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Stabilization of fluorine-containing industrial waste by production of sintered glass-ceramics

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Abstract

Calcium hydroxide is normally used to neutralize acid fumes escaping from furnaces in glass and ceramic manufacturing processes, leading to huge amounts of waste material known as ‘‘exhausted lime’’. The presence of calcium fluoride greatly complicates the use of this waste as Ca-rich secondary raw material. The present study is aimed at the development of a new type of glass-ceramics, allowing a significant fixation of fluorine (maintained as CaF_2 or in the form of calcium silicon oxyfluorides), by direct sintering of exhausted lime mixed with clay and recycled glass from dismantled cathode ray tubes. The low softening temperature of recycled glass allowed a substantial viscous flow at relatively low temperature.

Sintered glass-ceramic samples of optimized composition (glass/clay/waste weight proportion equal to 50/30/20), featured a water absorption below 2%, a good specific strength and, above all, a substantially unchanged F content, compared to the starting mixture. The obtained glass-ceramics could be used as low cost tiles, especially for insulation purposes, exploiting the residual porosity (30–40%).
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1. Introduction

Elemental fluorine F is a member of the halogen family. In combination, it comprises 0.065% of the earth’s crust, being the 13th element in abundance, and it is inevitably present in the raw materials for the ceramic industry [1]. A significant drawback of F-containing raw materials is the hazardousness of F-rich gaseous compounds that could evolve upon thermal processing; in fact, especially in recent years, environmental legislation in the European Union has set strict limits on the emission of fluorine-containing compounds into the atmosphere, the specific emission limit values for ceramic industries being about 5–10 mg HF/N m^3 at 18% O_2 [2,3].

Both glass and ceramic industries are known to abate F emissions by treating acid fumes with calcium hydroxide. This strategy provides some fluorine stabilization, by the formation of CaF_2 [4], but also implies the accumulation of huge amounts of waste, known as ‘‘exhausted lime’’, with limited valorization possibilities. In fact, any thermal treatment applied to F-contaminated calcium hydroxide may cause fluorine to escape again, by the decomposition of calcium-based compounds.

Previous studies exploited exhausted lime simply as Ca- and F-rich raw materials, for the development of waste glasses (i.e. glasses from combinations of waste materials), to be converted into frit-derived glass-ceramics (‘‘sinter-crystallized’’ glass-ceramics) [5–7], with no specific control of fluorine evolution. The present paper starts from a different approach, leading to glass-ceramics by direct sintering mixtures of exhausted lime, clay and recycled glass. The approach resembles that of traditional ceramics (e.g. porcelain stoneware), in which wastes are no longer introduced in limited quantities (as shown by a vast literature [8–11]), but can

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represent the basic raw materials. Glass is a fundamental component, since it allows viscous flow sintering at much lower temperatures than those required for feldspar fluxes; in addition, it reacts with the other raw materials, giving rise to silicate and alumino-silicate crystals [12,13].

Exhausted lime has been already recycled in conventional ceramic bodies, but it should be noted that several problems arise concerning the rheology of slips, the formation of undesired crystal phases and microstructural changes, so that the waste is reinserted in small amounts (not exceeding 2%) [14–16]. The approach here presented is essentially aimed at presenting a new type of glass-ceramics that could be seen as a hybrid between conventional ceramics, for the direct sintering of a mixture of raw materials and glass-ceramics, for the microstructural development, with the distinctive characters of low processing temperatures (900–1100 °C), remarkable waste recovery and substantial residual porosity. More precisely, we referred to a glass being hardly recycled in the manufacturing of the original articles, i.e. panel glass from dismantled cathode ray tubes (CRTs); like exhausted lime, this glass has been already considered for conventional ceramics, but in limited quantities [17]. The porosity is not reputed as a negative point: the new glass-ceramics, in fact, could be addressed to innovative applications, such as tiles for ventilated façades (lightweight tiles constituting a thermally insulating structure [18]).

Although we considered lime with a relatively low “exhaustion degree” (i.e. overall F contamination), selected sintering conditions led to a substantial fixation of F and could be the basis for further studies. Additional experiments concerned the application of a glassy layer at the surface of the sample to increase the mechanical properties and promote fluorine fixation.

2. Experimental procedure

The starting materials consisted of exhausted lime, glass from dismantled CRTs and pure kaolin clay. Exhausted lime comes from fume abatement systems of a plant for the production of blue-colored glass frits (Colorobbia SpA, Vinci, Italy), whereas CRT glass (provided by SASIL SpA, Biella, Italy) is actually a mixture of glasses from the recovery of panels of old TV and PC screens (Ba–Sr glasses, with a very limited content of PbO). The chemical composition of exhausted lime, according to XRF analysis (performed by the same Colorobbia SpA) and the composition ranges of CRT glass (provided by SASIL) are reported in Table 1.

Table 1
Chemical composition of the employed exhausted lime and panel glass.

