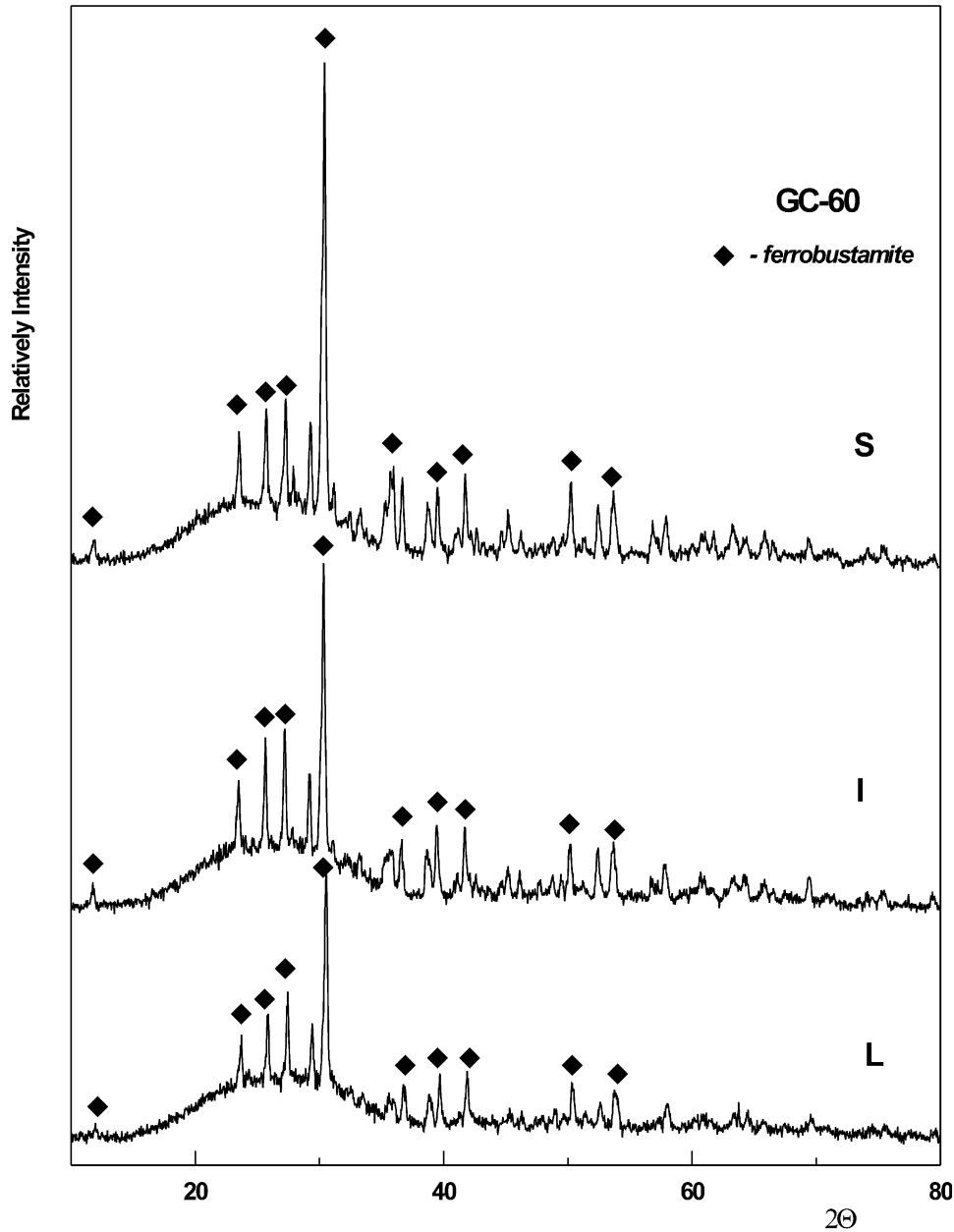


Fig. 4. XRD spectra of L, I and S glass-ceramics after 1 h heat-treatment at 1020 °C.

treatment regime insures complete crystallisation of glass particles up to 2–2.5 mm size.

Fig. 4 reports the XRD spectra of the L, I and S samples, obtained after 1 h heat-treatment at 1020 °C. The analysis highlighted the formation of only one crystal phase identified as ferrobustamite ( $\text{CaO}_{1-x}\cdot\text{FeO}_x\cdot\text{SiO}_2$ ),<sup>10</sup> in amounts of  $22\pm 3$ ,  $33\pm 3$  and  $39\pm 3\%$  for L, I and S samples, respectively. This phase has a pyroxenoid triclinic structure, very similar to that of  $\beta$ -wollastonite ( $\text{CaO}\cdot\text{SiO}_2$ ).<sup>11</sup>

The final appearance is influenced by the size of the glass fraction used and the length of the crystals formed during the thermal treatment: the glass-ceramics have the grained structure of granite. Fig. 5 shows the

