J Mater Sci (2007) 42:2706–2711
DOI 10.1007/s10853-006-1378-8

Al_2O_3-platelet reinforced glass matrix composites from a mixture of wastes

E. Bernardo · R. Castellan · S. Hreglich

Received: 12 October 2005 / Accepted: 22 February 2006 / Published online: 4 January 2007

Abstract Wastes consisting of mining residues from feldspar excavation, lime from fume abatement systems of the glass industry and panel glass from dismantled cathode ray tubes have been converted into an opaque fluorine-containing glass, featuring the precipitation of CaF_2 crystals just upon cooling. Fine glass powders were added with Al_2O_3 platelets (from 5% to 15% by vol.) and viscous flow pressureless sintered at 800 °C for 1 h, leading to dense glass matrix composites. Due the overall mechanical properties, approaching those available for glass–ceramics, coupled with a simple and economical manufacturing procedure, the obtained products could find applications in the building industry and constitute a promising way for the absorption of the investigated wastes.

Introduction

Glass matrix composites have been increasingly considered, for the last 10 years, as new engineering materials prepared by employing several wastes [1]. The first glass matrix composites, dating back to the end of the 1960s [2, 3], were developed with the specific aim of imparting to glass an enhanced fracture toughness and flaw tolerance, essential for many structural applications, by introducing various reinforcing phases. Even though this aim was generally fulfilled with the preparation of several fibre-reinforced systems, capable of outstanding mechanical properties (for example, fracture toughness may exceed 25 Mpa $m^{0.5}$) [3], glass matrix composites encountered several difficulties in their industrial development, due to their very expensive manufacturing procedures, almost completely based on hot pressing. On the contrary, most recent research is focused on low-cost manufacturing processes, based on cold pressing and viscous flow sintering of glass [4–6]. The aim is still obtaining materials with enhanced mechanical properties (bending strength, hardness, fracture toughness) compared to the matrix materials, but the composites are mostly intended to be a valid and cheaper alternative to other glass-based products, like glass–ceramics, for specific applications in the building industry (i.e. pavings, facings etc.). This approach is particularly important when the matrix glasses come from recycling activities or from the melting of several wastes, since sintering treatments are generally shorter and performed at lower temperatures than traditional nucleation and crystal growth treatments for producing glass–ceramics. Recent research has also evidenced the possibility of coupling the sintering process and the introduction of reinforcements with glass–ceramics manufacturing, by means of a sinter-crystallization process (sintering with concurrent crystallization of fine glass powders), thus producing novel glass–ceramic matrix composites with excellent mechanical properties [7, 8].

Al_2O_3 platelets represent probably the most widely reported reinforcement in pressureless sintered glass [4–6] and glass–ceramic [7] matrix composites. This is

E. Bernardo (✉) · R. Castellan
Dipartimento di Ingegneria Meccanica, settore Materiali,
Università di Padova, Via Marzolo 9, 35131 Padova, Italy
e-mail: enrico.bernardo@unipd.it

S. Hreglich
Stazione Sperimentale del Vetro, Via Briati 10, 30121
Murano, Venezia, Italy

due both to the specific reinforcing mechanism provided, i.e. crack deflection (the propagation of cracks in the glass matrix is altered by a system of residual stresses, caused by the thermo-elastic mismatch between the matrix and the reinforcement and enhanced by the particular aspect ratio of platelets [9]), and to the low commercial cost (alumina platelets are commonly employed as abrasives, so that they are produced in very large amounts), consistent with the overall cheap processing of the composites.