Compound	Exhausted lime (wt%)[a]	CRT glass (wt%)
SiO_2	6.40	59–61
CaF_2	14.50	–
CaO	52.40	0–2
B_2O_3	6.21	<0.2
K_2O	2.60	6–7
Na_2O	1.11	7.5–8
MgO	0.69	0–1
Al_2O_3	0.37	1.5–3
CoO_2	0.16	–
Fe_2O_3	0.10	<0.1
MnO_2	0.03	–
TiO_2	0.02	<0.6
PbO	–	<0.3
BaO	–	10–12
SrO	–	4.5–8.5
ZrO_2	–	1–5
LOI	Balance	–

LOI = lost on ignition.
[a] Tested after calcination at 500 °C.

Exhausted lime was first characterized by means of X-ray diffraction analysis (Bruker D8 Advance, Karlsruhe, Germany—CuKα radiation, 0.15418 nm, $2\theta = 15–60°$), DTA/TG analysis (DTA/TGA, STA409, Netzsch Gerätebau GmbH, Selb, Germany), and FTIR (FTIR model 2000, Perkin Elmer Waltham, MA), and then mixed with the other components, in three different weight proportions, labeled A (lime/glass/clay = 20/70/10), B (20/60/20) and C (20/50/30). The amount of lime was kept constant in order to assess the impact on sinterability, phase evolution and stabilization of F of different glass/clay ratios.

The components were mixed together in water (35–40% of the total solid), obtaining aqueous slips, homogenized by mechanical stirring. The slips were cast in wide aluminum containers (to avoid interaction of lime with glass containers) and dried at 110 °C overnight. The solid residues were manually ground and sieved to get fine granules of about 200 μm diameter and about 7% humidity. The granules were pressed at 40 MPa in different dies, to form discs (30 mm diameter, 2 mm height) and rectangular tiles (dimensions of 50 mm × 35 mm × 5 mm). The molded specimens were dried at 110 °C for 1 h and then directly put in an electric muffle furnace operating at the desired temperature (800 °C, 900 °C, 1000 °C and 1100 °C). Disc samples were directly removed from the furnace after 30 min holding time, whereas small tiles were subjected to a cooling procedure, aimed at minimizing the thermal shock (furnace turned off, natural cooling at a rate of approximately 20 °C/min just at the end of the holding stage, and 5 °C/min later).

Immersion in boiling water was done for the evaluation of the water absorption, according to the current norms [19]. The apparent density of the sintered materials was estimated by means of the Archimedes principle, whereas the true density was assessed by He pycnometry (Micromeritics AccuPyc 1330, Norcross, GA).

The main crystalline phases of all heat-treated samples and untreated ground mixtures were identified by XRD analysis (on powdered samples; same conditions applied to exhausted lime). Phase identification was achieved by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database

(ICDD—International Centre for Diffraction Data, Newtown Square, PA). Powdered samples were subjected also to FTIR spectroscopy (the same conditions as above) and X-ray fluorescence analysis. In particular, the fluorescence analysis was conducted with a wavelength dispersive spectrometer (WDXRF, ADVANT'XP+, Thermo ARL, Ecublens, Switzerland) operating on pressed powder pellets (six measurements performed on each sample; the net intensities of the FKα line – $\lambda = 1.83$ nm – were determined as the difference between the gross and the background counts).

For the evaluation of mechanical properties, small beams of 40 mm × 3 mm × 4 mm were cut from bigger tiles and carefully polished up to a 5 μm finish and chamfered at the edges, by using diamond tools. The elastic modulus was measured by non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, Belgium). Four-point flexural tests (24 mm outer span, 8 mm inner span) were carried out by using an Instron 1121 UTS (Instron, Danvers, MA), at a cross-head speed of 1 mm/min; each data point represents the average of at least 10 individual tests.

To elucidate their microstructures, the two most significant glass-ceramic samples were subjected to scanning electron microscopy (ESEM Quanta 200, FEI Company, Eindhoven, The Netherlands).

3. Results and discussion

As shown in Fig. 1a exhausted lime, in the as-received condition, featured calcium hydroxide (PDF#01-1079) and $CaCO_3$ (calcite, PDF#86-2339) as the main crystal phases. Weaker diffraction peaks were attributed to CaF_2 (fluorite, PDF#87-0971) and quartz (PDF#85-1780).

The thermal plots in Fig. 1b are consistent with the characteristics of the phases detected by X-ray diffraction: the thermogramimetric (TG) plot exhibits two weight loss effects, at 450–500 °C and 750–800 °C, both with endothermic character, according to the DTA. These effects are consistent with decomposition reactions, occurring at 450 °C for $Ca(OH)_2$ (evolution of water vapor [20]) and 750 °C for $CaCO_3$ (evolution of CO_2 [21]). The weight change between the two reactions is also consistent with the preliminary information about chemical composition of exhausted lime, shown in Table 1. Finally, the weak loss above 1000 °C, accompanied by not well defined endothermic effects, may be attributed to the decomposition of calcium fluoride, as reported in the literature [22].

