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Journal of the European Ceramic Society 29 (2009) 2921–2927

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Sintered esseneite–wollastonite–plagioclase glass–ceramics from vitrified waste

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Received 11 February 2009; received in revised form 28 April 2009; accepted 13 May 2009
Available online 11 June 2009

Abstract

Dense sintered esseneite–wollastonite–plagioclase glass–ceramics have been successfully prepared from a vitrified mixture of important inorganic waste (Bayer process red mud, fly ash from lignite combustion and residues from the polishing of porcelain stoneware tiles). The enhanced nucleation activity of fine glass powders, favoured by particular oxidation conditions, caused a substantial crystallisation, even in the case of very rapid thermal treatments at 900 °C, which led to remarkable mechanical properties (bending strength and Vickers micro-hardness exceeding 130 MPa and 7 GPa, respectively) and a promising chemical durability.

Keywords: Sintering; Mechanical properties; Glass–ceramics; Structural applications

1. Introduction

Glass–ceramics manufacturing has been considered as a very effective method for recycling and utilising many types of industrial waste since the early 1960s.[1] The key technological point is the preliminary dissolution of waste into glasses, which allows the practically permanent stabilisation of pollutants, whereas the main applications are in the building industry (as floor and roof tiles or road surfacing panels). The first applications of this approach correspond to the glass–ceramic tiles from glasses of the $CaO–Al_2O_3–SiO_2$ system, derived from several slag of ferrous and non-ferrous metallurgy, ashes and waste from mining and chemical industries,[2,3] known as "Slagsitall"[4] and "Slagceram"[5] glass–ceramics.

Although glass–ceramics manufacturing from inorganic waste is quite well established, some improvements in the overall processing are currently under investigation. In particular, the conventional processing of glass–ceramics is based on long nucleation and crystal growth thermal treatments, performed on almost defect free glass articles, shaped as the final product. An alternative approach has been focused on the sintering route, introduced in Japan for the marble-like "Neoparies" glass–ceramics in 1970s.[6] The processing is based on the viscous flow sintering of glass frits, with concurrent crystallisation, also known as "sinter-crystallisation".[7–10]

For sintered glass–ceramics the parent glass is used in powder form. This limits the need for an expensive refining after vitrification, aimed at removing defects, like gas bubbles. This feature is particularly interesting for the treatment of waste glasses,[11–22] for which the refinement is not easy (waste glasses are usually dark, so that the heat transfer via radiation is quite difficult)[1] nor recommended (a long treatment at high temperatures is very expensive and may promote the volatilisation of poisonous oxides, like PbO). The crystallisation process, owing to a surface mechanism of nucleation, is active even without nucleating agents such as TiO_2, Cr_2O_3, etc., in the glass formulation. When using fine glass powders further advantages are possible: (i) glass–ceramic tiles could be shaped by simple uniaxial pressing, (ii) the green density can be optimised by a controlled particle size distribution and (iii) the high specific surface of fine powders enhances the surface nucleation, so that glass–ceramics with not frequently encountered crystal phases, like alkali feldspars and feldspathoids,[17–19] or processed with very rapid heating,[21,22] have been successfully prepared.

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doi:10.1016/j.jeurceramsoc.2009.05.017

In the present paper we discuss the feasibility of ternary sintered glass–ceramics, featuring esseneite ($CaFe^{3+}AlSiO_6$), wollastonite and plagioclases (Ca-, Na-, feldspars) as the main crystal phases, from a glass frit obtained by melting a mixture of important inorganic waste materials (Bayer process bauxite residue, i.e. "red mud", fly ash from lignite combustion, residues from the polishing of porcelain stoneware tiles), subjected to both conventional and rapid thermal treatments. Due to the achieved mechanical properties and the very simple and cost effective manufacturing process, the investigated glass–ceramics are promising for applications as construction materials.

