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Sintered sanidine glass-ceramics from industrial wastes

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Abstract

Glass obtained from melting a mixture of industrial wastes (panel glass from dismantled cathode ray tubes, mining residues from feldspar excavation and lime from fume abatement systems of the glass industry) has been employed for the production of sanidine-based glass-ceramics. The glass-ceramics were developed by a sintering treatment with concurrent crystallization, from fine powders ($<37\ \mu$m), at a relatively low temperature (880 °C). The enhanced nucleating activity of glass surfaces likely promoted the formation of sanidine, hardly found in glass-ceramics, as the main crystal phase. Due to the achieved mechanical properties (bending strength of about 120 MPa, Vickers' microhardness exceeding 7 GPa) and aesthetic appearance, resulting from a compact and homogeneous microstructure, the obtained sanidine glass-ceramics may find applications as construction materials.

Keywords: Sintering; Mechanical properties; Glass; Glass-ceramics; Structural applications; Waste materials; Sanidine

1. Introduction

Since the early 1960s, the production of glass-ceramics for the building industry has been considered as an effective way in recycling and utilizing a number of industrial wastes.[1] The approach has a two-fold benefit, as potentially dangerous wastes are dissolved in the parent glass, i.e. in a material with a high chemical stability, and the wide dimensions of the specific market of construction materials allow large quantity of wastes to be absorbed. Well known commercial examples of glass-ceramics from wastes are those of "Slagsitall"[2] and "Slagceram",[3] developed from several slags of ferrous and non-ferrous metallurgy, ashes and wastes from mining and chemical industries.[4,5]

Although well established and leading to materials with excellent properties (Boccaccini et al.[6] and Öveçoğlu,[7] for example, obtained materials with a bending strength exceeding 240 and 300 MPa, respectively) the common production of glass-ceramics from wastes presents some disadvantages. It is well known that the vitrification of wastes is capital and energy intensive; the conversion of the achieved glasses into glass-ceramics may bring remarkable additional costs. Even with the employment of catalysts (nucleating agents) in the glass formulation (TiO_2, Cr_2O_3, etc.[4,5]), the conventional two step thermal treatment of nucleation and crystal growth is generally slow and expensive (the processing times being in the order of 10 h). Moreover, extensive refining of the parent glass is required to remove its defects (for example gas bubbles from vitrification reactions), detrimental to the mechanical properties, which may remain in the final product upon crystallization. The refining treatment represents a pressing problem especially for waste glasses, which are usually dark, due to a large content in heavy metals. The colouration causes a low thermal conductivity by radiation, which in turn imposes very long holding times[1]; in addition, a long refining may promote the volatilisation of certain dangerous oxides (like PbO), no longer immobilized in the glass structure.

As an alternative to common processing of glass-ceramics, a sintering approach is particularly promising for the treatment of waste glasses. Sintered glass-ceramics, investigated since the 1960s, start from heating powdered glass to a certain temperature, at which densification occurs together with crystallization. Since free glass surfaces are preferred sites for devitrification,[8–11] glass particles, featuring large specific surfaces, are easier to crystallize than bulk pieces with the same

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composition, so that nucleating agents in the glass formulation are not essential and the processing times are limited. The enhanced nucleating activity of powdered glass leads to materials with a pleasant aesthetic appearance, comparable to that of natural stones and traditional ceramics, generally unavailable for traditional glass-ceramics.[1] As an example, marble-like materials for architectonic applications, with different main crystalline phases, such as β-wollastonite in "Neoparies" (a well established commercial product in Japan since 1970s),[12] cordierite[13] and diopside[14] have been produced.

Applying the sintering route to the production of glass-ceramics from waste glasses enables the reduction of the processing times, in the fact that a short time vitrification treatment can be used, with no need to refine the melt before casting into a frit, thus limiting cost and potential volatilisation of poisonous oxides. A wide range of sintered glass-ceramics from waste glasses has been developed, in Bulgaria[14] and in Italy,[15–20] since the early 1990s.