In this paper, we present the reinforcement of a glass prepared by employing three different wastes as the only raw materials. The main wastes came from mining and glass industries and consisted of residues from feldspar excavation, i.e. fractions of feldspar minerals not employed in the ceramic industry (due to excessive silica content), and calcium hydroxide (lime) employed to react with acidic fumes coming from opal glass melters, featuring several pollutants like nitrates, sulphates and fluorides etc. (coupled with traces of heavy metals) and consequently hardly used as a source of CaO in conventional glass-making. The third waste consisted of panel glass from dismantled cathode ray tubes (CRTs), a Ba-based glass (corresponding to the front part of CRTs) currently employed in new CRTs only in low percentages (15 wt%) [10]; in fact, only high-quality pristine glass, from selected raw materials and with no lead contaminations, is desirable [6], so that a huge amount of glasses from dismantled CRTs is landfilled (CRT glasses represent the 4% of municipal wastes, but they are expected to increase by more than 15% every 5 years [11]). The usage of a waste glass, added to the main wastes, was intended to provide a viscous liquid mass at relatively low temperatures, thus shortening the vitrification process and reducing the overall costs of glass preparation. The obtained glass constituted the basis of Al_2O_3 platelet-reinforced glass matrix composites exhibiting a complex of mechanical properties comparable to those of glass–ceramics for tiles applications.

Experimental

The chemical composition of the employed wastes is available in Table 1 (the composition of lime is that after calcination). The powdered wastes were mixed in the proportion mining wastes-lime-panel 47%–25%–28% by wt., and treated at about 1300 °C for 1.5 h. The glass was not extensively refined but drastically cooled by pouring it on a steel plate, thus producing large fragments. A chemical analysis was conducted on the glass by means of X-ray fluorescence analyser (Philips XRF Sequential Spectrometer PW 2400, Eindhoven, The Netherlands). The glass was dry ball-milled and sized to grains <37 μm.

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

	Panel glass	Lime	Mining residues	Glass
SiO_2	60.7	10.1	67.3	51.1
Al_2O_3	2.1	0.9	18.3	9.4
Na_2O	8.0	9.6	8.7	8.7
K_2O	7.2	6.2	1.1	4.1
CaO	1.0	29.8	1.9	8.6
MgO	0.3	0.2	1.1	0.2
BaO	9.9	0.1		2.8
SrO	8.4	0.1		2.4
Fe_2O_3	0.1		1.5	0.7
Cr_2O_3		0.2		0.1
TiO_2	0.4		0.1	0.2
ZrO_2	0.8	0.6		0.4
PbO	0.3	5.2		1.3
ZnO	0.3	2.6		0.7
As_2O_3		7.5		1.8
Sb_2O_3	0.4	1.0		0.4
P_2O_5		0.2		0.1
F		26.2		6.6
Cl		0.8		0.2
SO_3		1.0		0.3

The material was subjected to dilatometric and differential thermal analysis, in the form of a rod and fine powders, respectively (402E and DTA/TGA, STA409, Netzsch Gerätebau GmbH, Selb, Germany, 10 °C/min heating rate), as illustrated by Fig. 1. From the dilatometric analysis (Fig. 1a) a thermal expansion coefficient of 11.2 10^{-6} $°C^{-1}$ was inferred. The glass transition temperature (T_g) and the dilatometric softening point are clearly visible at about 510 and 580 °C, respectively. The glass transition is also shown in the differential thermal analysis (Fig. 1b). Unlike analogous glass compositions feldspar residues/lime/panel glass, which were successfully converted into sintered glass–ceramics at relatively low temperatures (880–930 °C) [12], there is no pronounced exothermic crystallization peak.

Fine glass powders were mixed with alumina platelets in 5, 10, 15% concentrations by volume, homogenised in a dry ball mill for 1 h, and finally uniaxially pressed at 40 MPa in a steel die at room temperature, without any binder. Also glass powders with no alumina addition were considered. The obtained green tiles were sintered in air at 800 °C for 1 h, with a heating rate of 10 °C/min, leading to dense samples with a light green opaque colouration.

