Effect of waste glass (TV/PC cathodic tube and screen) on technological properties and sintering behaviour of porcelain stoneware tiles

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Abstract

In the present work, the effects of TV and PC cathodic tube and screen glasses additions (5 and 10 wt.%) to a porcelain stoneware body, in replacement of feldspar, were evaluated simulating the tilemaking process. The presence of glass allows to preserve good technological and mechanical properties, complying with the latest requirements of the industrial practice. The sintering pattern of the glass-added bodies, evaluated by hot stage microscopy, is modified according to the different glass amount and typology; in particular, cathodic tube glass when present at 5 wt.% brings about a lowering of the maximum densification temperature and of the activation energy.
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1. Introduction

Nowadays, recycling processes became more and more important mostly due to the impressive increase in the production of wastes and to the growing attention to the environmental safeguard. In modern society, the improvement of life standards and the technological development have brought about a significant growth in the consumption of computer (PC) and TV-sets. The consequent increasing of wastes, coming from electronic and electrical devices, requires to make their recycling technically and economically feasible [1,2]. Currently, the level of reutilization of both PC and TV wastes is about 5 wt.% of the total production, but the latest trend is moving towards an increasing of these levels; for this purpose, recent investigations within European countries [2] estimated the necessity to allocate about $1 \times 10^6 \ m^3$/year of TV glass wastes per million people.

The 85 wt.% of PC and TV waste is made up of cathodic ray tubes and screen glasses, and, notwithstanding their particular chemical composition due to the presence of some hazardous elements, it has been demonstrated that their recycling on an industrial scale is possible [3].

In the literature, the reuse of different waste glasses has been investigated [4–7], so that, in the latest years, these waste glasses became a commercial alternative to traditional raw materials (mainly feldspar and quartz-feldspathic sands) in ceramic bodies [8]. The use of waste glasses in the production of building materials has been successfully pursued since it can reduce both the consumption of natural resources and the cost of waste disposal, protecting the environment from their harmful action. Moreover, being the glass one of the predominant constituent of vitrified ceramic bodies, i.e. porcelain stoneware, in which it is formed in situ by the reaction of quartz and clay minerals with feldspars, many authors have considered this as the most suitable field for the potential recycling of waste glasses [9–12]. In fact, due to both the large amount of liquid phase (50–65%) developed during firing and the flexibility of the tilemaking process, glassy materials may be introduced into porcelain stoneware bodies without modifying significantly the manufacturing cycle.

Recently, some papers considered the introduction of soda–lime waste glasses as raw materials for both ceramic bodies and glazes [8–10]. In porcelain stoneware bodies, where soda–lime glasses substitute feldspathic fluxes, additions of up to 5 wt.% do not bring about any significant change in the technological behaviour, and a reduction of the sintering temperature was observed [9–12]. On this basis, commercial fluxes have been developed as a mixture of feldspar plus different amounts of

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soda–lime glass and they are currently utilized for porcelain stoneware tiles [8].

However, since waste glasses present a variable chemical composition, their utilization cannot be easily modelled; in particular, the recycling of TV and PC cathodic tube and screen glasses involves technological problems due to the high lead content and the great amount of Ba and Sr, respectively [2]. In the last decade, many authors exploited the possibility of fabricating high density bodies at relatively low temperature by mixing raw materials with TV and PC glass powders. In particular, Boccaccini et al. [13] studied the sintering behaviour of compact bodies, made of TV glass powder, suitable as tiles for radiation protection use. Recycled TV screen glasses were also mixed by Minay et al. [14] with Al_2O_3 platelets to produce composite materials having enhanced mechanical performance for wear resistant applications. The reutilization of TV waste glass in porcelain stoneware tiles has been recently investigated by Rambaldi et al. [15] which highlighted the strong fluxing power of the lead-based glass, being able to improve the formation of both liquid phase and mullite when present in a low amount (<2 wt.%).

In this work, TV/PC cathodic tube and screen glasses were added to a typical porcelain stoneware body as partial replacement of fluxes, in particular sodic feldspar. Simulating the tilemaking process at a laboratory scale, it was appraised whether the waste glass additions determined any change in the technological and mechanical properties of both fired and unfired tiles, taking a waste-free porcelain stoneware body as a reference. Particular attention was paid to the sintering behaviour of waste-bearing tiles as well as on the phase composition, microstructure and chemico-physical properties of the liquid phase.

2. Experimental

Two different types of glass, coming from the recovery of TV/PC cathodic tube (C) and screen (S), respectively, were selected together with a porcelain stoneware body (V0)

Table 1
Formulation of experimental porcelain stoneware bodies

wt.%	V0	VC5	VC10	VS5	VS10	VCS5
Ball clay	40	40	40	40	40	40
Quartz sand	10	10	10	10	10	10
Na–feldspar	40	35	30	35	30	30
K–feldspar	10	10	10	10	10	10
Cathodic tube glass	–	5	10	–	–	5
Screen glass	–			5	10	5

consisting of a mixture of ball clay, quartz sand, sodic and potassic feldspars. In the design of the porcelain stoneware formulations, the recycled glasses were introduced in 5 wt.% (VC5, VS5) and 10 wt.% (VC10, VS10), in partial replacement of the sodium feldspar. In addition, a mixture containing 5 wt.% of each glass (VCS5) was also formulated (Table 1).

Raw materials were characterized from the chemical point of view by inductively coupled plasma emission measurements (ICP-OES, Varian Liberty 200) on solutions obtained by melting the samples with lithium tetraborate at 1200 °C (Table 2).