In this paper, we describe the production of sintered glass-ceramics based on a glass obtained by the treatment of a mixture of various wastes as the exclusive raw materials. The investigated wastes consisted of panel glass from dismantled cathode ray tubes (CRTs), mining residues from feldspar excavation and lime from fume abatement systems of the glass industry. Panel glass, a barium–strontium-based glass, corresponds to the front part of the CRT (i.e. the "screen").[21] The usage of expensive oxides like BaO and SrO, instead of PbO (chosen for the formulation of the glasses of the inner parts of CRTs), prevents the precipitation of metallic clusters from easily reducible oxides (like PbO), induced by high-energy electrons, which in turn may cause an undesirable darkening effect of the screens ("solarization" effect).[22] The lower specific absorption of radiations of Ba–Sr glasses, compared to Pb glasses, is compensated by the relevant thickness of the screens, resulting in the fact that almost two thirds of the total weight of glass components in CRTs are attributable to the panel glass. Panel glass, unlike the other glasses in a CRT, is hardly employed in manufacturing new CRTs (the percentage of "used" glass is lower than 15%[23]), since only high-quality pristine glass, from selected raw materials and with no lead contaminations is desirable. The situation is complicated, at the same time, by the replacement of standard-definition television with high-definition television (without cathode ray tube); the difficult and insufficient recycling will be less and less suitable, as a drastic reduction of CRTs production is probable.[24] It has been estimated that the amount of end-of-life CRTs in Western Europe is in the range of 300 kt/year,[25] so that an enormous quantity of panel glass requires recycling. Residues from feldspar excavation correspond to fractions of feldspar minerals which cannot be employed in the ceramic industry due to their high silica content, currently stored in very large quantities (the production of feldspar residues from a typical Italian excavation company is in the range of 40–50 kt/year). Lime consists of calcium hydroxide employed to react with acidic fumes coming from vitrification plants: besides $Ca(OH)_2$, the composition features several pollutants, like nitrates, sulphates, fluorides etc., or traces of heavy metals so that this waste is hardly used as a source of CaO in conventional glass-making.

The achieved mechanical properties and visual appearance of sintered glass-ceramics together with the very simple and cost effective manufacturing process, are promising for applications as construction materials.

2. Experimental

The chemical composition of the employed wastes is given in Table 1, which also lists the lime composition after the calcination step. The wastes were mixed in the proportion panel–lime–mining residues 28–25–47% by wt. The reference composition for the glass formulation was that of wollastonite-based glass-ceramics,[4,12] but the high content of alkali (more than 10% by wt. instead of 5% in wollastonite glass-ceramics) had to be compensated by a more pronounced alumina content (10% by wt.). This choice was intended to determine alumino-silicate phases, since the anorthite field of composition was approached.[4] The mixture of wastes was melted at about 1300 °C in an AZS crucible for about 1.5 h followed by pouring the melt on a steel plate, thus determining a drastic cooling and causing the obtained glass to break into large fragments. The results of the chemical analysis, conducted by means of an X-ray fluorescence apparatus (Philips XRF Sequential Spectrometer PW 2400, Eindhoven, The Netherlands), is shown in the same Table 1. The glass was dry-ball milled and sized in order to achieve powder particulates having powder sizes <37 μm (400 mesh).

Dilatometry and differential thermal analysis (DSC 404, Netzsch Gerätebau GmbH, Selb, Germany, 10 °C/min heating rate) were performed on the glass, in the form of a rod and fine powders, respectively.

The powders were uniaxially pressed in a steel die at the room temperature, by using an hydraulic press operating at 40 MPa, without any binder. The obtained green compacts were sintered in air at 880 °C for different times (from 0 to 3 h), with a heat-

Table 1
Chemical analysis of the starting wastes and of the investigated glass

	Panel glass	Lime	Mining residues	Glass
SiO_2	60.7–64.6	10.7–16.8	67.3	51.85
Al_2O_3	2.1–2.8	1.1–1.4	18.3	9.46
Na_2O	8.0–9.4	3.0–3.2	8.7	7.14
K_2O	7.2–7.5	0.4–2.6	1.1	3.24
CaO	0.5–1.0	59.9–65.9	1.9	16.18
MgO	0.3	0.1 – 2.4	1.1	0.78
BaO	9.1–12.7	0.0–0.2		3.07
SrO	1.0–8.4	0.0–0.1		1.29
Fe_2O_3	0.1	0.0–0.1	1.5	0.74
TiO_2	0.4		0.1	0.19
ZrO_2	0.1–0.9	0.0–0.6		0.24
PbO	0.1–0.3	0.0–1.1		0.37
ZnO	0.1–0.4	0.0–2.6		0.13
As_2O_3		0.1–0.9		0.23
Sb_2O_3	0.4–0.5	0.9–1.3		0.62
P_2O_5		0.2		0.05
B_2O_3		0.8–5.9		1.48
F		6.4–9.5		2.37
Cl		0.4–0.8		0.12
SO_3		0.2–1.7		0.43