2. Experimental procedure

The investigated waste materials consisted of Bayer process bauxite residues, called "red mud", obtained from Aluminium of Greece, labelled as RM, fly ash from lignite combustion, labelled as FA, obtained from the Public Power Industry of Greece in Megalopolis plant, and residues from the industrial polishing of porcelain stoneware tiles, labelled as PR, coming from a landfill site in Emilia–Romagna in Italy. Their chemical compositions are reported in Table 1. The industrial wastes were mixed with reagent grade $CaCO_3$ (Sigma–Aldrich, Gillingham, UK) in the weight proportion RM/FA/PR/$CaCO_3$ = 10/29/40/21. The mixture was converted into a glass at 1400 °C for 2 h. After quenching, by pouring on cold steel plates, the resulting glass broke in a number of fragments, subsequently dry ball milled and sized to two kinds of powders having a maximum dimension of 37 μm and 75 μm. The chemical composition of the glass, reported in Table 2, was determined by using an atomic emission spectroscopy (PerkinElmer ICP, OES Optima 3200 XL, NL). Dilatometric analysis (402E Netzsch Gerätebau GmbH, Selb, D) was performed on a glass rod, while differential thermal analysis (DTA/TGA, STA409, Netzsch Gerätebau GmbH, Selb, D), operated at 10 °C/min heating rate, was performed on both coarse and fine powders (with a maximum dimension of 75 μm or 37 μm respectively). Dilatometric and DTA plots are reported in Fig. 1.

The powder, having maximum dimension of 37 μm, was uniaxially pressed at 40 MPa (without any binder) in steel dies, obtaining both discs, with a diameter of about 31 mm, and rectangular tiles, with dimensions of about 40 mm × 30 mm × 3 mm.

Table 1
Chemical composition (wt.%) of the starting waste.

Oxide	RM	FA	PR
SiO_2	7.8	49.4	64.1
Al_2O_3	17.1	22.7	16.5
TiO_2	5.1	1.1	0.5
Fe_2O_3	44.1	7.4	0.5
CaO	11.7	8.9	1.4
MgO	0.6	1.6	4.6
K_2O	0.1	1.4	2.1
Na_2O	3.2	0.9	4.4
ZrO_2	0.0	0.0	1.1
Others	0.5	5.3	0.8
LOI	9.8	1.3	4.0

Table 2
Chemical composition of the glass from RM/FA/PR/$CaCO_3$ mixture.

Oxide	wt.%
SiO_2	46.06
Al_2O_3	15.29
TiO_2	1.32
Fe_2O_3	8.61
CaO	22.72
MgO	2.13
K_2O	1.08
Na_2O	2.53
ZrO_2	0.02
Others	0.24

The disk specimens were sintered by using two different heating cycles. Initially it was applied a "conventional" sintering at 900 °C (i.e. the crystallisation temperature, see Fig. 1), with soaking time of 0–3 h and heating rate of 10 °C/min. When 0 h soaking time was used, the samples were cooled down just at the reaching of the sintering temperature. Based on the results, "rapid" sintering was also investigated: pressed powders were directly inserted in the furnace at 900 °C, with a soaking time of 0.5–1 h. Both treatments led to dense samples having a brown colour. Natural convection inside the furnace was used for cooling in all cases.

Small beams of about 3 mm × 2 mm × 30 mm were cut from sintered rectangular tiles. The beams were carefully polished to a 6 μm finish and chamfered at the edges, by using abrasive papers and diamond paste. The Young's modulus was measured by means of non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, B). Four point bending tests (24 mm outer span, 8 mm inner span) were performed by using an Instron 1121 UTS (Instron, Danvers, MA), with a crosshead speed of 0.5 mm/min. Each data point represents the average of at least 10 individual tests. Selected polished samples were employed for Vickers indentation tests at low load, 5N, which yielded the micro-hardness, HV.