All ceramic bodies underwent a laboratory simulation of the industrial tilemaking process by:

- mixing and wet grinding in a porcelain jar with dense alumina media for 20 min in a planetary mill;
- slip drying at 105 ± 5 °C, powder deagglomeration (by hammer mill) and humidification with 7–8% water;
- uniaxial pressing (40 MPa) of 110 mm × 55 mm × 6 mm tiles;
- drying in an electric oven at 105 ± 5 °C overnight;
- firing in an electric roller kiln at maximum temperature ranging from 1180 to 1220 °C with a thermal cycle of 51 min cold-to-cold.

Technological properties were investigated on powders and slips as well as on unfired and fired tiles. It has to be pointed out that particular attention is necessary during the treatment of the

Table 2
Chemical composition of raw materials

wt.%	Ball clay	Quartz sand	K–feldspar	Na–feldspar	Cathodic tube glass (C)	Screen glass (S)
SiO_2	58.0	94.5	67.6	69.2	51.6	62.7
TiO_2	1.5	0.1	0.0	0.2	0.1	0.4
ZrO_2	<0.1	<0.1	<0.1	<0.1	0.2	1.9
Al_2O_3	27.0	3.1	18.0	18.6	3.6	2.3
Fe_2O_3	0.9	0.2	0.1	0.1	0.1	0.1
Sb_2O_3	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
B_2O_3	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
MgO	<0.1	0.2	0.3	0.1	1.9	0.3
CaO	<0.1	0.1	0.1	0.6	3.8	1.0
ZnO	<0.1	<0.1	<0.1	<0.1	0.1	0.2
SrO	<0.1	<0.1	<0.1	<0.1	0.7	7.6
BaO	<0.1	<0.1	<0.1	<0.1	0.8	8.4
PbO	<0.1	<0.1	<0.1	<0.1	23.1	0.4
Na_2O	0.2	0.1	2.8	10.4	6.1	7.4
K_2O	0.2	1.5	10.8	0.2	7.5	7.1
Li_2O	<0.1	<0.1	<0.1	<0.1	0.1	0.1
L.O.I.	7.4	0.4	0.3	0.5	<0.1	<0.1

Table 3
Technological properties of semi-finished products

Product	Property	V0	VC5	VC10	VS5	VS10	VCS5
Slip	Water content (wt.%)	65.4 ± 0.2	65.5 ± 0.2	65.4 ± 0.2	65.3 ± 0.2	64.6 ± 0.2	64.8 ± 0.2
	Weight/volume (g/cm³)	1.65 ± 0.01	1.64 ± 0.01	1.65 ± 0.01	1.66 ± 0.01	1.63 ± 0.01	1.63 ± 0.01
Powders	Median particle size (μm)	2.8 ± 0.1	3.0 ± 0.1	3.3 ± 0.1	2.7 ± 0.1	3.1 ± 0.1	3.2 ± 0.1
	Working moisture (wt.%)	7.6 ± 0.1	8.0 ± 0.1	7.4 ± 0.1	7.3 ± 0.1	7.2 ± 0.1	7.3 ± 0.1
	Specific weight (g/cm³)	2.63 ± 0.01	2.63 ± 0.01	2.65 ± 0.01	2.63 ± 0.01	2.63 ± 0.01	2.62 ± 0.01
Dry tiles	Bulk density (g/cm³)	1.96 ± 0.01	1.96 ± 0.01	1.95 ± 0.02	1.94 ± 0.01	1.93 ± 0.01	1.94 ± 0.01
	Total porosity (vol.%)	25.2 ± 0.1	25.5 ± 0.1	26.2 ± 0.1	26.3 ± 0.1	26.7 ± 0.1	26.0 ± 0.1
	Drying shrinkage (cm/m)	0.42 ± 0.05	0.38 ± 0.04	0.45 ± 0.02	0.38 ± 0.05	0.42 ± 0.05	0.45 ± 0.03
	Modulus of rupture (MPa)	2.4 ± 0.3	2.7 ± 0.3	2.4 ± 0.5	3.5 ± 0.5	3.4 ± 0.3	2.9 ± 0.6

cathodic tube wastes, because a rubber layer, usually present as antielectrostatic coating, could influence the rheological behaviour and, in particular, the slip viscosity.

Slips were characterized by measuring their weight/volume and water content by the gravimetric method, while particle size distribution (ASTM C958) and moisture content (ASTM C324) were determined on powders. Bulk density (BD) (ASTM C329), drying shrinkage (ASTM C326) and 3-point flexural strength (ISO 10545-4) were measured on dry tiles.

All the fired samples were characterized through the determination of firing shrinkage (ASTM C326), water absorption, open porosity (OP) and bulk density (ISO 10545-3) and 3-point flexural strength (ISO 10545-4); specific weight (SW) and total porosity (TP) of both fired and unfired tiles were evaluated by He pycnometry (Micromeritics MVP 1305) and by the equation: $TP = [1 - (BD/SW)] \times 100$. The closed porosity (CP) was calculated by the difference: $CP = TP - OP$. CIE-Lab colourimetry (ISO 10545-16, Hunterlab MSXP-4000) of sintered tiles was also performed; the chromatic difference between the reference body and the waste-added samples was expressed as: $\Delta E^* = (\Delta L^* + \Delta a^* + \Delta b^*)$, where ΔL^*, Δa^*, and Δb^* are the difference of the CieLab parameters L^*, a^* and b^*.

Leaching tests (DIN 38414-S4) were performed on both types of waste glasses (C and S) and on the samples fired at 1200 °C in order to evaluate the inertization degree of waste glasses achieved into the ceramic matrix.

The phase composition of stoneware tiles was quantitatively determined by XRPD (Rigaku Miniflex, Cu Kα radiation, 10–80° 2θ range, 0.02° stepscan) using the RIR method with CaF_2 as internal standard. The experimental error is within 5%.

The chemical composition of the glassy phase was calculated on the basis of bulk chemistry and phase composition of the tiles, allowing the calculation of viscosity and surface tension of the liquid phase at high temperature [16,17].