The presence of calcium carbonate and its decomposition explains the generally decreasing trend of density with increasing temperature, as illustrated by Fig. 2. In fact, $CaCO_3$ is known to cause some foaming when mixed with glasses having a low softening point, such as CRT glasses [23]. Due to the direct insertion of samples at the firing temperature the water release also from the decomposition of $Ca(OH)_2$ and clay dehydration (occurring at 550 °C [24]) probably contributed to the foaming.

Water absorption has more complex trends. All formulations generally led to a decrease of water absorption, up to 900 °C; above this temperature, the different balances among glass, clay and exhausted lime are associated to different behaviors. The formulation featuring the

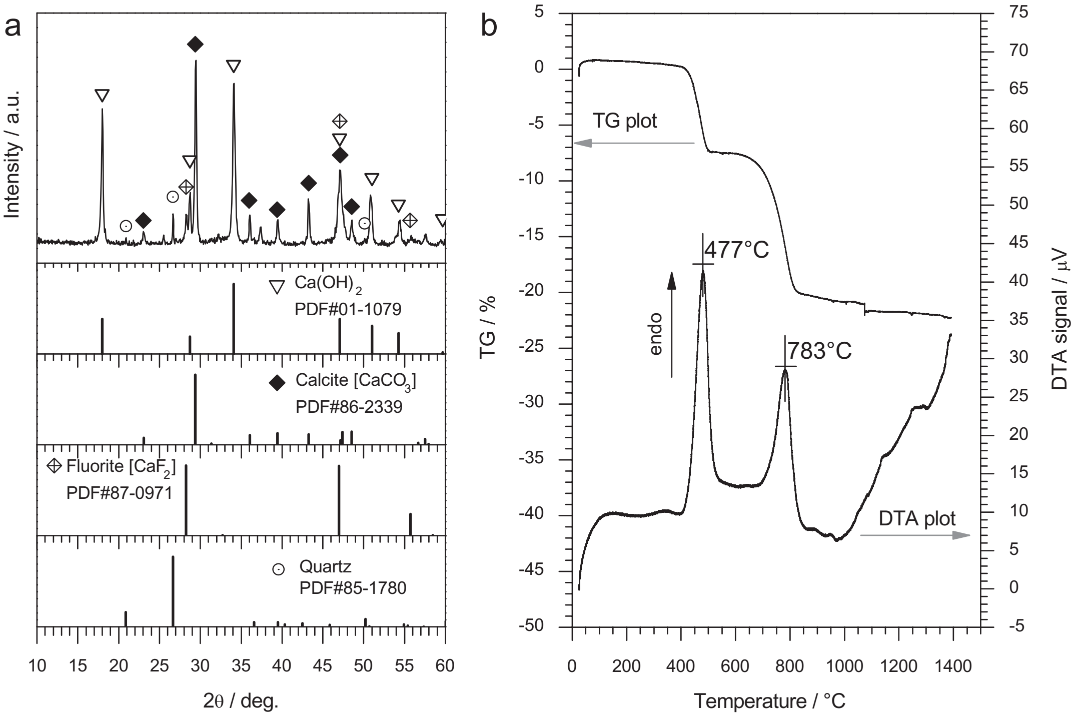

Fig. 1. Preliminary analysis on exhausted lime in the as-received condition: (a) X-ray diffraction analysis and (b) thermal analysis (DTA/TG plots).

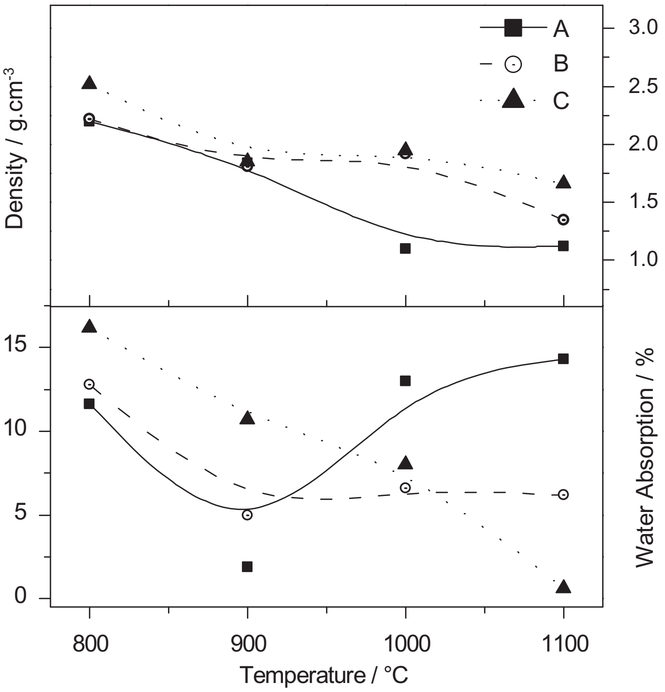

Fig. 2. Water absorption and apparent density trends with firing temperature (lines are simply guides for the eye—disc samples).

highest glass/clay ratio (formulation A) exhibited a dramatic increase of water absorption above 900 °C, whereas the one with the lowest glass/clay ratio (formulation C) exhibited a further decrease; the intermediate formulation had a stationary absorption above 900 °C.