The bulk density of the sintered compacts was measured by the Archimedes' principle. At least ten fragments were analysed for each sample. The true density of the composite materials was evaluated by

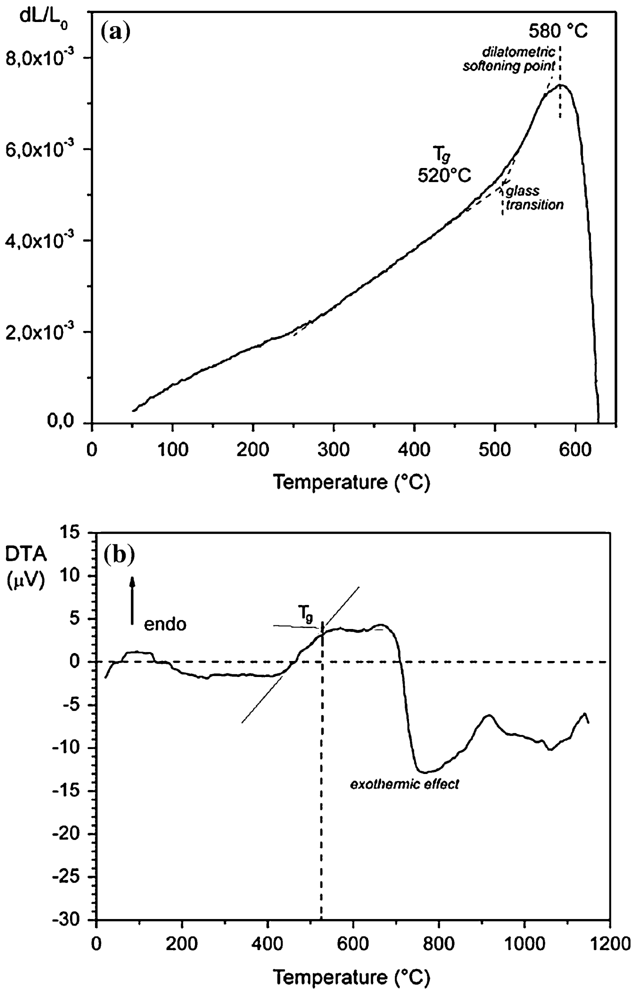

Fig. 1 Dilatometric and DTA plots of the investigated glass

means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA).

Beam samples of about 3 × 2 × 30 mm, for bending strength determinations were cut from larger sintered tiles. 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, which yielded the hardness (H_v), at low load (5 N) and the indentation fracture toughness (K_{IC}), at high load (20 N), of the investigated materials. The fracture toughness was calculated by using the well-known equation of Anstis et al. [13], after the measurement of the length of cracks emanating from the corners of the Vickers indents.

The 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 K_α radiation (0.15418 nm). The phase identification was performed by using Match! (Phase Identification from Powder Diffraction, Crystal Impact, Bonn, Germany) [14].

Results and discussion

The selected waste mixture led to an opaque glass. This was due to the precipitation, just at the cooling from the vitrification temperature, of fluoride crystals, as in the common manufacturing process for "opal" glass. This fact was confirmed by the evaluation of the X-ray diffraction pattern, shown in Fig. 2a (see the plot for the