The microstructure of the graphite-coated polished surface of V0, VC10 and VS10 samples, fired at 1220 °C, was also investigated through SEM micrographs obtained with a Leica Cambridge Stereoscan 360 microscope. The bulk chemical composition was assessed by XRF-EDS (Link—Analytical electron microprobe).

The sintering behaviour of waste-added bodies was evaluated by isothermal (heating rate 80 °C/min to 1100, 1125, 1150, 1175 and 1200 °C) and constant rate (40 °C/min up to 1200 °C, plus 5 min soaking) optical dilatometry analyses obtained by a hot stage microscope (Expert System, Misura 2), allowing to calculate kinetic parameters such as sintering rate and apparent energy of activation [18–20].

3. Results and discussion

3.1. Semi-finished products

Slip properties and particle size distribution (Table 3 and Fig. 1) of all waste glass-added mixtures (VC, VS and VCS) are quite similar to those of the waste-free one (V0), complying with the latest requirements of the industrial practice. However, the median particle diameter slightly increases with the glass percentage, leading to the conclusion that the waste presence could somehow affect the grindability of porcelain stoneware bodies. An interference of soda–lime glass with slip rheology was effectively observed in porcelain stoneware bodies [6,7]. It is possible that the slightly coarser particle size distribution of cathodic glass-bearing bodies is due to the occurrence of rubber particles from the tube coating.

On the other hand, VC, VS and VCS semi-finished tiles present a slightly higher porosity (and a lower bulk density) than V0, with exception of the VC5 sample, whose data are practically unchanged with respect to the waste-free body. This circumstance can be probably explained by the higher working moisture of both V0 and VC5, that ensures a better powder
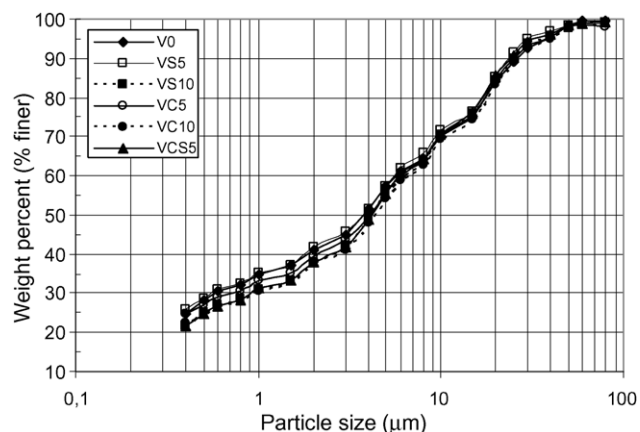

Fig. 1. Particle size distribution of porcelain stoneware bodies.

compaction during pressing [8]. However, the slightly lower compaction degree of the VS bodies can be possibly ascribed to their different behaviour during pressing connected with their finer particle dimensions.

As already observed in the literature [8–11], mechanical resistance of dry tiles is improved by the recycled glass, especially when the screen glass S is added, though the trend does not correspond to the porosity differences. Probably, glass addition promotes local microstructural modifications, not detected by the measurements of a global property such as porosity, but which are able to enhance the product performance as a result of internal residual stresses.

On the whole, the characterization of the waste-added semi-finished products highlights their good technological and mechanical properties, which allow them to provide performances similar to those of the reference industrial bodies.

3.2. Firing behaviour

Waste glass-added porcelain stoneware bodies behave in a different way during the firing cycle (Table 4). Generally, in the presence of waste glass C, the maximum shrinkage is shifted towards lower temperature. In particular, VC5 and VC10 bodies reach their maximum densification already at 1180 °C, while their structural coarsening begins just above this temperature. Moreover, with increasing of the waste glass percentage, the coarsening rate becomes very fast, as can be detected comparing the VC10 firing shrinkage at 1200 and 1220 °C.

The maximum densification temperature, the linear shrinkage and the kinetic pattern of the VS bodies depend on the waste glass percentage: VS5 presents the maximum densification degree at 1200 °C, while VS10 is still contracting at 1220 °C;

moreover, in the 1180–1200 °C range, the presence of a higher amount of waste glass seems to promote the body densification. The behaviour of VCS5, which presents the highest shrinkage at 1200 °C and the beginning of coarsening just after this temperature, is an average of that shown by the bodies containing the two types of glass.

As far as water absorption and open porosity are concerned, at 1220 °C all bodies present about the same value, but with a different trend from 1180 up to 1220 °C due to their different densification kinetics. At 1200 °C, the porosity of the VC bodies is essentially made up of closed pores, while, at the same temperature, the VS bodies still preserve a residual amount of open porosity. Generally, total porosity of waste-added samples is higher than the value presented by the V0 samples; besides, total porosity is higher in VS than in VC samples. The trend of bulk density is consistent with these conclusions, even if a small contribution to the higher density values of VC samples should be attributed to the presence of PbO.

The above mentioned circumstances are further confirmed by the analysis of the SEM micrographs of Fig. 2, obtained on samples fired at 1200 °C. The presence of spherical closed porosity in the VC10 sample clearly stands out, being the result of structural coarsening already under way at this temperature. In addition, the irregular morphology of the porosity present in VS10 testifies that at 1200 °C, in agreement with the firing shrinkage values, the densification is still in progress and that, notwithstanding that porosity is practically completely closed, the bloating phenomenon has not yet started.