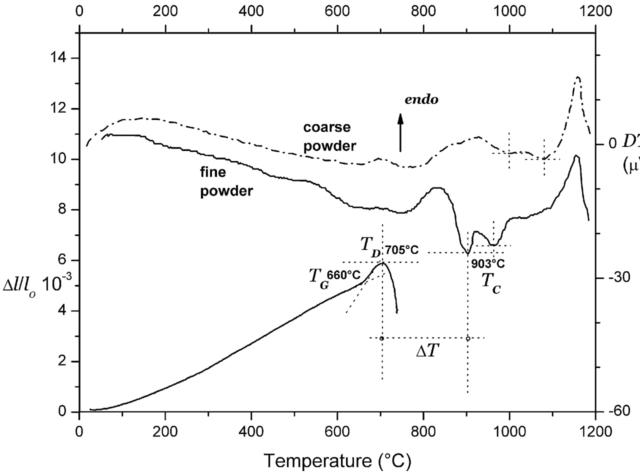

Fig. 1. Dilatometric and DTA plots of the investigated glass.

The bulk density of the sintered glass–ceramics was measured by the Archimedes' principle. At least ten specimens were analysed for each sample. The true density of the glass–ceramics was evaluated by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA) on powdered samples.

Polished samples were analysed by Scanning Electron Microscopy (Philips XL 30 ESEM, Eindhoven, NL). Powdered glass–ceramics were investigated by X-ray diffraction (Philips PW 3710, Eindhoven, NL), by using Cu Kα radiation (0.15418 nm). The diffraction patterns were analysed by means of the Match! program package (Crystal Impact GbR, Bonn, D), supported by data from the PDF-2 database (International Centre for Diffraction Data, ICDD, Newtown Square, PA). A semi-quantitative analysis was performed, on a selected sample, by means of the MAUD (Material Analysis Using Diffraction) program package,[23] supported by crystallographic data from the from ICSD (Inorganic Crystal Structure Database, v. 2005-1, Fachinformationszentrum Karlsruhe, D) database.

The samples, conventionally sintered for 2 h at 900 °C, were subjected to a preliminary chemical attack, following the standard for ceramic glazed tiles.[24]

3. Results and discussion

While the investigated waste materials have been considered individually in several applications,[25,26] the present study focuses on combining the wastes to obtain a glass suitable for the preparation of sintered glass–ceramics. The reference glass was that derived from the melting of sediments from the Venice Lagoon, belonging to the $CaO–MgO–Al_2O_3–SiO_2$ system.[15] Compared to the reference, the glass from the present wastes features slightly enhanced contents of Al_2O_3, from 13 to 15 wt.%, and Fe_2O_3, from 6 to 9 wt.%, and a substantial decrease of MgO, from about 6 to 2 wt.%, approximately. The relatively high content of Fe_2O_3 is mainly due to the presence of red mud, while the fly ash provided mainly SiO_2, Al_2O_3 and CaO. The polishing waste and $CaCO_3$ were employed to increase the content of silica and CaO, respectively. In practice, the new composition is slightly shifted towards the composition of natural basalt rocks, well known to possess a significant iron oxide content and good chemical durability: in fact, when melted and crystallised, the obtained basalt glass–ceramics are comparable to ordinary soda–lime–silica glass.[2]

Fig. 1 reveals that the glass, coming from the selected mixture of inorganic waste, is prone to surface nucleation: while fine powders exhibit two significant exothermic peaks in the DTA plots, at about 900 and 960 °C, coarse powders show two slight peaks, at about 1000 and 1080 °C. The temperature of the first exothermic peak, for fine powders, was taken as a reference for sinter-crystallisation treatments. It may be observed that this temperature is considerably higher than the dilatometric softening point, about 700 °C, also evidenced by Fig. 1. The difference between the two temperatures (ΔT), about 200 °C, can be seen as a promising aspect for obtaining dense glass–ceramics from the sintering of fine glass powders. In fact, several experiences in the literature[27–29] provide evidence that enhanced viscous flow sintering occurs at a temperature 50–100 °C higher than the dilatometric softening point, i.e. 750–800 °C for the present glass. If sintered at the crystallisation temperature, 900 °C, the glass was expected to have a good "sinterability". This was effectively confirmed by the relatively low total porosity, <6% (Table 3), comparable to that for porcelain stoneware tiles.[30]