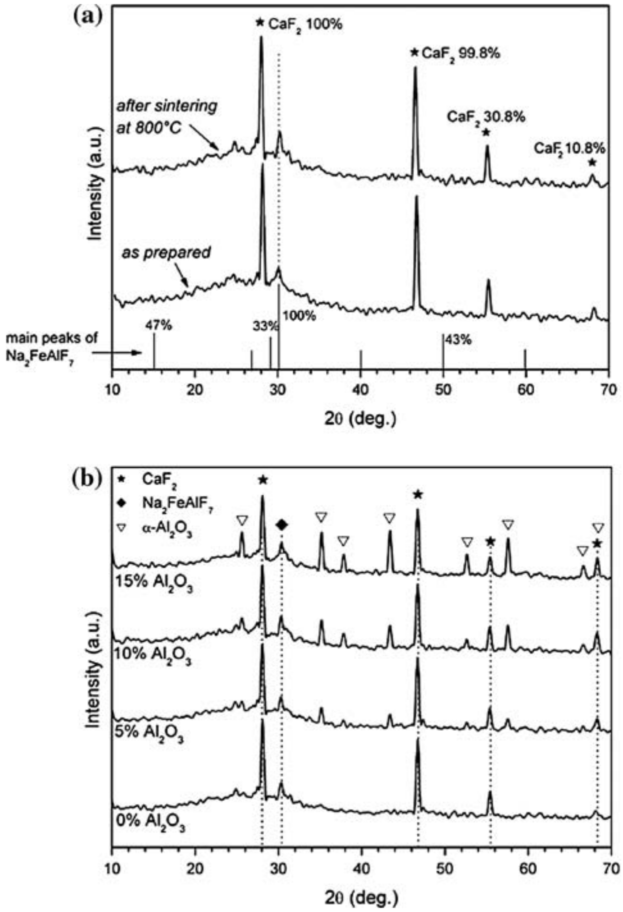

Fig. 2 XRD spectra of the starting glass and of sintered materials

“as prepared” glass). The main crystal phase is calcium fluoride, CaF_2 (ICSD PDF #870971), together with disodium iron aluminium fluoride (Na_2FeAlF_7, PDF #410394). The fact that only the highest peak (at about 30°) is visible suggests that the content of the second phase should be low. The precipitation of fluorides was not surprising, since the lime waste was itself due to the manufacturing process of opal glasses, and consequently retained a remarkable amount of fluorine.

$$E_{\mathrm{comp}} = E_{\mathrm{m}}\left\{1-\frac{\pi}{A}\left[1-\frac{1}{9\left(1+\frac{1.99}{B}\left\{\frac{E_{\mathrm{m}}}{E_{\mathrm{p}}}-1\right\}\right)}-\frac{1}{3\left(1+\frac{1.68}{B}\left\{\frac{E_{\mathrm{m}}}{E_{\mathrm{p}}}-1\right\}\right)}-\frac{1}{\frac{9}{5}\left(1+\frac{1.04}{B}\left\{\frac{E_{\mathrm{m}}}{E_{\mathrm{p}}}-1\right\}\right)}\right]\right\} \tag{1}$$

The densification degree of the sintered materials at 800 °C was relevant, as illustrated by Table 2. Despite the expected retardation in sintering of glass provided by Al_2O_3 platelets (it has been reported [15] that plate-like inclusions retard densification by greatly increasing the viscosity of the system), highly dense samples were obtained even for the largest reinforcement content (the calculated porosity being lower than 3%). This fact is probably due to the chosen processing temperature, significantly higher than the minimum temperature for viscous flow sintering, well known to be 50–100 °C above the dilatometric softening point [5, 6, 16] (580 °C for the investigated glass, see Fig. 1a). The beginning of the exothermic effect at about 700 °C, in the DTA plot (Fig. 1b), is consistent with the occurrence of sintering; the energy release may be due to the dramatic decrease of specific surface when passing from fine powders (before sintering) to a dense monolith (after sintering).

Figure 2a shows that no substantial crystallization occurred upon sintering of fine glass powders at 800 °C (the plot for un-reinforced sintered glass is identical to that of the “as-prepared” glass except for a very slight modification of the peak related to Na_2FeAlF_7). Also the introduction of Al_2O_3 platelets did not provide any significant modification in the XRD patterns, except for the presence of peaks corresponding to the same reinforcement (consisting of α-Al_2O_3), as illustrated by Fig. 2b.

The addition of platelets resulted in an overall improvement of the mechanical properties, summarized in Table 2. The measured elastic moduli were compared to those calculated by means of the Mazilu–Ondracek equation, as reported in [17], as follows:

where E_{comp}, E_{m}, E_{p} are, respectively, the moduli of the composite, the matrix and the inclusion phase (E_{m} being 380 GPa [17]). A and B are factors to be calculated as follows:

$$A = \frac{\left(\frac{4\pi}{3V_{\mathrm{f}}}\right)^{2/3}\left(\frac{z}{x}\right)^{-1/3}}{\sqrt{1+\left(\left[\left(\frac{z}{x}\right)^{-2}-1\right]\cos^2\alpha\right)}};$$

$$B = \left(\frac{4\pi}{3V_{\mathrm{f}}}\right)^{1/3}\left(\frac{z}{x}\right)^{1/3}\sqrt{1+\left(\left[\left(\frac{z}{x}\right)^{-2}-1\right]\cos^2\alpha\right)} \tag{2}$$

where V_{f} is the volume fraction of the reinforcement, (z/x) the axial ratio and α is the average angle between the rotational axis of platelets and the stress direction. The equation refers to the hypothesis of full densification; applied to the present data, which refer to a limited porosity content, the equation fits the experimental data for ($z/x = 0.2$), a typical value for Al_2O_3 platelets, and α = 75–80°. This α angle corresponds to platelets oriented almost parallel to the stress direction, reasonably due to uniaxial