The highest values of flexural strength do not belong to samples fired at the maximum temperature, but, in agreement with the densification pattern, the mechanical strength reaches its maximum at 1180 °C in the VC series and at 1200 °C in VS

Table 4
Technological properties of porcelain stoneware tiles

| Body	Firing temperature (°C)	Firing shrinkage (cm/m)	Water absorption (wt.%)	Open porosity (vol.%)	Closed porosity (vol.%)	Total porosity (vol.%)	Bulk density (g/cm³)	Modulus of rupture (MPa)	Color CIE-Lab			
									L^*	a^*	b^*	ΔE^*
V0	1180	6.5 ± 0.1	1.5 ± 0.1	3.5 ± 0.2	3.4 ± 0.3	6.9 ± 0.7	2.36 ± 0.01	49.6 ± 2.0	80.4 ± 0.1	2.4 ± 0.1	11.6 ± 0.1	ref.
	1200	6.8 ± 0.1	0.3 ± 0.1	0.7 ± 0.1	2.2 ± 0.2	2.8 ± 0.3	2.41 ± 0.01	49.9 ± 0.9	78.3 ± 0.1	2.0 ± 0.1	12.5 ± 0.1	ref.
	1220	6.8 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	1.5 ± 0.2	1.7 ± 0.2	2.41 ± 0.01	41.5 ± 9.2	76.8 ± 0.1	0.7 ± 0.1	12.5 ± 0.1	ref.
VC5	1180	7.1 ± 0.2	0.3 ± 0.1	0.6 ± 0.2	3.6 ± 0.4	4.2 ± 0.4	2.41 ± 0.01	48.9 ± 1.7	77.6 ± 0.1	2.2 ± 0.1	13.5 ± 0.1	3.3 ± 0.1
	1200	7.0 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	2.8 ± 0.3	2.9 ± 0.3	2.41 ± 0.01	45.8 ± 0.7	75.9 ± 0.1	1.7 ± 0.1	13.4 ± 0.1	2.6 ± 0.1
	1220	6.7 ± 0.1	0.05 ± 0.02	0.1 ± 0.1	3.0 ± 0.3	3.1 ± 0.3	2.37 ± 0.01	35.3 ± 8.3	76.6 ± 0.1	0.3 ± 0.1	14.4 ± 0.1	1.4 ± 0.1
VC10	1180	7.0 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	4.2 ± 0.4	4.3 ± 0.4	2.42 ± 0.01	49.9 ± 0.3	75.9 ± 0.1	2.1 ± 0.1	14.3 ± 0.1	5.3 ± 0.1
	1200	6.8 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	5.3 ± 0.5	5.4 ± 0.5	2.37 ± 0.01	41.4 ± 0.9	75.6 ± 0.1	1.6 ± 0.1	14.3 ± 0.1	3.3 ± 0.1
	1220	6.0 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	6.0 ± 0.6	6.1 ± 0.6	2.31 ± 0.01	31.0 ± 6.3	77.4 ± 0.1	0.3 ± 0.1	13.7 ± 0.1	1.4 ± 0.1
VS5	1180	6.4 ± 0.1	1.9 ± 0.2	4.5 ± 0.4	3.5 ± 0.4	7.9 ± 0.8	2.33 ± 0.01	43.3 ± 1.6	81.3 ± 0.1	2.2 ± 0.1	11.7 ± 0.1	0.9 ± 0.1
	1200	7.2 ± 0.1	0.4 ± 0.1	0.9 ± 0.2	3.6 ± 0.4	4.5 ± 0.5	2.39 ± 0.01	48.5 ± 0.7	79.3 ± 0.1	1.6 ± 0.1	13.1 ± 0.1	1.2 ± 0.1
	1220	7.0 ± 0.2	0.05 ± 0.02	0.1 ± 0.1	2.4 ± 0.2	2.5 ± 0.3	2.40 ± 0.01	40.7 ± 7.5	75.9 ± 0.1	0.5 ± 0.1	12.9 ± 0.1	1.0 ± 0.1
VS10	1180	5.1 ± 0.1	3.4 ± 0.4	7.6 ± 0.7	4.5 ± 0.5	12.1 ± 0.9	2.24 ± 0.02	36.9 ± 2.2	84.2 ± 0.1	1.9 ± 0.1	11.9 ± 0.1	3.9 ± 0.1
	1200	6.3 ± 0.1	1.4 ± 0.2	3.2 ± 0.4	4.4 ± 0.4	7.6 ± 0.8	2.32 ± 0.01	43.8 ± 0.6	76.7 ± 0.1	1.8 ± 0.1	12.3 ± 0.1	1.6 ± 0.1
	1220	7.0 ± 0.2	0.05 ± 0.01	0.1 ± 0.1	3.7 ± 0.4	3.8 ± 0.4	2.38 ± 0.01	34.9 ± 13.9	76.4 ± 0.1	0.4 ± 0.1	14.2 ± 0.1	1.8 ± 0.1
VCS5	1180	6.4 ± 0.1	1.1 ± 0.2	2.6 ± 0.4	5.0 ± 0.5	7.6 ± 0.8	2.33 ± 0.01	42.0 ± 1.3	78.3 ± 0.1	2.0 ± 0.1	13.7 ± 0.1	2.9 ± 0.1
	1200	7.2 ± 0.2	0.1 ± 0.1	0.2 ± 0.1	4.1 ± 0.4	4.3 ± 0.4	2.34 ± 0.01	48.4 ± 1.3	75.5 ± 0.1	1.7 ± 0.1	14.3 ± 0.1	3.4 ± 0.1
	1220	6.7 ± 0.1	0.04 ± 0.03	0.1 ± 0.1	4.6 ± 0.5	4.7 ± 0.5	2.35 ± 0.01	38.9 ± 1.5	76.5 ± 0.1	0.5 ± 0.1	13.8 ± 0.1	2.0 ± 0.1
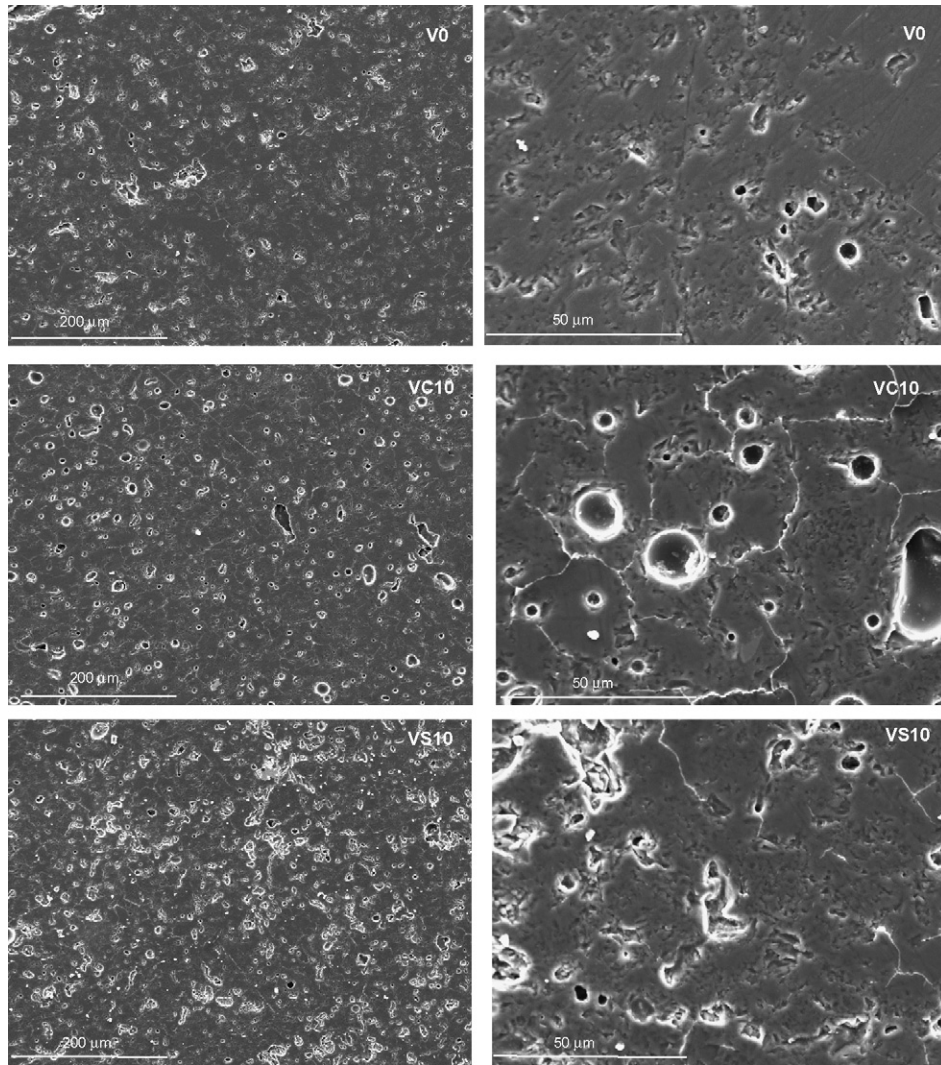
Fig. 2. SEM micrographs of the V0, VC10 and VS10 samples, fired at 1200 °C.