ing rate of 10 °C/min, leading to dense samples having a white colour. In the case of a 0 h holding, the samples were cooled down just at the reaching of the sintering temperature.

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 composite materials was evaluated by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA). Beam samples of about 3 mm × 2 mm × 30 mm, for bending strength determinations were cut from larger sintered compacts. All samples were carefully polished to a 6-μm finish, by using abrasive papers and diamond paste. The edges of the bars were bevelled by using fine abrasive papers and diamond paste. The Young's modulus was measured by means of non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, Belgium). 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 0.2 mm/min. Each data point represents the average of at least 10 individual tests.

Polished samples were employed for Vickers indentation tests, using a low load of 5 N. The thermal expansion coefficient of the glass-ceramics was measured by means of a dilatometric analysis on the specimens similar to those employed for bending tests.

The polished and fracture surfaces of sintered samples were characterized by Scanning Electron Microscopy (Philips XL 30 ESEM Eindhoven, The Netherlands). Powdered samples were investigated by X-ray diffraction (Philips PW 3710, Eindhoven, The Netherlands), employing Cu Kα radiation (0.15418 nm).

3. Results and discussion

The dilatometric analysis of the parent glass, as illustrated by Fig. 1, yielded a glass transition temperature T_g of 595 °C, and a dilatometric softening point T_d of 680 °C; the thermal expansion coefficient (in the range 25–450 °C) was measured to be equal to $9.5 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$. The density of the parent glass was 2.64 g/cm^3.

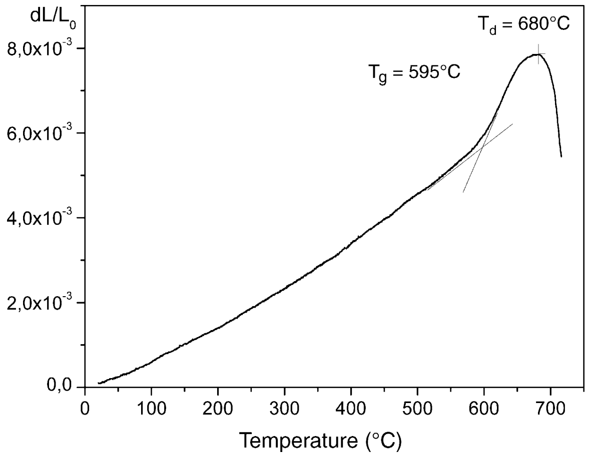

Fig. 1. Thermal expansion plot as a function of temperature of the investigated glass.

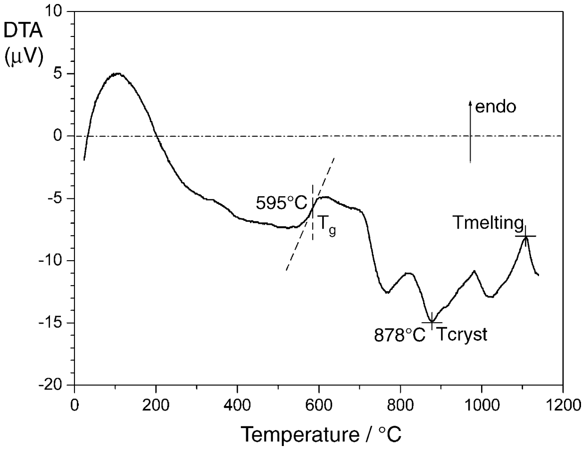

Fig. 2. DTA plot of the investigated glass.