Table 2 Densification and mechanical properties of the sintered materials

Al_2O_3 platelet vol. fraction (%)	Density (g/cm^3)		Porosity (%)	Young’s modulus (GPa) #	Bending strength (MPa)	Vickers Hardness H_V (GPa)
	Bulk density	True density				
0	2.68 ± 0.01	2.75 ± 0.01	2.5	73.0 ± 1.4	79.2 ± 8.5	7.0 ± 0.7
5	2.73 ± 0.01	2.80 ± 0.01	2.5	76.7 ± 1.1 [77.4]	84.6 ± 8.4	7.4 ± 0.3
10	2.77 ± 0.01	2.85 ± 0.01	2.8	82.1 ± 1.0 [83.1]	91.8 ± 11.4	7.9 ± 0.4
15	2.85 ± 0.01	2.93 ± 0.01	2.7	87.9 ± 2.6 [90.1]	100.2 ± 9.8	8.9 ± 0.6

Data fitting by Mazilu–Ondracek’s equation given between square parenthesis

pressing of the powders prior to the sintering treatment.

Like in previous experiences [5–7], the increase of both bending strength and Vickers hardness were substantial, despite the relatively low amount of platelets added to glass powders. The bending strength and the Vickers hardness reached 100 MPa and almost 9 GPa (for 15% vol. Al_2O_3), respectively. In Fig. 3 are reported both the indentation fracture toughness and the so-called brittleness index, i.e. the ratio between the Vickers hardness and the same fracture toughness [18]. More than a 40% increase of fracture toughness and more than 17% decrease of brittleness were achieved with 15% vol. Al_2O_3; it may be observed, in addition, that both the trends of fracture toughness and brittleness index are almost linear with the platelet volume fraction.

The SEM micrographs reported in Fig. 4 illustrate that the roughness of the fracture surfaces of composites (see Fig. 4b, showing a composite with 15% vol. Al_2O_3) was notably higher than that of un-reinforced glass (Fig. 4a); in particular, in Fig. 4c some pieces of platelets may be observed as protruding from the fracture surface of a composite material, due to a local rupture of the glass–alumina interface. This morphology is consistent with the expected development of residual tangential tensile stresses in the glass around the reinforcement upon cooling from the sintering temperature, due to the higher thermal expansion of the glass (11.2 10^{-6} °C^{-1}) compared to that of alumina (8.9 10^{-6} °C^{-1}) [19] (the contraction of glass was locally impeded by the lower contraction of platelets). Cracks propagating within the matrix were attracted towards the reinforcement, and advanced through the rupture of the glass/alumina interface, leading to rough fracture surfaces (compared to the relatively smooth surface of un-reinforced glass, Fig. 4a). The generally strong bond between glass and alumina [5, 6], in the composites, caused an enhanced energy absorption during crack propagation, as evidenced by the progression of fracture toughness with the reinforcement content. Figure 4 also illustrates the low residual porosity of the sintered materials, consistent with the density measurements; the small white dots were found to correspond to fluoride crystals, as evidenced by XRD analysis.