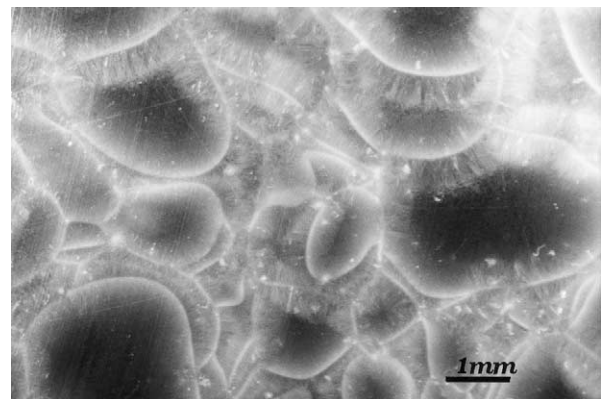


Fig. 5. Microscopic photos of the L glass-ceramics grain structure.

polished surface of the L sintered sample, obtained at 10 °C/min heating rate, followed by 1 h at 1020 °C. The picture highlights the texture of the sintered glass-ceramics with needle-like crystals growing from the surface towards the centre of the grains and the absence of residual porosity. If a higher heating rate and a shorter holding time are used, the crystal length is shorter and a semi-transparent appearance is obtained.

Fig. 6 shows samples of polished glass-ceramics. In sample 6-a L, I and S fractions were mixed together, in samples 6-b and 6-c the L fraction was sintered at 10 °C/min for 60 min and at 15 °C/min for 20 min,

respectively, while in sample 6-d the I fraction was used. When the S fraction was sintered, the grains are not distinguishable and the sample appearance is homogeneous and not attractive.

### 3.2. Properties of the glass-ceramics

The mechanical, thermal and chemical properties of the L, I and S glass-ceramics are summarised in Table 2. The same properties for marble and granite are reported for the sake of comparison.<sup>1,2</sup>

Table 2  
Properties of the obtained sintered glass-ceramics (GC), granites (G) and marbles (M)<sup>12</sup>

Properties	GC (S)	GC (I)	GC (L)	G	M
Density (g/cm <sup>3</sup> )	2.611±0.012	2.652±0.003	2.651±0.004	2.6–2.8	2.6–2.8
Compression strength (MPa)	220±70	300±80	360±100	60–300	90–230
Bending strength (MPa)	69±8	58±4	48±13	12–15	14–17
Modulus of Elasticity (GPa)	85±1.5	84±2.5	85.5±2	43–61	28–84
Vickers hardness (MPa)	5572±10	5876±30	5670±20	–	–
Mooh's hardness	6.0	6.0	6.0	4–6.5	3–5
Thermal expansion (×10 <sup>-7</sup> deg <sup>-1</sup> )	68.1	79.0	88.1	70–150	70–150
Chemical resistance (% loss) in 0.01 N HCl			1.1±0.2	2.2–4.2	>5
in 0.01 N NaOH			1.0±0.2	2.4–3.6	>5