The differential thermal analysis plot is shown in Fig. 2. The transition temperature, available from dilatometric analysis, is confirmed. Large exothermic and endothermic effects, which correspond, respectively, to crystallization and melting processes, are clearly evident at about 880 and 1100 °C. This thermal analysis constituted an essential reference point for glass-ceramics manufacturing since, like in previous experiences,[18,19] the processing temperature for achieving glass-ceramics was coincident with the crystallization temperature. This choice was suggested by the expected high nucleating activity of fine-grained glass (maximum size of 37 μm), and may represent a desirable feature from an economic point of view, due to the lower processing temperature than in other experiences of sintering with concurrent crystallization of glass.[15,16,17]

The sintering temperature of 880 °C was effective to produce glass-ceramics with limited processing times. In Fig. 3a, it may be seen that the crystallization was almost complete within a couple of hours (the X-ray diffraction pattern for 3 h did not differ substantially from that for 2 h). The precipitated phases are reported in Fig. 3b. The main crystal phase in the sintered glass-ceramics was sanidine,[26] $(K,Na)AlSi_3O_8$. The formation of sanidine is rather surprising, since this phase corresponds to the group of alkali feldspars, summarized by the formula $M_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, where M is a Na or K cation. With respect to the reference formula $Na_xK_{1-x}AlSi_3O_8$, x varies from 0 to about 0.6. It must be noted that alkali ions may be replaced by Ca on octahedral sites, the charge balance being maintained by the substitution of Al for Si on tetrahedral sites, so that sanidine may be regarded as an effective member of the ternary system albite–orthoclase–anorthite ($NaAlSi_3O_8$–$KAlSi_3O_8$–$CaAl_2Si_2O_8$).[27] Despite their wide natural occurrence (they comprise ~60% of the earth's crust),[27] alkali feldspars are known to be easily vitrified but hardly converted to a glass-ceramic: glasses from feldspars are known to be unable to crystallize in practical times.[4]

Feldspathoid phases, consisting of trikalsilite[28] and panunzite[29] were also revealed. Trikalsilite and panunzite are polymorph tectosilicates belonging to the nepheline group, with the same reference formula, $(K,Na)AlSiO_4$, and they may be considered as intermediate phases between nepheline

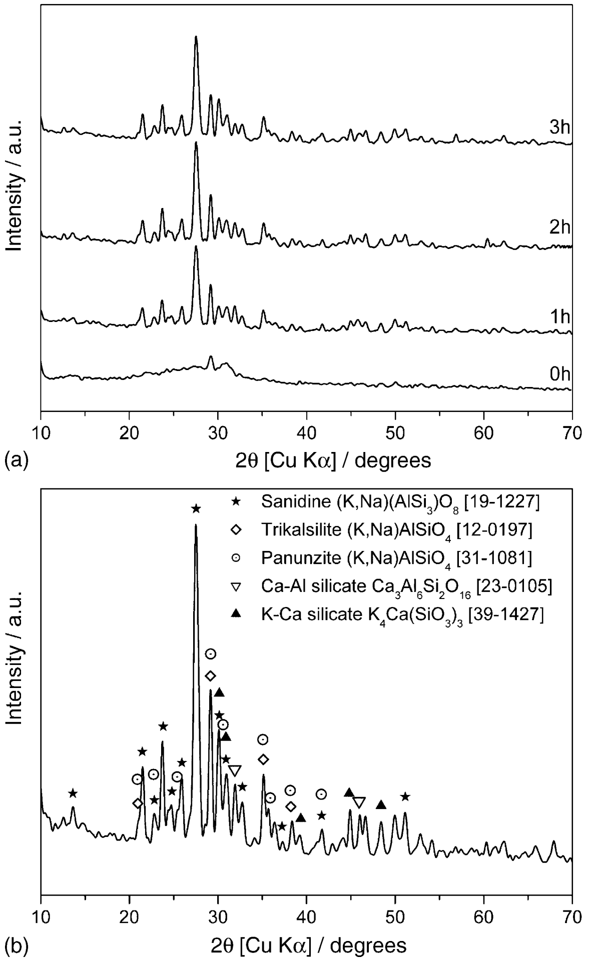

Fig. 3. XRD patterns of the investigated glass-ceramics: (a) evolution of crystallization with increasing holding time at 880 °C; (b) phase identification (glass-ceramic 2 h at 880 °C).