In our opinion, densification and absorption trends could be caused by conflicting effects, involving the reduction of viscosity of the liquid phase, provided by the glass component, with increasing temperature. On one hand, the viscous flow promotes the sealing of open porosity and the decrease of water absorption; on the other hand a low viscosity favors uncontrolled foaming by gas escape. In particular, water absorption might be enhanced by the collapse of gas bubbles at the surface of samples (reasonably the hottest part of the samples, upon firing).

Operating with a high glass/clay ratio, the viscosity of the mixture was obviously lower than in the other cases, so that the "sealing effect" occurred at much lower temperature (900 °C) than extensive foaming (1000–1100 °C). On the contrary, for a low glass/clay ratio sealing and foaming likely occurred progressively and "simultaneously" (water absorption and density with similar decrease with increasing temperature).

For all the formulations, the viscous flow was complicated by the crystallization, as illustrated by the diffraction patterns reported in Fig. 3. The proposed approach does not properly lead to glass-ceramics, since there is no glass undergoing controlled crystallization by itself [25]. However, we can observe that most of the crystal phases are "newly formed", i.e. they were formed by the reaction among the components.

The signals for both $Ca(OH)_2$ and $CaCO_3$, well recognizable in exhausted lime (even if the pattern, already shown in Fig. 1a, is represented out of scale, for comparison purposes), are practically absent in samples fired at only 800 °C. The calcium oxide available from the decompositions led to other Ca-rich crystal phases, by reaction with CRT glass, dominant above 900 °C. In fact, the main crystalline phase is wollastonite, in its low temperature form (β-$CaSiO_3$, PDF#84-0655), accompanied by pseudowollastonite (α-$CaSiO_3$, PDF#74-0874), i.e. its high temperature polymorph, appreciable especially above 1000 °C. The two phases are consistent with the formulation; more precisely the same phases were developed in frit-derived glass-ceramics, i.e. starting from a melting process (involving both CRT glass and exhausted lime as raw material) [6].

Quartz and CaF_2, the other two phases detected in the waste, were substantially maintained, but only in samples sintered at low temperatures. The quartz peaks are less intense for the mixture with the highest glass/clay ratio (formulation A)—the lower viscosity of the system upon firing reasonably evidently promoted also an intense quartz dissolution.

According to Fig. 2, some conditions could be taken as references. In fact, two formulations, for specific firing temperatures, i.e. composition A fired at 900 °C (A900) and C at 1100 °C (C1100), exhibited a water absorption below 2%, a sort of threshold limit for building materials to be applied on external walls; coupled to the low density (close to 2 g/cm^3), the low water absorption makes the products suitable for ventilated façades [18].

Fig. 4, reporting the detailed phase identification of the two reference samples (we report the most probable phases according to Match!), allows some clarification about the minor phases. CaF_2 was actually replaced by another F-containing phase, that is cuspidine ($Ca_4Si_2O_7F_2$, PDF#41-1474), due to the interaction among the constituents of the studied mixtures; the transformation is partial, for A900, whereas it is reputed to be complete for formulation C1100. For formulation C, anorthite ($CaAl_2Si_2O_8$, PDF#85-1415) is also present, in agreement with the formulation (anorthite and related solid solutions have been already found to develop by the reaction between Ca-rich compounds or glasses and kaolin clay [12,13]).

FTIR analysis allowed a confirmation of the development of cuspidine. CaF_2 is infrared-transparent (it is known to be used for commercial IR windows), so that it is not surprising to find signals that are attributable only to the other phases [26] in the spectrum for as-received exhausted lime, as shown in Fig. 5a. However, in sintered glass-ceramics, A900 and C1100, there are signals compatible with those for cuspidine, as illustrated in Fig. 5b [27] (the symbols refer to the typical bands as described in the reference).

Table 2 summarizes the properties of test specimens cut from small tiles, sintered reproducing the reference conditions. The density and water absorption values practically confirm those determined for disc samples; the bending strength, considering the remarkable porosity, is quite