samples. Generally, the mechanical strength of fired tiles is lowered by the presence of the recycled glasses; however, all waste glass-added samples show values of modulus of rupture fulfilling the standard requirements (>35 MPa).

Waste glass additions also induced some small variations of colour (Table 4); ΔE^*, expressing the total chromatic change with respect to the reference body, decreases with the firing temperature, being almost negligible in the highly vitrified bodies. The main changes concern the L parameter: all bodies were progressively darker for increasing firing temperature, with the glass-bearing samples exhibiting slightly higher values of both a^* and b^*.

In order to evaluate the lead inertization into the ceramic matrix, a SEM-EDS investigation on VC5 and VC10 samples, fired at 1200 °C, was performed. The EDS analyses revealed the residual presence of PbO in VC5 and VC10 in percentage of 0.96 and 2.02, respectively.

Considering the waste-added amount and its contribution to the PbO fraction (100% cathodic tube glass = about 10 mg/kg, i.e. 10% = 1 mg/kg versus 0.7 mg/kg of the body VC10), it is

confirmed that a value between 20% (VC10) and 30% (VC5) of PbO is lost during firing, corresponding to approximately 0.2 and 0.3 wt.%. According to the leaching test results (Table 5) a quite complete inertization of lead into the ceramic matrix can be confirmed.

Table 5
Amount of lead from the two different glass typologies and samples fired at 1200 °C