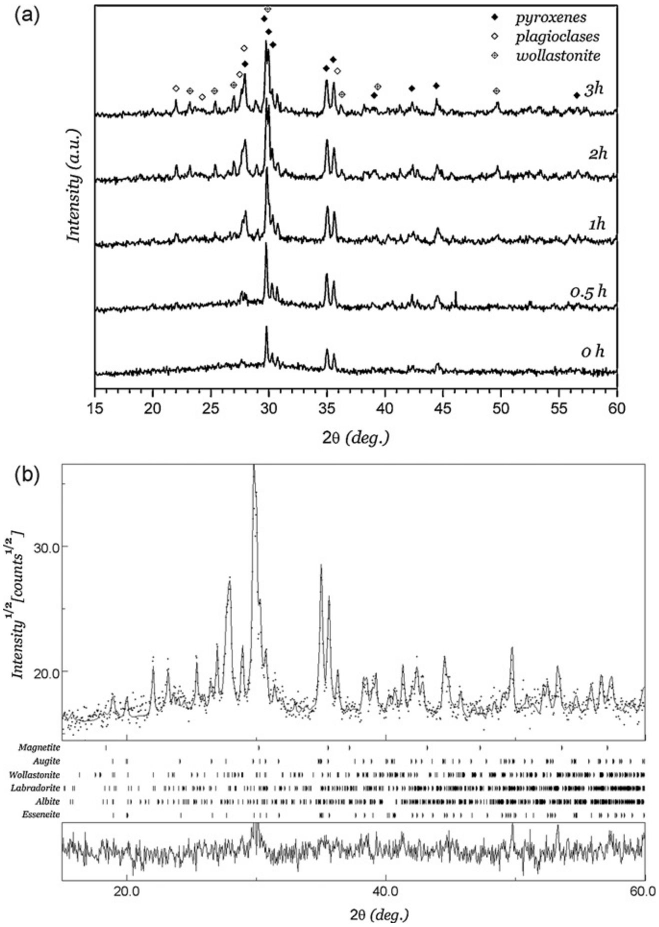

Fig. 2. (a) X-ray diffraction pattern showing phase evolution of glass–ceramics with increasing sintering time; (b) Rietveld refinement (provided by the Maud program package) of the X-ray diffraction pattern of a sample sintered for 2 h at 900 °C [dots: experimental points; continuous curve: refinement].

Fig. 2a shows that the sinter-crystallisation process was effective in yielding a remarkable crystallisation even for relatively short soaking times. Indeed, crystals are visible even in the sample with a 0 h holding time. The qualitative analysis of the X-ray diffraction pattern revealed that the crystal phases correspond to pyroxenes, i.e. esseneite ($CaFe^{3+}AlSiO_6$) and augite ($(Mg_{0.6}Fe^{3+}{}_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$), plagioclases, i.e. Ca–Na feldspars (labradorite, $Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$, and albite, $NaAlSi_3O_8$), and wollastonite (β-$CaSiO_3$). From the automatic phase identification provided by the Match! program package also magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) was detected, but it must be noted that its peaks overlap with those of pyroxenes.

The crystallisation sequence probably starts with pyroxenes, present even with a 0 h soaking time, and ends with wollastonite,

Table 3
Physical and mechanical properties of the investigated sintered glass–ceramics.