($NaAlSiO_4$) and its solid solutions and kalsilite ($KAlSiO_4$), corresponding to a K/Na ratio equal to 3.[4,30,31] A clear distinction between the two feldspathoids is practically difficult, except for a few peaks. Although sanidine peaks are more relevant for the glass-ceramics sintered at 880 °C for 1 h (or more), feldspathoids were likely the first crystal phases to precipitate, as shown by Fig. 3a (see the slight peak at 2θ—29°, corresponding to the main peaks of both trikalsilite and panunzite). Such observation is in a good agreement with the ability of nepheline crystals to separate, in powder processed glass-ceramics, after limited sintering times, reported in recent works.[19,32] The precipitated feldspathoids likely acted as nucleating agents for other alumino-silicate phases.

In addition to sanidine and feldspathoid phases, traces of Ca alumino-silicate $Ca_3Al_6Si_2O_{16}$[33] and Ca–K silicate $K_4Ca(SiO_3)_3$[34] were also found. Besides to the alumina content, the absence of wollastonite ($CaSiO_3$) in the precipitated phase might be attributable to the sintering temperature (880 °C), far lower than the temperature of maximum wollastonite formation (which is about 950 °C[4]).

The results of XRD analysis were followed by density measurements and SEM investigation coupled with energy dispersive X-ray analysis. In Fig. 4, both bulk and true density are reported. It can be observed that the crystallization caused a slight increase in true density values (from 2.65 to 2.66 g/cm^3) with respect to the parent glass, in agreement with the density of the main crystalline phases formed ($d_{\text{sanidine}} = 2.62$ g/cm^3 [35], $d_{\text{trikalsilite}} = 2.64$ g/cm^3 [36]); as for the XRD plots, the true density for 3 h did not differ from that for 2 h. As a consequence, the differences between bulk and true density were caused mainly by the residual porosity, varying from 4% to almost 0% (see the plot for the relative density, i.e. the ratio between bulk and true densities). Nearly full density is achieved after 1 h. The densification of the fine powders is consistent with the findings in the literature about the pressureless viscous flow sintering of glass, which is found to occur rapidly (in the range of a few hours) when the firing temperature exceeds, for more then 50 °C, the dilatometric softening point of the studied glass.[37–40] In the present investigation, owing to the dilatometric softening temperature of the glass, 680 °C, and the sintering temperature, 880 °C, the condition was satisfied. A remarkable nucleating activity, despite of the reduction of surface area caused by sintering, was likely to be allowed by the extremely rapid formation of trikalsilite or panunzite, as mentioned above.

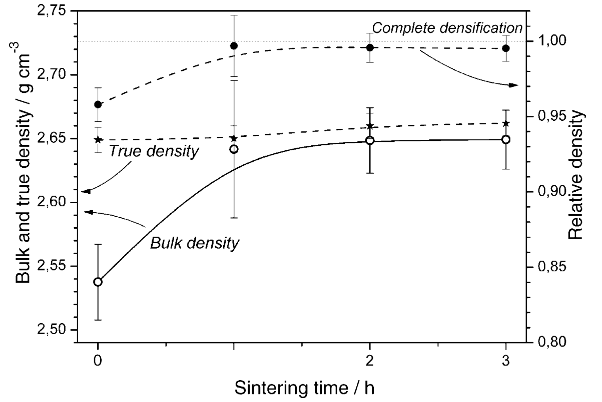

Fig. 4. Bulk, true and relative density of the sintered products as a function of the sintering time.

The microstructural evolution with increasing holding time at 880 °C, observed by means of SEM, is illustrated by Fig. 5. The above mentioned residual porosity of samples from a 0 h holding time is clearly visible in Fig. 5a. After 1 h holding time, the glass-ceramics exhibited an almost complete removal of porosity (see Fig. 5b), consistent with the density measurements, together with the formation of a network of fibrous crystals. After 2 h holding time (Fig. 5c), the glass-ceramics reached an almost stationary microstructure consisting of small fibrous crystals (length of about 5 μm, width of about 1 μm), homogeneously distributed, attributable to sanidine formation.