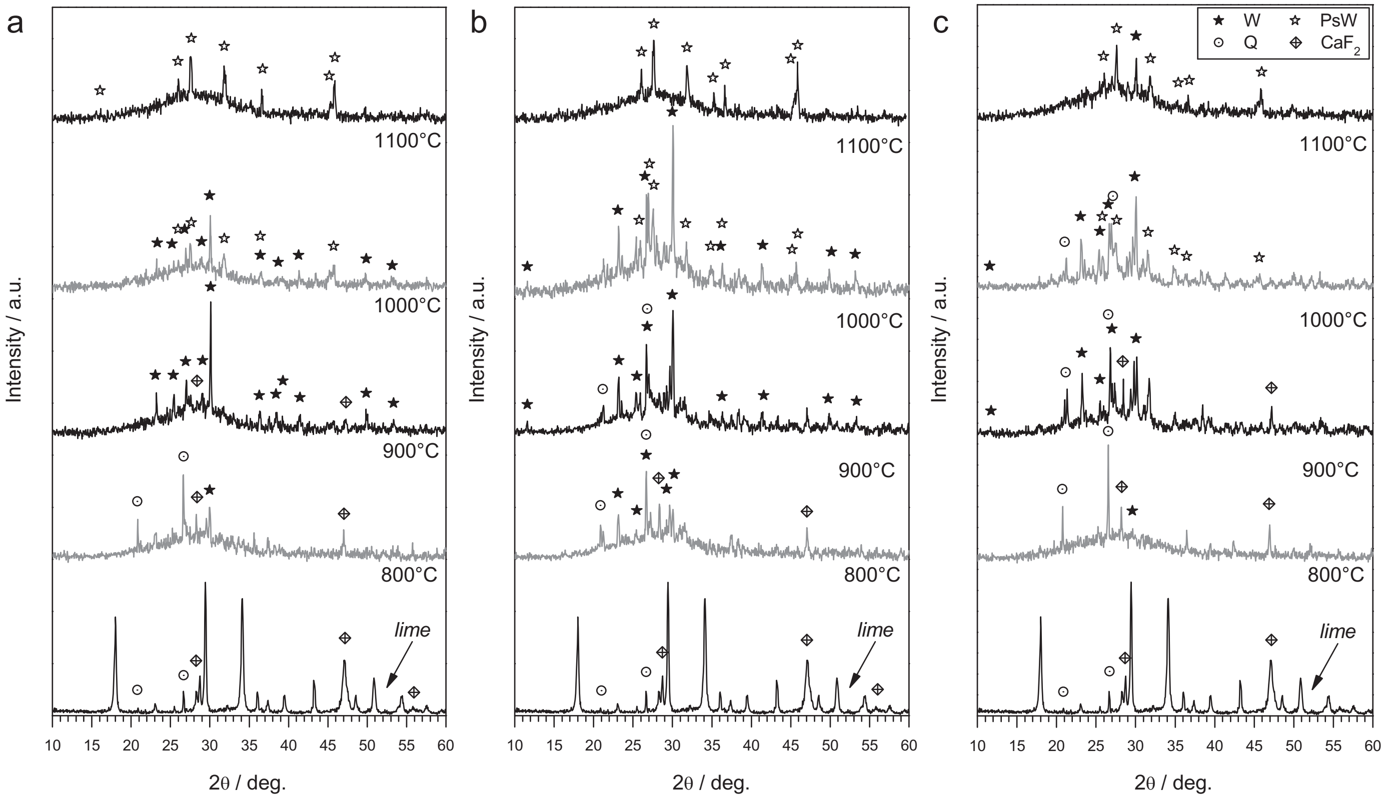

Fig. 3. Phase evolution with increasing firing temperature: (a) formulation A; (b) formulation B and (c) formulation C (pattern for exhausted lime represented out of scale—W = wollastonite; PsW = pseudowollastonite and Q = quartz).

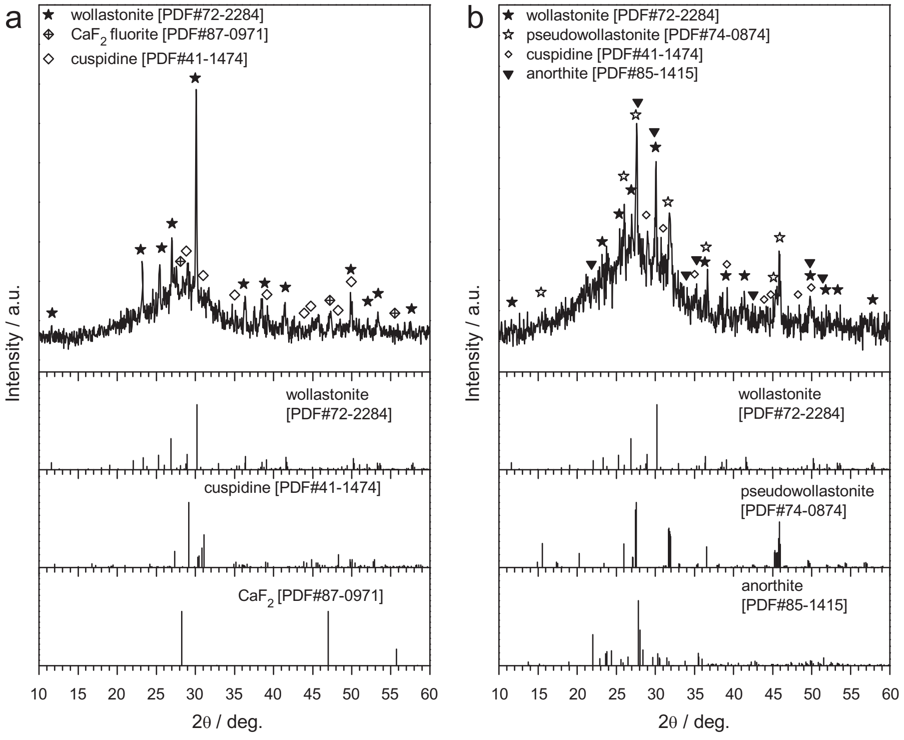

Fig. 4. Phase identification for reference sintered materials: (a) formulation A sintered at 900 °C (A900) and (b) formulation C sintered at 1100 °C (C1100).