Sintering temperature (°C)	Soaking time (h)	Heating mode	Bulk density (g/cm^3)	Closed porosity (vol.%)	Elastic modulus (GPa)	Bending strength (MPa)	HV (GPa)
900	0.5	Conventional	2.82 ± 0.01	4.2	99.4 ± 1.2	89.6 ± 22.6	
900	1	Conventional	2.84 ± 0.02	4.9	99.9 ± 0.7	100.9 ± 14.4	
900	2	Conventional	2.84 ± 0.01	4.4	125.8 ± 4.6	132.6 ± 16.5	7.3 ± 0.3
900	0.5	Rapid	2.80 ± 0.02	5.6	97.2 ± 7.0	96.5 ± 15.7	
900	1	Rapid	2.82 ± 0.01	3.8	103.2 ± 6.9	102.9 ± 20.5	7.0 ± 0.3

present at increased levels for a 2 h soaking time. A longer treatment does not seem to further enhance crystallisation: the X-ray diffraction pattern for 3 h does not show any new peak or increase in intensity of the peaks already present.

The semi-quantitative analysis, via Rietveld refinement (Fig. 2b), of the sample sintered for 2 h by using conventional heating, indicates a rather high degree of crystallisation of about 80 vol.%. Esseneite and labradorite correspond to 30 vol.% of the total crystal phase, approximately; wollastonite corresponds to about 19 vol.%, while both augite and albite contents are about 10 vol.%.

Esseneite belongs to the large family of pyroxenes, typically found in basalt glass–ceramics and in the sintered glass–ceramics of the previous investigations.[2,15] However, there are important differences to be highlighted, both in the specific type of pyroxene and in the other crystal phases. Monoclinic pyroxene crystals, in basalt glass–ceramics, are generally complex solid solutions between "double silicates", featuring Ca^{2+}/Mg^{2+} ($CaMgSi_2O_6$, diopside), Ca^{2+}/Fe^{2+} ($CaFeSi_2O_6$, hedenbergite) and Na^{+}/Fe^{3+} ($NaFeSi_2O_6$, acmite) ion couples, and monosilicates like $MgSiO_3$, $FeSiO_3$ and $MnSiO_3$.[2] The sintered glass–ceramics from vitrified Venice Lagoon sediments, with a higher MgO/Fe_2O_3 ratio, were based on augite, coupled to gehlenite.[15] Esseneite, found in the present glass–ceramics, is a rather unusual "double silicate" with a Ca^{2+}/Fe^{3+} ion couple, the charge balance being provided by a substantial replacement of Si^{4+} ions with Al^{3+} ions.[31]

The crystallisation of feldspars is also remarkable, unlike what happens in basalt glass–ceramics, where the feldspathic components remain essentially in the residual glass phase (a complex alkali–aluminosilicate phase).[2] Due to the high amount of both esseneite and alumino-silicates, the present glass–ceramics find analogies only with those developed by Leroy *et al.*,[32] for glasses derived from the melting of coal fly ashes, featuring esseneite associated with a feldspathoid, i.e. nepheline.

The oxidation state of iron ions is a key point in the overall crystallisation sequence. Iron oxide is known to promote the nucleation via clustering of Fe^{3+} in glasses from basalt melting, yielding magnetite, typically from 650 to 800 °C, persisting in the final microstructure or resorbed in pyroxene solid solutions.[2] In the present glass–ceramics, on the basis of the Rietveld refinement, the Fe^{3+} ions were incorporated in the esseneite and augite crystals: in fact, the calculated amount of magnetite, about 1%, is comprised in the error of the computational process, so that the presence of this phase can be excluded.

The surface conditions likely played an important role, similarly to glass–ceramics from melted basalts.[1,33,34] An effective way to promote the nucleation of basalt glass–ceramics is the simple grinding of the rock before melting in air. In the present case, fine glass powders (with a dimension <37 μm) likely promoted the oxidation, i.e. the formation of Fe^{3+} clusters, directly upon sintering, due to their high specific surface. Fig. 3 illustrates that the fine glass powders had a slight weight increase in the temperature range 650–800 °C, consistent with the oxidation; the effect is similar for coarse glass powders (<75 μm), but it takes place in a wider temperature range. This delay could be a reason for the less significant crystallisation peaks, for coarse powders, observed at about 1000 °C.