The energy dispersive analysis confirmed the above reported phase identification. In Fig. 6, the spectra of selected points are shown. Grey zones can be attributed to feldspathoids (A) and sanidine (B, see the above mentioned fibrous crystals). The spectra of the two phases differ mainly for the Ca content, higher for sanidine, in a good agreement with the possibility of the same crystal to incorporate Ca ions. Lighter regions (C) show a more

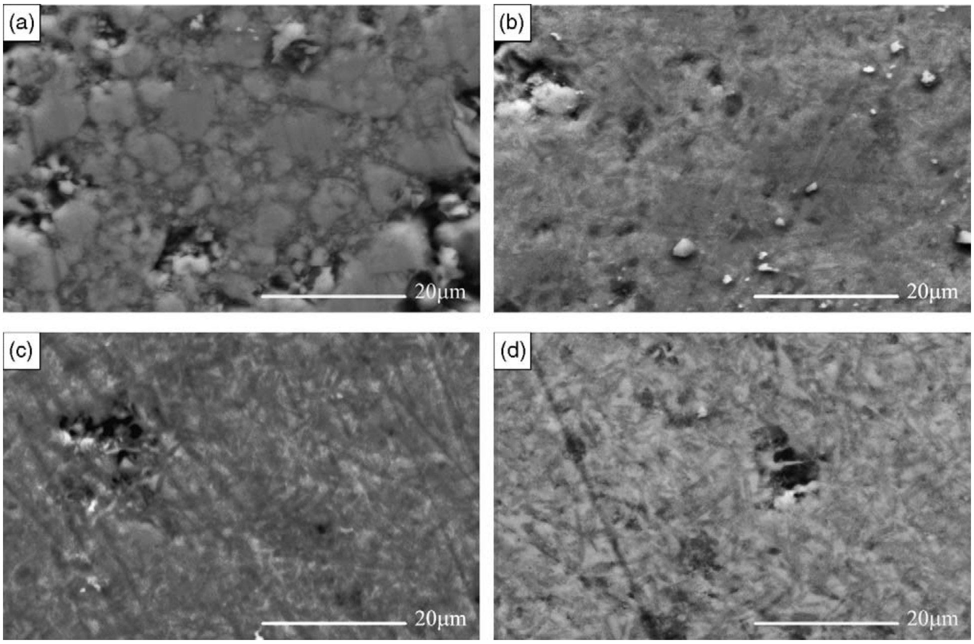

Fig. 5. SEM micrographs of sintered glass-ceramics taken at different holding times at 880 °C: (a) 0 h; (b) 1 h; (c) 2 h; (d) 3 h.

pronounced Ca, Ba and Sr content, and they may be attributed to a residual calcium alumino-silicate glass phase together with the revealed traces of Ca alumino-silicate crystals.

The elastic modulus of the glass-ceramics, as illustrated by Fig. 7, was found to reach an almost stationary level of about 70 GPa for a holding time longer than 1 h. The increase of Young's modulus need to be attributed both to the crystallization and to the increase of relative density, which reached itself an almost stationary level after 1 h. The elastic modulus for a porous material depends on the elastic modulus E_0 of corresponding pore-free material and the porosity P, following the equation[41] (in the hypothesis of spherical pores):

$$E = E_0(1 - \varepsilon P^n) \quad (1)$$

where, following Rice[41], $\varepsilon = 3^{1/2}$ and $n = 2/3$. The glass-ceramics from a 0 h holding had a relative density $\rho_{\text{rel}} = 0.958$, so that the porosity content was $P = 1 - \rho_{\text{rel}} = 0.042$; by substituting P and $E = 48.5$ GPa, we infer $E_0 = 61.3$ GPa, which may be seen as the intrinsic elastic modulus for slightly crystallized samples. From an analogous calculation, for 1 h holding, $E_0 = 75.7$ GPa (almost stationary with increasing sintering time, being $E_0 = 74.8$ GPa and $E_0 = 72.5$ GPa for 2 and 3 h holding, respectively): the completion of crystallization resulted in a 25% increase of the elastic modulus with respect to the value for 0 h holding.