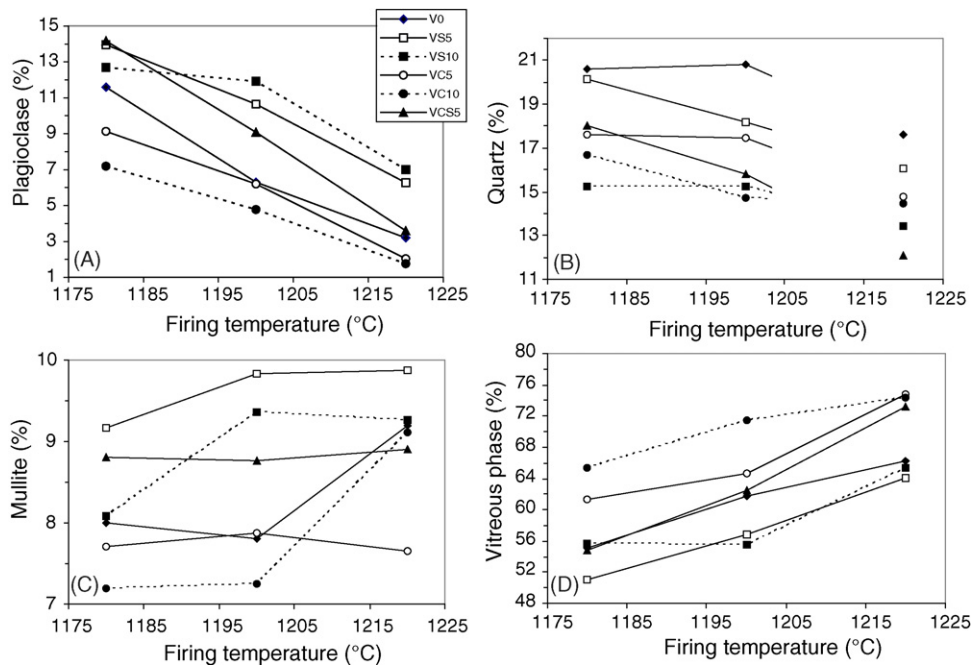| Body	Pb in the fired product (EDS) (mg/kg)	Leached Pb (DIN 38414-4) (mg/kg)
V0	–	<0.10
VC5	8900	0.37
VC10	18800	0.71
VS5	–	<0.10
VS10	–	<0.10
VCS5	–	0.23
Cathodic tube glass	–	9.97
Screen glass	–	0.22

Fig. 3. Quantitative phase analyses of the ceramic tiles: (A) plagioclase; (B) quartz; (C) mullite; (D) vitreous phase.

3.3. Phase composition

A typical porcelain stoneware is composed of quartz, mullite and plagioclase embedded in a very abundant glassy phase. The trends of quantitative phase analyses of the ceramic tiles are shown in Fig. 3.

As the firing temperature increases, plagioclase (Fig. 3(A)) melts very quickly, following a similar trend for all compositions, with a dissolution rate which seems to be a little bit lower in the VS10 sample. Considering the amount of plagioclase with respect to the reference body V0 in the 1180–1220 °C range, it is always present in higher concentration in the VS samples and lower in the VC sample, with VCS5 presenting an intermediate content.

The amount of quartz in VS5 and VCS5 samples steadily decreases when temperature change between 1180 and 1220 °C, while, in the case of VC5 and VS10 samples, its dissolution starts just above 1200 °C (Fig. 3(B)); this latter behaviour also belongs to the reference sample, in which the total amount of quartz is always higher than that in the modified bodies. For both VC and VS products, in fact, the presence of recycled glass from 5 to 10% progressively reduces the total amount of quartz.

The mullite content (Fig. 3(C)) does not significantly change when temperature increases from 1180 to 1220 °C in all samples, even if a different influence of the waste glass typology on mullite amount may be detected. Waste glasses C and S bring about, respectively, the occurrence of a lower or a higher amount of mullite when compared to the V0 sample.

The glassy phase (Fig. 3(D)) increases regularly with firing temperature, with VC and VS samples showing the highest and the lowest content, respectively. The total amount of vitreous phase is proportional to the waste glass percentages just in samples VC and for firing temperatures up to 1200 °C. In the

other cases, a similar quantity of glassy phase is developed independently of the waste amount.

Overall, the presence of waste glasses C and S brings about a modification of the crystalline/glassy phase ratio:

- The screen glass involves the persistence of mullite (9–10%) at temperatures of 1200–1220 °C, independently of its relative amount in the starting formulation. The residual amount of plagioclase (8–9%) is larger when compared with all the other formulations, while the quartz dissolution rate seems to be lowered by increasing the waste glass percentage. On the contrary, a lowest quantity of glassy phase is developed.
- The cathodic tube glass is the most effective in promoting the formation of glassy phase, mainly at expenses of plagioclase, whose dissolution is practically complete at 1200 °C; its occurrence brings about a lower amount of mullite, but for VC10 at 1220 °C, while an intermediate content of quartz is detected.
- The trends shown by the mineralogical transformations of VCS5 seem to confirm the opposite effect exerted by C and S glasses, resulting often in an averaged behaviour.

The chemico-physical properties of the glassy phase, summarized in Table 6, vary according with the firing temperature, and the percentage and typology of waste glasses. In particular, when recycling glass is present, the glassy phase becomes richer in SiO_2 and poorer in Al_2O_3, while Na_2O and K_2O content are, respectively, lower and higher. These chemical variations bring about different values of the liquid phase viscosity; generally, it decreases with glass additions, which is related to the progressive decrease of the Na_2O/K_2O ratio. Moreover, the influence of screen glass on these parameters seems to be the most effective.

Table 6
Chemical and physical properties of the glassy phase calculated at the different firing temperature