A high amount of crystals had a very positive effect on the mechanical properties, as reported by Table 3. The values for elastic modulus, bending strength and Vickers micro-hardness (for selected samples) are significantly higher than those exhibited by the most common ceramic tiles and by the previously mentioned esseneite–nepheline glass–ceramics.[32] The values of bending strength, significantly higher than 100 MPa, and micro-hardness, exceeding 7 GPa, are consistent with those exhibited by the glass–ceramics from Venice Lagoon sediments.[15]

Table 4, reporting preliminary results on the chemical stability of the developed glass–ceramics, underlines as after chemical attack with acetic acid, do not show a significant release of heavy metal ions, in particular no cadmium and lead were revealed. The concentration of Cr, V, Co and Ba ions are all below the Ital-

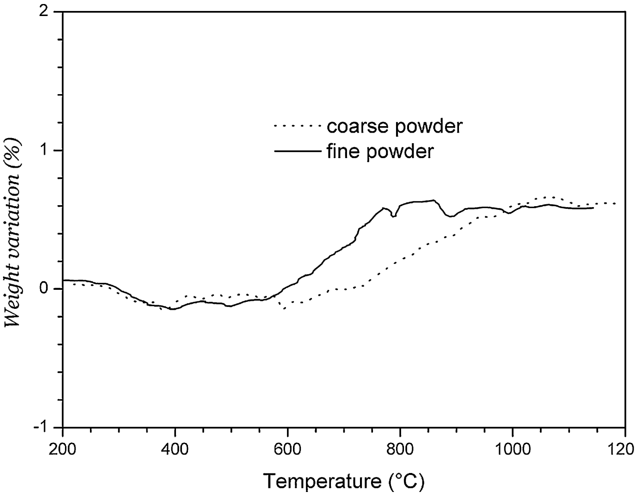

Fig. 3. Thermogravimetric plots of the investigated glass with different powder sizes.

Table 4
Results from the preliminary leachability test on the investigated glass–ceramics.

Metal	Release (mg/dm^2)	Limit (mg/dm^2)
Ba	0.020	
Cr	0.042	
V	0.046	
Co	0.064	
Cd	–	0.07
Sr	0.154	
Pb	–	0.80

ian standard limits for Cd, while Sr ions are below the limits for Pb.[24] This behaviour represents a very promising point for the actual industrial production of the presented materials. Further chemical analysis, however, will undoubtedly constitute the focus of future investigations.

The observed rapid crystallisation triggered for the investigation of a relatively novel thermal treatment. The approach consists in the direct insertion of glass compacts in the sintering furnace at the crystallisation temperature, for limited holding times of 0.5 and 1 h. This treatment has been recently applied to glasses from other mixtures of inorganic waste[21,22] and represents an attempt to apply the fast sintering cycles, typical for traditional ceramics, to glass–ceramics.

The comparison of the X-ray diffraction patterns of samples “conventionally” and “rapidly” sintered, with the same soaking time (Fig. 4), shows that rapid sintering did not affect significantly the crystallisation degree. The intensities of the crystals peaks are slightly lowered in the rapidly sintered body. That was expected, since samples from conventional heating rate were maintained to a high temperature for a longer time than the directly heated ones. Only the peak at about 28°, associated to labradorite and albite, increases with the conventional firing. It can be also observed that the samples sintered with a rapid treatment do not show a practical difference in elastic modulus and bending strength, compared to those conventionally sintered, see Table 3.