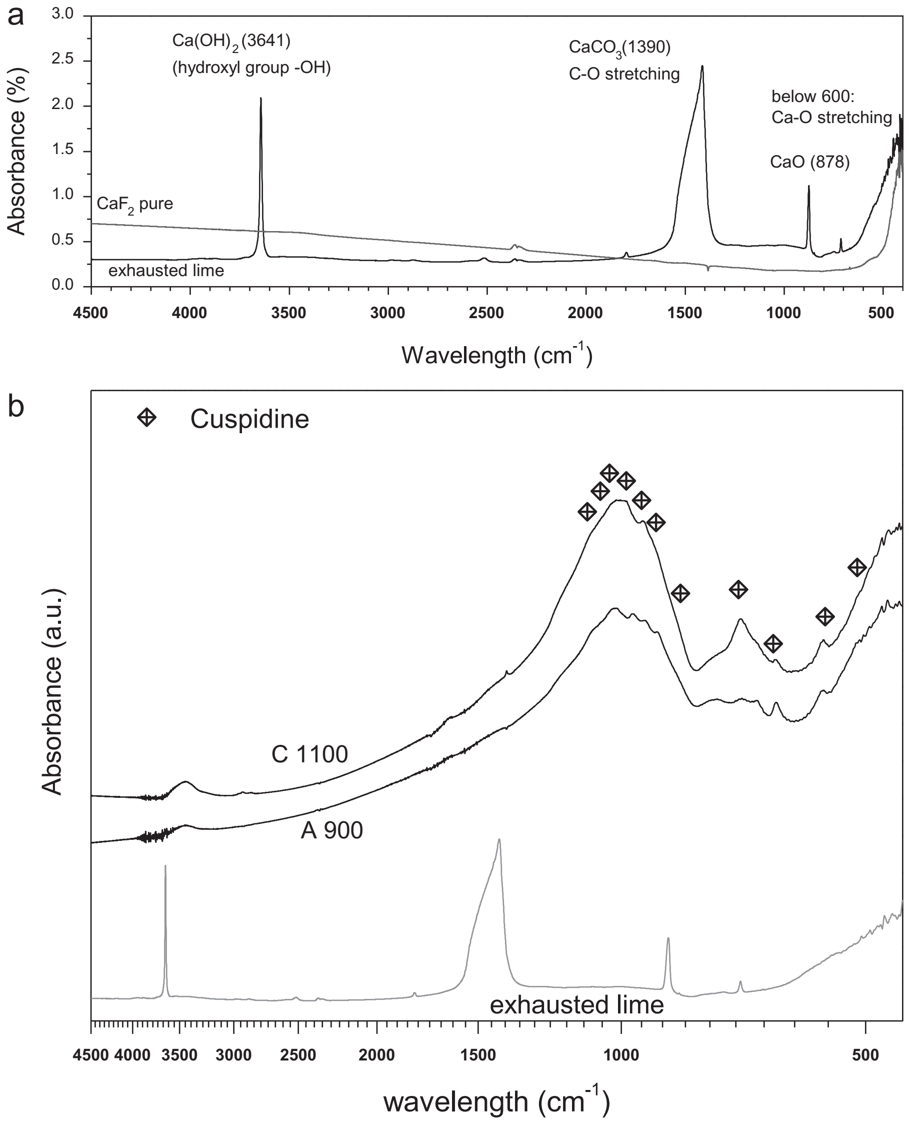

Fig. 5. FTIR characterization of the starting waste and of reference sintered glass-ceramics.

Table 2
Mechanical properties of selected sintered samples (small tiles).

Sample	Apparent density, ρ (g/cm^3)	Water absorption[a] (%)	Total porosity (%)	Elastic modulus (GPa)	Bending strength, σ_f (MPa)	Specific strength, $\sigma_f^{0.5}/\rho$ (MPa$^{0.5}$ cm^3/g)
A900	1.84 ± 0.04	1.9 ± 0.1	31 ± 2	28 ± 2	20 ± 4	2.4
C1100	1.66 ± 0.04	0.6 ± 0.2	37 ± 3	21 ± 1	15 ± 3	2.3
C1100 glazed	1.62 ± 0.04	0.5 ± 0.1	39 ± 1	36 ± 3	20 ± 2	2.8
Lightweight porcelain stoneware, sintered at 1260 °C [18]	1.70 ± 0.05	1.5 ± 0.1	30	34 ± 2	22 ± 2	2.8

[a] Test performed on tiles.

substantial. Compared to a reference material, i.e. lightweight porcelain stoneware, specifically conceived for thermally insulating structures, samples from both formulations are denser, but possess almost the same specific strength (we considered, according to Ashby [28], an index specifically concerning the structural efficiency of panels).