	V0[a]			VC5[a]			VC10[a]			VS5[a]			VS10[a]			VCS5[a]		
	1180[b]	1200[b]	1220[b]	1180[b]	1200[b]	1220[b]	1180[b]	1200[b]	1220[b]	1180[b]	1200[b]	1220[b]	1180[b]	1200[b]	1220[b]	1180[b]	1200[b]	1220[b]
SiO_2	66.7	67.1	69.5	67.1	66.4	68.3	66.2	67.1	69.1	67.0	68.7	69.8	68.5	69.13	69.85	65.89	68.14	69.5
TiO_2	1.2	1.1	1.1	1.1	1.1	1.0	1.0	1.0	0.9	1.3	1.2	1.1	1.2	1.2	1.1	1.3	1.1	1.0
Al_2O_3	22.7	22.3	19.9	20.5	21.2	19.9	19.6	18.9	17.0	20.5	19.3	18.2	18.2	17.3	17.3	19.2	18.2	17.2
Fe_2O_3	0.8	0.7	0.7	0.7	0.7	0.6	0.6	0.6	0.6	0.8	0.7	0.7	0.7	0.7	0.6	0.8	0.7	0.6
MgO	0.1	0.1	0.1	0.3	0.2	0.2	0.4	0.4	0.4	0.1	0.1	0.1	0.2	0.2	0.1	0.3	0.3	0.2
CaO	0.3	0.3	0.3	0.6	0.6	0.5	0.8	0.8	0.8	0.4	0.4	0.4	0.4	0.4	0.4	0.7	0.6	0.6
SrO	–	–	–	0.1	0.1	0.1	0.1	0.1	0.1	0.7	0.6	0.6	1.2	1.3	1.14	0.8	0.6	0.6
BaO	–	–	–	0.1	0.1	0.1	0.1	0.1	0.1	0.8	0.7	0.7	1.4	1.4	1.2	0.8	0.7	0.7
PbO	–	–	–	1.5	1.5	1.3	3.0	2.9	2.8	0.1	0.1	0.1	0.1	0.1	0.1	1.7	1.5	1.4
Na_2O	5.9	6.2	6.4	5.4	5.7	5.6	5.0	5.2	5.4	5.4	5.5	5.7	4.8	4.9	5.2	4.9	5.1	5.3
K_2O	2.4	2.2	2.1	2.8	2.7	2.4	3.1	3.0	2.9	3.1	2.8	2.7	3.4	3.4	3.1	3.8	3.2	3.0
Viscosity (kPa s)	8.4	5.8	3.2	5.7	5.2	4.5	4.5	5.0	2.1	5.9	3.5	2.6	4.3	2.9	2.4	4.4	3.9	2.2
Surface tension (mN/m)	335	334	328	332	333	329	331	329	324	330	327	325	325	323	322	328	326	323

[a] wt.%.
[b] T (°C).

The surface tension of the liquid phase, which in turn indicates its wetting capacity, is lowered by the waste glass additions, even if there are no significant variations with the amount and typology of glasses.

3.4. Sintering behaviour

Constant rate optical dilatometry, showing the dimensional variations as a function of the temperature (Fig. 4), indicates that the body densification by viscous flow starts at different temperatures, following different sintering kinetics: the reference body begins to densify at 1020 °C, while the presence of glass lowers this temperature to 980–990 °C (5 wt.% addition) and 950–960 °C (10 wt.% addition), with the lowest values achieved with the glass C (Fig. 4(B)).

The sintering rate of porcelain stoneware tiles is more clearly detected by the isothermal curves of Fig. 5, where the dimensional variations have been contrasted with the elapsed time. It is somehow affected by the different recycled glass amount and typology: at 1200 °C, which is the typical industrial firing temperature of porcelain stoneware, the VC5, VS5 and VCS5 samples reach the maximum densification in a few minutes, while the densificaton rate of the VS bodies is slower. In any case, shrinkage values are about 8–10%. The presence of a higher amount of glass wastes reduces the final shrinkage and/ or causes an elongation of the time necessary to achieve the same densification degree. Moreover, once the maximum densification degree is reached, VC and VS samples show an inversion of their sintering curves, with the consequent decrease of density due to a bloating phenomenon, which in turn is directly linked to the waste glass amount.

The sintering rate, calculated as the volumetric dimensional variation per unit time, obviously increases with the firing temperature, but has a different trend for the two glass
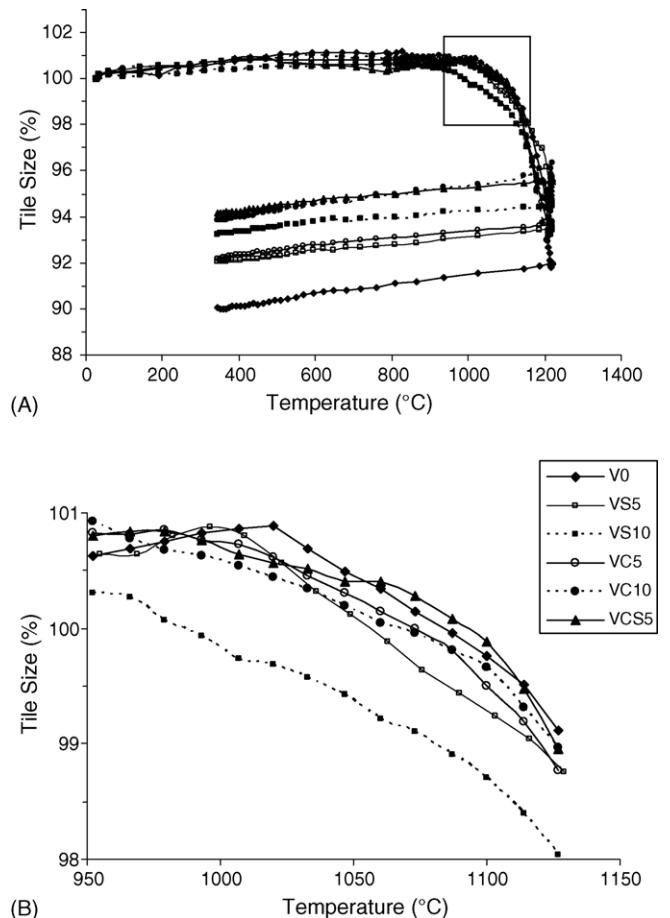