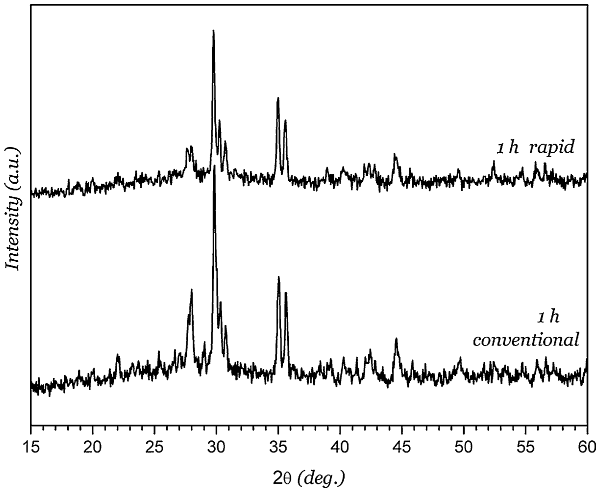

Fig. 4. Comparison in the X-ray diffraction patterns between conventionally sintered and rapidly sintered samples (1 h soaking time at 900 °C).

The high levels of crystallinity were confirmed also by the SEM analysis (Fig. 5). A large amount of crystals is visible for both conventional and rapid heat treatments. For a very short holding time, 30 min, see Fig. 5a and c, a complex “coast and island” microstructure may be recognised, as observed in the backscattered images, with many areas, i.e. “isles”, surrounded by light crystals, i.e. “coasts”. The light-grey coloured, crystals reasonably correspond to pyroxenes, for the presence of iron, developing from the surface of the former glass granules. The formation of isles can be attributed to both the mechanism and morphology of crystallisation. Some isles are attributable to the growth of crystals from the surface of former glass granules towards the centre, see zone “A” in Fig. 5a, in which the light crystals exhibit an almost radial distribution; some others are due to the interlocking of dendrites, see zone “B” in Fig. 5a, also starting from the surface of former glass granules. The dendritic crystallisation, common for the crystallisation of pyroxenes,[2] is consistent with the present glass–ceramic system.

The “isles” developed after the two types of thermal treatment differ in terms of crystal population and dimensional range. The conventional heating caused the formation of “clouds” of small crystals, see Fig. 5a, less evident with rapid heating, Fig. 5c. These “clouds” of small crystals are consistent with the crystallisation of feldspars, as observed in previous works,[17–19] and with the differences in the X-ray diffraction patterns of Fig. 4. A longer soaking time, 1 h, causes a very widespread crystallisation, see Fig. 5b and d. For conventional heating it could be observed the formation of quite long fibrous crystals, see zone “C” in Fig. 5b, attributable to wollastonite, the last phase to be developed.

The reduced dimensions of the isles, observed when the rapid treatment was applied, might be caused by the direct “exposition” of free glass surfaces at high temperatures, enhancing the surface nucleation. Although the overall crystallisation degree is lower, as previously discussed, the fast treatment seems advantageous in giving a more homogeneous crystallisation (many small isles with a thin contour instead of big isles with a thick contour, as those provided by conventional heating), which in turn could justify the mechanical properties. Although further characterisations are needed, the results from rapid sintering are undoubtedly promising for the manufacturing of glass–ceramics with economic sintering plants, comparable to the ones employed for traditional tiles, to be coupled to vitrification furnaces.

A final remark should be given to the porosity. The SEM images of samples sintered for 1 h seem to demonstrate some increasing of the porosity, in contradiction with the density measurements, especially for the rapid treatment. This could be due, to our opinion, to artefacts (not all the black regions could be associated to pores) and to sub-micrometric pores in the glass–ceramics. The closed porosity in Table 3 was inferred from the difference between bulk density (measured with the Archimedes’ method) and true density, on powdered samples. Due to their dimensions, the powders (100–150 μm) for pycnometric measurements probably still contained sub-micrometric pores, thus causing the true density to be underestimated. The presence of sub-micrometric pores in sintered glass–ceramics is caused by the volume variations, associated to the crystallisa-