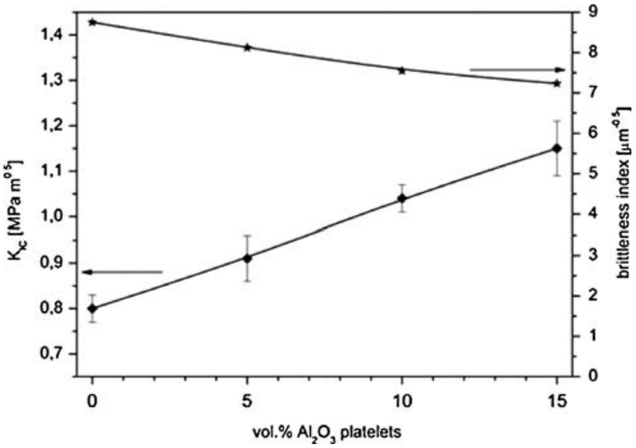

Fig. 3 Indentation fracture toughness and brittleness index (HV/KIC) as functions of the Al_2O_3 platelet volume fraction

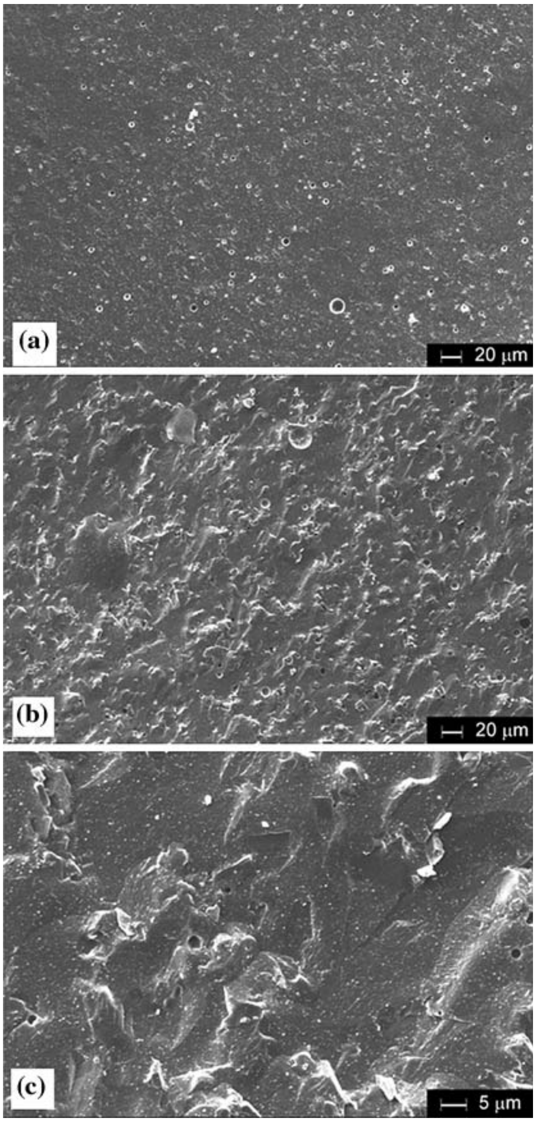

Fig. 4 SEM micrographs of the fracture surfaces of the investigated sintered material

The complex of the mechanical properties of the composites could be compared to that of glass–ceramics for building applications (see Table 3), which in turn may be developed from a number of wastes (for example the well known Slag-Sitalls) [20, 21] but need

Table 3 Physical properties of a glass matrix composite compared to those of other building materials

Property	Glass matrix composite (15% vol. Al_2O_3)	Slag-Sitalls glass–ceramics	Marble	Granite
Elastic modulus (GPa)	87.9 ± 2.6	93	27–82	42–60
Flexural strength (MPa)	100.2 ± 9.8	90–130	13.7–16.7	13.5–14.7
Vickers Hardness (GPa)	8.9 ± 0.6	Not available	1.47–4.22	1.28–5.59
Coefficient of Thermal Expansion [30–380 °C]/ (10^{-6} K^{-1})	10.9	7.2–9.0	8.0–26.0	5.0–15.0
Apparent density (g cm^{-3})	2.85 ± 0.01	2.60–2.80	2.70	2.60
True density (g cm^{-3})	2.93 ± 0.01	Not available	Not available	Not available

a crystallization process after vitrification. A comparison between the properties of the investigated glass matrix composites and those of Slag-Sitalls and other building materials [22, 23] is available in Table 3. The produced composites are thought to be promising especially for applications requiring a good wear resistance, due to their remarkable microhardness.