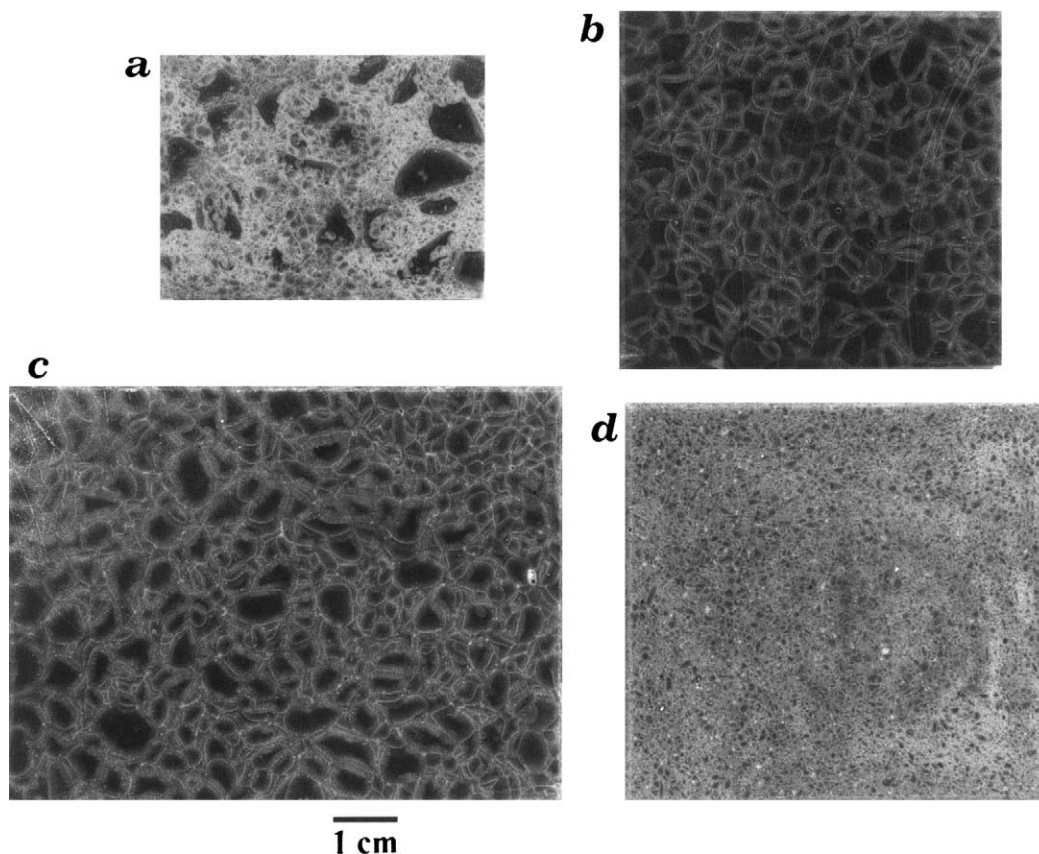


Fig. 6. Appearance of the sintered glass-ceramics obtained by different thermal treatment and particle size (see text).

The densities of the I and L samples are similar to that of the parent glass ( $2.648 \pm 0.004 \text{ g/cm}^3$ ), while the S sample shows a lower value. In wollastonite forming glasses, the density change due to crystallisation is negligible,<sup>13,14</sup> therefore in G-60 glass-ceramics the variation of this property may be used as an indication of the degree of sintering. It was inferred that no porosity is retained in the L and I samples while in the S samples a 2% closed porosity is attained. After polishing and lapping the surface of the S sample, the presence of pores was confirmed by microscopic observations.

This might explain the decreasing trend of the compression strength together with the decreasing of the particle size in S glass-ceramics. The bending strength showed the opposite behaviour, i.e. the strength increased by decreasing the fraction size. This result may be related to the higher percentage of crystal phase formed in the S sample and to the shorter size of the crystals compared to L glass-ceramics. In this later sample, the retained glassy phase in the centre of the bigger particles might introduce a source of weakness in the bending strength since it can act as a preferential path for the fracture. In fact, when the fracture passed through glassy phase, the minimum value of 35 MPa was measured.

The thermal expansion coefficient shows large differences among the investigated samples: the L ( $88.1 \times 10^{-7} \text{ deg}^{-1}$ ) is similar to the parent glass ( $86.2 \times 10^{-7} \text{ deg}^{-1}$ ) while the S ( $68.1 \times 10^{-7} \text{ deg}^{-1}$ ) is considerably lower. In order to highlight the relation between thermal expansion coefficient and preferred orientation of the crystals, the following experiment was carried out. A bulk glass with 40/5/5 mm<sup>3</sup> size was heat-treated for 1 h at 1020 °C. A ferrobustamite crystalline formation was grown perpendicularly from the surface to the centre of the specimen. Two samples were obtained and, after polishing, the thermal expansion coefficient was measured in the direction parallel and perpendicular to the crystal growth. A value of  $79.6 \times 10^{-7} \text{ C}^{-1}$  and  $68.4 \times 10^{-7} \text{ C}^{-1}$  were obtained for the parallel and perpendicular directions, respectively. It was concluded that the orientation and length of the silicate chains formed during the crystallisation as well as the degree of crystallisation might have a significant influence on the thermal expansion coefficient. Considering, the grain size of the glass as an additional variable, no clear explanation about the thermal expansion coefficient behaviour can be proposed for these sintered glass ceramics. A similar anomaly was reported by other authors on anorthite sintered glass-ceramics.<sup>15</sup>

Compared to G-70 glass, investigated in the previous study,<sup>7</sup> G-60 composition contains a lower percentage of MSWA (60% instead of 70) and a higher percentage of glass-formers, therefore, the chemical durability is expected to be improved. For G-60 parent glass, L, I and S glass-ceramics the DIN procedure for commercial

glasses was employed. The results, reported in Table 2, show that the chemical resistance of parent glass, L, I and S glass-ceramics is similar for both acid and basic solutions, i.e. the chemical resistance of the parent glass, crystalline phase and residual glassy phase are comparable and are not influenced by the percentage of crystal phase.

The resulting values demonstrated that the overall properties of the G-60 composition are comparable with the glass-ceramic obtained by sinter-crystallisation of natural raw materials glass frits<sup>3,4</sup> and are consistently higher than marble and granite.

#### 4. Conclusions

The investigated G-60 glass composition, obtained by mixing MSWA, glass cullet and sand showed low crystallisation rate and resulted in being suitable in order to obtain nonporous sintered glass-ceramics by glass frits at 900–950 °C. The maximum rate of crystal growth occurred at 1020 °C and yielded a 35% ferrobustamite crystalline phase. The thermal and mechanical properties were affected by the grain size of the glass frit and the sinter-crystallisation behaviour but no consistent correlation could be drawn on the basis of the experimental results.

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