The obtainment of lightweight construction materials, at relatively low temperature and using waste materials instead

Table 3
Estimation of F fixation by WDXRF analysis.

Counts for F line Kα (E:0.68 keV, λ:1.83 nm)	Reference: exhausted lime, as received	A900	C1100	C1100 glazed
Average value (10^3 counts/s)	5.04 ± 0.33	1.16 ± 0.02	0.54 ± 0.08	0.55 ± 0.03
Normalized counts (counts for sample/counts for reference)	1	0.23	0.11	0.11
% exhausted lime in formulation (%)	100	20	20	18

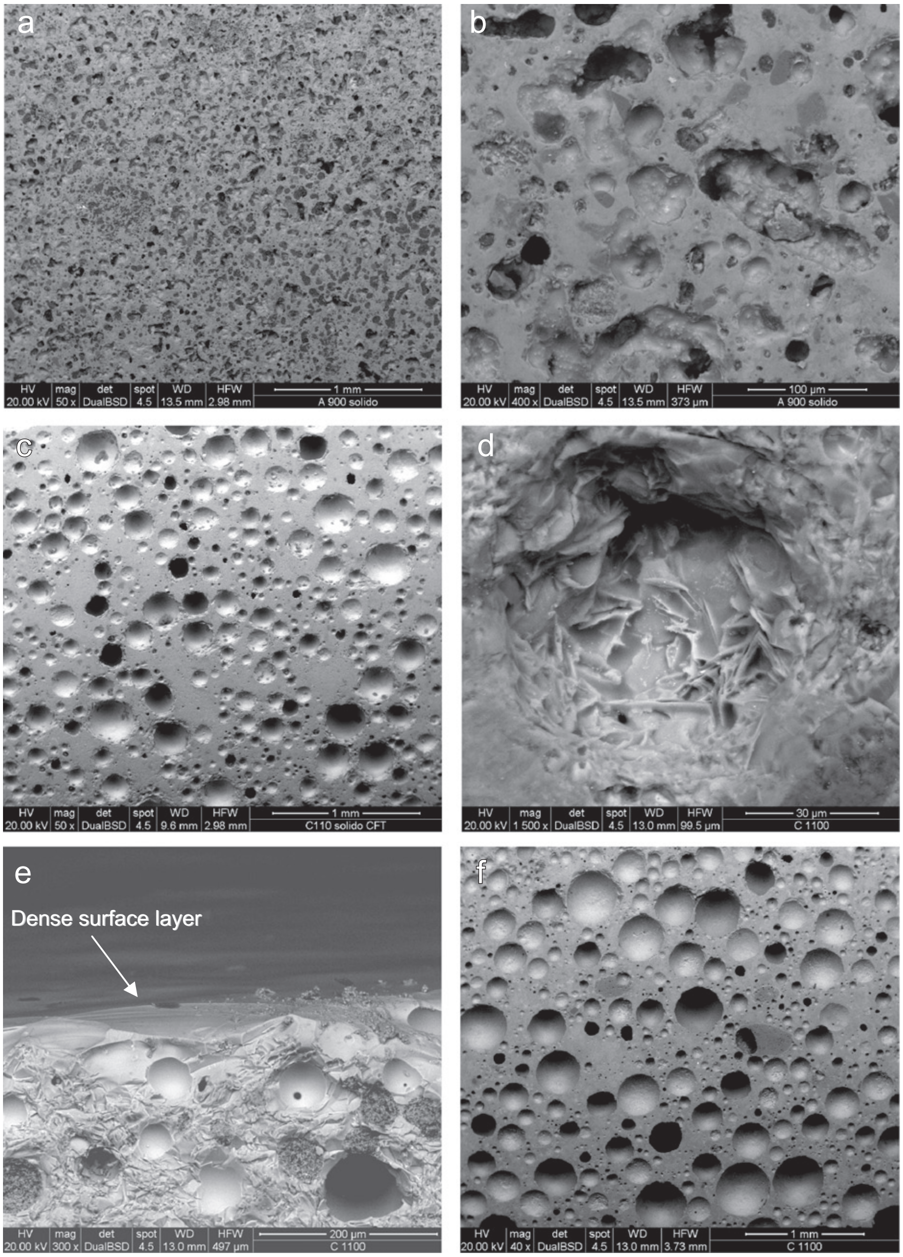

Fig. 6. Microstructural details of selected glass-ceramic samples: (a,b) A900; (c,d) C1100 and (e,f) C1100 with coating.

of valuable raw materials (lightweight porcelain stoneware, presented in recent papers [18,29], is sintered above 1200 °C and is obtained due to the addition of expensive foaming agents, such as CeO_2 and SiC, to conventional raw materials), cannot be considered as separate from the stabilization of pollutants. In particular, fluorine evolution is a critical issue—any product should be accompanied by a significant fixation of the element, in order to reduce the need for new lime upon manufacturing (if all F is lost, the same amount of lime recycled is needed to neutralize the fumes from the new process, i.e. the overall amount of waste is constant).