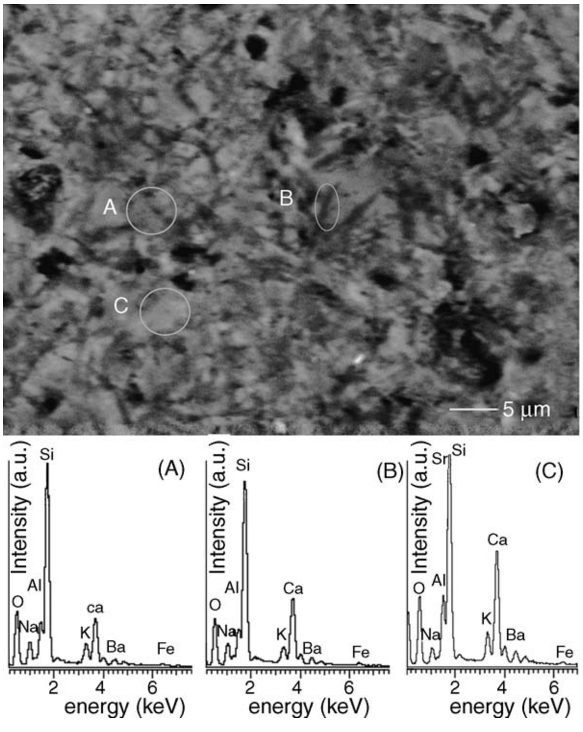

Fig. 6. EDS spectra of selected zones of a sintered glass-ceramic.

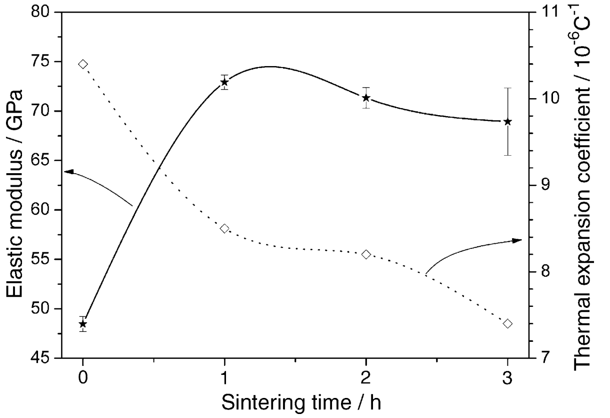

Fig. 7. Elastic modulus and thermal expansion coefficient of the sanidine glass-ceramics as functions of the sintering time.

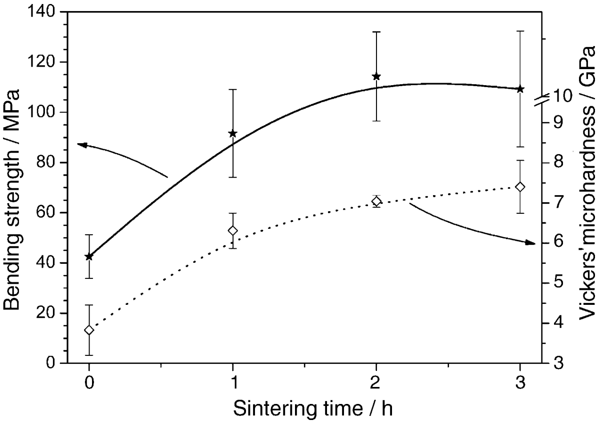

Fig. 8. Bending strength and Vickers' microhardness of the sanidine glass-ceramics as functions of the sintering time.

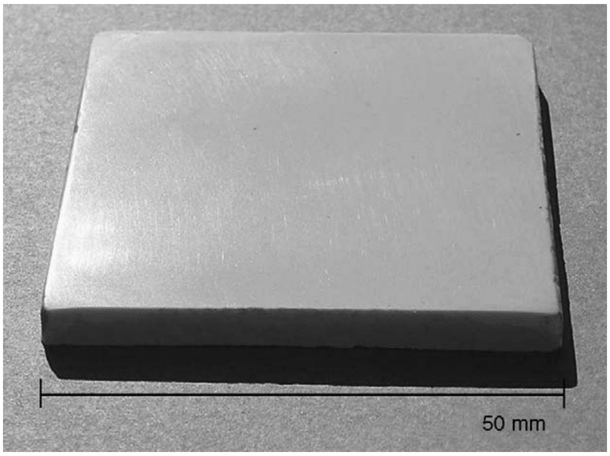

Fig. 9. Visual appearance of sintered sanidine glass-ceramics.