Preliminary durability tests showed that the glass considered for the preparation of composites is comparable to ordinary soda-lime glass. More detailed chemical tests will be topics for future research.

Conclusions

The main findings of the present investigation may be summarized as follows:

- A new glass for the preparation of sintered glass-matrix composites was made from the vitrification of a selected mixture of wastes.
- The large amount of fluorine in the raw materials caused the glass to be opaque, due to the formation, just upon cooling, of fluoride crystals. The sintering of fine glass powders at 800 °C did not cause further crystallization.
- Dense glass matrix composites were successfully prepared by the sintering of fine glass powders added with a relatively low quantity (from 5 to 15% vol.) of alumina platelets; due to their mechanical properties, the composites may be considered as a valid alternative to glass–ceramics and natural stones in building applications.
- The simple and economical manufacturing process of the composites (the sintering temperature, 800 °C, is far lower than those employed for the preparation of glass–ceramics) could be highly profitable for a large absorption of the investigated wastes.

Acknowledgements The authors would like to thank Prof. Giovanni Scarinci (Università di Padova, Dipartimento di Ingegneria Meccanica, settore Materiali) for a very fruitful and stimulating discussion, Roberto Falcone (Stazione Sperimentale del Vetro) and Marzia Zanesco (Università di Padova, Dipartimento di Innovazione Meccanica e Gestionale) for experimental assistance.

References

1. Colombo P, Brusatin G, Bernardo E, Scarinci G (2003) Curr Opin Solid State Mater Sci 7:225
2. Boccaccini AR, Rawlings RD (2002) Glass Technol 43C:191
3. Boccaccini AR (2001) J Ceram Soc Japan 109[7]:99
4. Boccaccini AR, M. Bücker, Bossert J, Marszalek K (1997) Waste Manag 17:39
5. Bernardo E, Scarinci G (2004) Ceram Int 30:785
6. Bernardo E, Scarinci G, Hreglich S (2005) J Eur Ceram Soc 25(9):1541
7. Bernardo E, Andreola F, Barbieri L, Lancellotti I (2005) J Am Ceram Soc 88(7):1886
8. Brusatin G, Bernardo E, Scarinci G (2003) Sintered glass–ceramics from waste inert glass. IV International Workshop VARIREI (Valorization and recycling of industrial residues), L'Aquila, Italy, June 2003
9. Chawla KK (1993) Ceramic matrix composites. Chapman & Hall, London
10. Siikamaki LAR (2003) In: Dhir RK, Newlands MD, Halliday JE (eds) recycling and reuse of waste materials. Thomas Telford Publishing, London, p 743
11. Hreglich S, Falcone R, Vallotto M (2001) In: Dhir RK, Limbachiya MC, Dyer TD (eds) Recycling and reuse of glass cullet. Thomas Telford, London, p 123
12. Bernardo E, Castellan R, Hreglich S (2007) Ceram Int 33:27
13. Anstis GR, Chantikul P, Lawn BR, Marshall DB (1981) J Am Ceram Soc 64(9):533
14. http://www.crystalimpact.com
15. Boccaccini AR (1998) Mater Lett 34:285
16. Ray A, Tiwari AN (2001) Mater Chem Phys 67:220
17. Boccaccini AR, Eifler D, Ondracek G (1996) Mat Sci Eng A207:228
18. Dlouhy I, Boccaccini AR (1996) Compos Sci Technol 56:1415
19. Dorre E, Hübner H (1984) Alumina. Springer Verlag, Berlin, Heidelberg
20. Höland W, Beall G (2002), Glass–ceramic technology. The American Ceramic Society, Westerville, OH
21. Sarkisov PD (1989) In: Glass '89. Survey papers of the XVth International Congress on Glass. Leningrad, p 411
22. Strnad Z (1986) Glass–ceramic Materials. Elsevier Science Publishers, Amsterdam
23. Hatta G, Kamei F (1987) Rep Res Lab Asahi Glass 37:149