An affordable estimation of fluorine content comes from the WDXRF analysis, summarized in Table 3. The total counts for the distinctive line of fluorine (FKα $\lambda = 1.83$ nm, corresponding to an energy of 0.68 keV) for A900 sample, compared to those for exhausted lime in the as-received condition, are in proportion with the content of exhausted lime in the mixture (the normalized count is 0.23, while the content of lime in the formulation is 20% = 0.2). For C1100 sample the signal for fluorine is much weaker, the total counts being one half of those for A900, despite the same content of exhausted lime adopted. This means that at 900 °C the fixation of F is practically complete, while higher temperatures are associated to some F evolution, in the form of gaseous compounds (e.g. hydrofluoric acid, silicon tetrafluoride [22]), in agreement with the thermal analysis (Fig. 1); the slight formation of alumino-silicates, for sample C1100, is also thought to favor the evolution, due to their ability to dissociate fluorine-retaining crystalline phases [22].

The fixation of F stimulated additional sintering experiments is based on double pressing. In fact, a second pressing operation was used to deposit a mixture of CRT glass and clay (in the proportion 63/37) on a base body of formulation C, thus forming a double layer green body with a weight proportion between top and substrate of 1:10. This procedure was mainly conceived to “seal” the F-containing body from the atmosphere, upon firing, with a F-free coating (glazes are effectively known to reduce gas emissions [22]). The results of WDXRF analysis, however, demonstrate that only limited F fixation was achieved with a slightly lower overall content of F-containing waste; the counts for F are almost the same than those available from C1100 with no coating. The most significant effect concerns the density, well below 2 g/cm^3, much lower than in the glass-ceramic with no coating and not accompanied by any strength degradation; the coating, in other words, had a positive effect on specific strength. The coating probably helped the entrapment of gaseous compounds.

The good mechanical properties of the coated glass-ceramic sample, practically matching those of lightweight porcelain stoneware (both strength and elastic modulus are nearly the same, see Table 2), are a consequence of the quite homogeneous microstructures, as shown in Fig. 6. The porosity is substantial (more than 30%, from density determinations), but uniform, as testified by the low magnification images of the two reference samples (Fig. 6a and c). The crystallization is also evident from the images—in Fig. 6b many micrometric grains are visible especially at the surface of pores, for formulation A; in Fig. 6d we can observe many interconnected acicular crystals, typical for wollastonite [25].

The shape of pores is quite interesting, to our opinion, as an evidence of the conflicting phenomena occurring upon firing, as discussed above. The pores in the sample from formulation A (A900, Fig. 6a) are uniformly distributed, but irregular, whereas the ones in the sample from formulation C (C1100, Fig. 6c) are almost spherical, and much bigger. In the first sample, the high glass content promoted the densification (and the sealing of open porosity) at low temperature, and crystallization likely “froze” the microstructural evolution. For the second sample, the lower glass content allowed a substantial viscous flow only at higher temperature, at which the escape of gasses is less controllable (spherical pores are typical of gas evolution in a pyroplastic mass [23]). The presence of a dense surface layer (see upper part of Fig. 6e) is confirmed to positively influence the porosity (the sample shown in Fig. 6f – C1100 with coating – is visibly more porous than that shown in Fig. 6c—C1100).

In conclusion, further studies are probably needed to clarify the gaseous emission upon firing. In any case, the presented glass-ceramics achieve the starting objective of a substantial F fixation, and could be addressed to a specific application, in which they could be competitive with well-established ceramics, due to the intrinsic inexpensive character (in turn associated to the recovery of waste and the adoption of low firing temperatures). Future investigations will be probably dedicated, in addition to lime with a higher overall F contamination, to “engineered coatings”, presented here only as an example, in order to improve both F-fixation and mechanical properties.

4. Conclusions

Exhausted lime, i.e. mainly F-contaminated calcium hydroxide, was successfully recycled in the formulation of lightweight glass-ceramics for building applications, based on low temperature sintering of glass-rich mixtures. The adopted strategy is particularly significant for its double impact; in fact:

(1) Rapid sintering treatments, for formulations comprising CRT glass (having a low softening point), promote some foaming, thus obtaining micro-porous components; due to the uniformity of pore distribution, the specific strength is substantial; considering the low water absorption, the products may be attractive for the specific application as lightweight panels in ventilated façades (similar results have been presented for traditional ceramics, sintered at higher temperatures and prepared with valuable raw materials).

(2) Optimized formulations allow a remarkable fixation of fluorine; operating at low temperature (formulation A, sintered at 900 °C), fluorine is practically completely maintained, in the form of CaF_2 or other F-containing compounds (cuspidine), while treatments above 1000 °C (formulation C, sintered at 1100 °C) determine only a partial stabilization; although preliminary, the present study evidenced possible improvements associated to a F-free coating.

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