The crystallization kinetics was likely the main reason for the decrease of thermal expansion coefficient (measured in the range 25–450 °C), also shown in Fig. 7: for a 0 h holding time the coefficient of thermal expansion was slightly higher than that of the parent glass, reasonably due to the precipitation of feldspathoid phases (trikalsilite and panunzite, as above described, are intermediate phases between nepheline and kalsilite, having a thermal expansion coefficient superior to $12 \times 10^{-6}\,°\mathrm{C}^{-1}$ [4,19,31]); after 1 h, the coefficient of thermal expansion was lower than $8 \times 10^{-6}\,°\mathrm{C}^{-1}$, reaching $7.4 \times 10^{-6}\,°\mathrm{C}^{-1}$ for a 3 h holding time, likely due to the formation of feldspar crystals (recent studies showed that sanidine thermal expansion coefficient is in the order of $4 \times 10^{-6}\,°\mathrm{C}^{-1}$ [42]). The achieved thermal expansion coefficient is close to that of natural stones (like granite and marble) and glass-ceramics for tile applications (Slagsitalls and Neoparies).[4,5]

The fine, compact and homogeneous distribution of crystals led to remarkable values for the bending strength and Vickers' microhardness, as shown in Fig. 8. The value of the bending strength is close to 120 MPa, thus being comparable to that of commercial glass-ceramics for applications in the building industry.[4] The poor bending strength for a 0 h holding time is reasonably due to the relevant porosity of the samples, at the start of densification. The completion of densification, after 1 h, caused an increase to 91.6 ± 17.5 MPa, improved to 114.3 ± 17.8, after 2 h, with the completion of crystallization. The dependence of the bending strength to the crystallization is confirmed by the fact that, as for the density and the crystal precipitation, the mechanical properties of glass-ceramics cannot be enhanced further by extending the holding time from 2 to 3 h.

The trend of Vickers' microhardness is analogous to that of the bending strength. The microhardness, after 2 h, exceeded 7 GPa, a value again comparable to those of other construction materials (natural stones and commercial glass-ceramics[4]), thus configuring products suitable for applications requiring good wear resistance.

In addition to the above reported combination of physical and mechanical properties, the achieved sanidine-based glass-ceramics exhibited a pleasant aesthetic appearance, due to a homogeneous white colouration (the morphology of a typical sample is illustrated by Fig. 9), favourable for architectural applications. Although further studies are needed to complete the characterization of the achieved glass-ceramics (for example, the chemical durability will be the object of our future experiences), the reported study has a remarkable potential for a large absorption of the investigated wastes in the market of construction materials.

4. Conclusions

In this investigation, a selected mixture of industrial wastes, consisting of panel glass from dismantled CRTs, mining residues and lime from fume abatement systems, was successfully converted into sanidine-based glass-ceramics by a simple and economic sintering treatment with concurrent crystallization. The main features of the obtained products may be summarized as follows:

(1) The enhanced nucleating activity of finely powdered glass caused a very rapid formation of feldspathoid crystals, i.e. trikalsilite and panunzite, which in turn allowed a diffuse crystallization of alkali feldspar crystals, consisting of sanidine. The formation of alkali feldspar crystals is particularly notable, since feldspars are known to be easily converted into glasses, however not capable of crystallization in practical times.
(2) The relatively high alumina content of the glass from wastes and the relatively low sintering temperature (880 °C) promoted the formation of alumino-silicates instead of calcium silicate (wollastonite), commonly developed from glasses having similar chemical compositions.
(3) The bending strength and the Vickers' microhardness values of the sintered sanidine-based glass-ceramics were remarkable, approaching 120 MPa and exceeding 7 GPa, respectively. The obtained product may be compared to commercial glass-ceramics like "Neoparies" and "Slagsitalls", intended for applications as construction materials.
(4) The optimum features of sanidine glass-ceramics were achieved for a very limited holding time, 2 h, much shorter than those required for traditional glass-ceramics. In addi-

tion to the low processing temperature with respect to traditional ceramics, the possibility of rapid manufacturing could be useful for the production of cheap building materials, highly profitable for a large absorption of the investigated wastes.

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