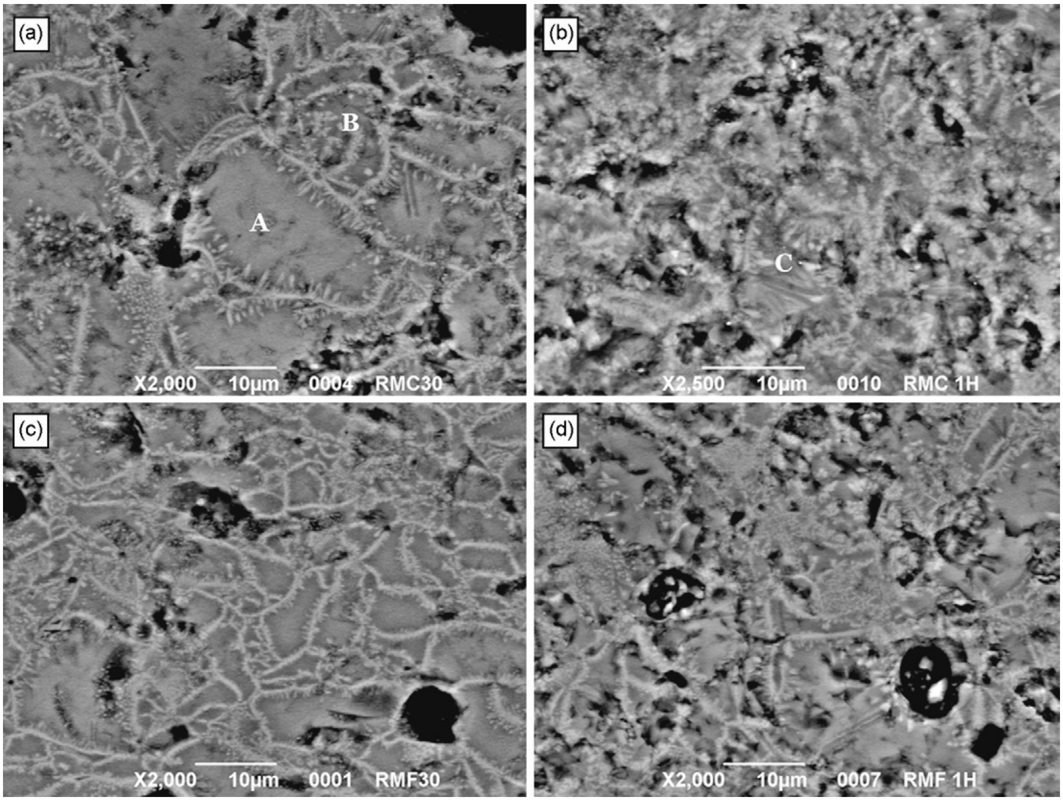

Fig. 5. SEM micrographs (backscattered electrons image) of the investigated glass–ceramics: (a) conventional sintering, 0.5 h at 900 °C; (b) conventional sintering, 1 h; (c) rapid sintering, 0.5 h; (d) rapid sintering, 1 h.

tion, that are not fully compensated by the viscous flow of the residual glass phase, and have been recently discussed in the literature.[35–37]

4. Conclusions

The key findings of the present investigation may be summarised as follows:

- waste materials, such as red mud, fly ashes and ceramic tile polishing wastes may be converted, by proper mixing, into a glass prone to surface crystallisation, leading to multiphase glass–ceramics;
- the fast surface crystallisation is reasonably associated to the oxidation state of iron ions, which also promotes the development of a not frequently encountered pyroxene (esseneite) as one of the main crystal phases;
- the enhanced nucleation activity of fine glass powders allows short thermal treatments; in particular, dense and well crystallised glass–ceramics may be obtained even with a "rapid sintering" treatment, promising for the manufacturing of glass–ceramics with the well known, simple and economic processing of traditional ceramic tiles;
- the substantial crystallisation led to remarkable mechanical properties, bending strength and Vickers micro-hardness exceeding 100 MPa and 7 GPa, respectively;
- preliminary chemical tests on glass–ceramics indicate a promising chemical durability.

Acknowledgement

The authors acknowledge Dr. Sandro Hreglich at Stazione Sperimentale del Vetro, Venice (Italy), for glass melting.

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