Fig. 4. Firing behaviour of the porcelain stoneware bodies in an industrial-like cycle (A); particular of the beginning of densification (B).
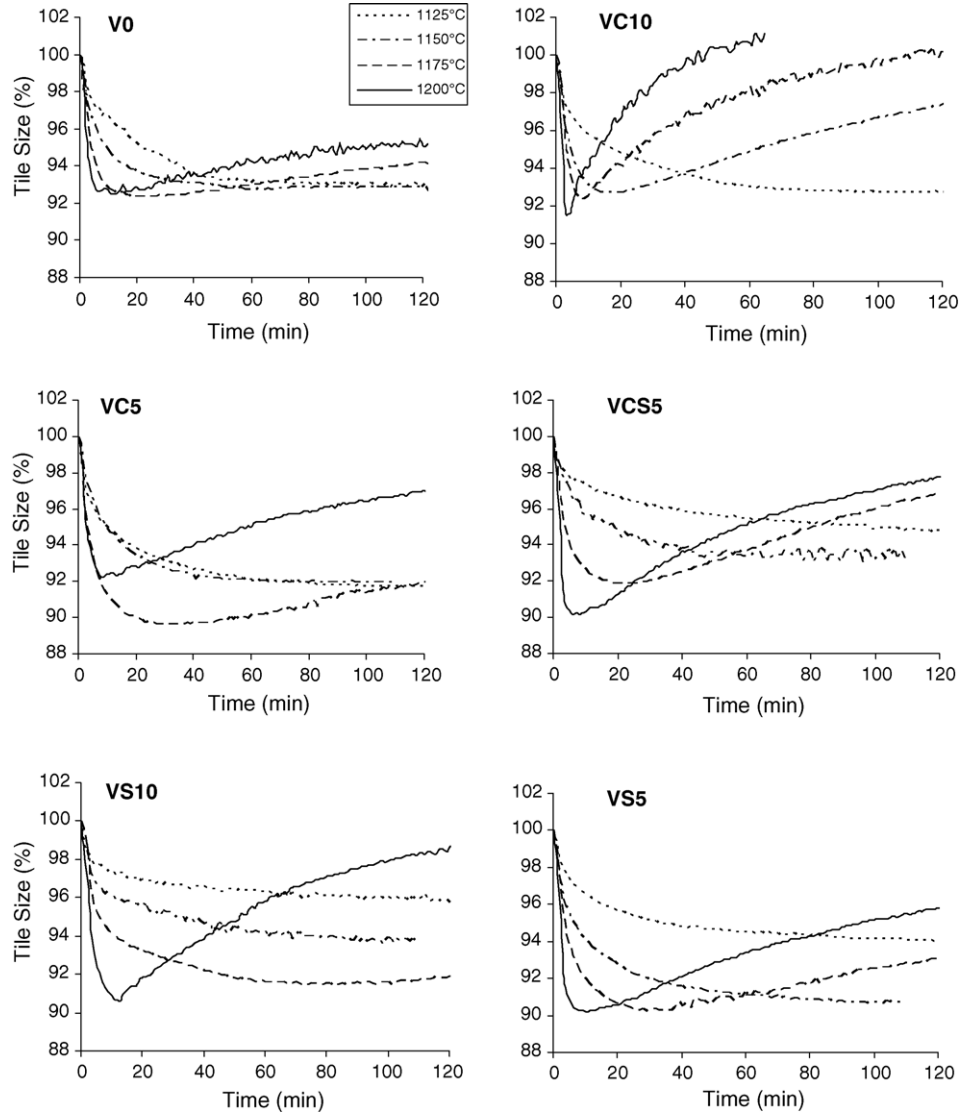
Fig. 5. Isothermal curves (heating rate 80 °C/min to 1125, 1150, 1175, 1200 °C) of porcelain stoneware bodies.

typologies (Table 7): while glass C improves the sintering rate, especially when present at the lower percentage, glass S has a moderate effect and, at temperatures up to 1175 °C, does not significantly change the sintering kinetics.

The addition of waste glasses induces a modification of the apparent energy of activation E_a, which is connected with the added amount (Table 7). According to these values, both cathodic and screen glasses at the lower percentage help the

Table 7
Shrinkage, sintering rate and apparent energy of activation of porcelain stoneware tiles

Parameter	Temperature (°C)	Sample					
		V0	VC5	VC10	VS5	VS10	VCS5
Linear shrinkage at maximum densification (cm/m)	1125	7.10	3.10	2.10	7.15	7.35	4.30
	1150	7.30	7.15	6.30	7.25	8.50	10.10
	1175	8.25	8.25	9.20	8.30	7.15	10.15
	1200	8.30	10.30	10.30	8.40	10.50	10.20
Sintering rate (min^{-1})	1125	2.4	2.9	2.4	2.3	1.9	1.7
	1150	2.9	5.1	3.7	3.1	3.0	2.1
	1175	4.0	4.5	4.5	4.2	4.2	4.0
	1200	4.0	7.0	5.6	5.8	4.5	5.2
Apparent energy of activation E_a (kJ/mol)		1241	861	1576	1078	2148	2169

sintering kinetics through the lowering of the E_a. However, when their amount is 10 wt.%, and especially for waste glass S, a noticeable increase of E_a is observed. In the case of glass S, this is consistent with the densification behaviour previously described, while the E_a value calculated for the VC10 sample is higher than expected on the basis of its densification pattern. For this purpose, some other factors, not easily identifiable at this stage, might play a significant role.

4. Conclusions

TV/PC cathodic tube and screen glasses, added to a typical porcelain stoneware body, are able to partially replace the conventional industrial fluxes, without significant impact on the technological process. The waste glass, however, affects in some way the compositional properties and the firing behaviour of the porcelain stoneware bodies. Nevertheless, the addition of these glasses ensures technological and mechanical performance similar to those of reference industrial bodies.

As far as the inertization of hazardous elements is concerned, some PbO is lost during firing (0.2–0.3 wt.%) and little after firing (<0.7 mg/kg).

The waste glass C is able to shift the temperature of maximum shrinkage towards lower values (1180 °C), with a greater influence on the sintering as shown by the amount of glassy phase of the added bodies.

The activation energy of the sintering process is lowered by the presence of both glasses at the percentage of 5 wt.%, while the liquid phase viscosity of the waste-bearing bodies generally decreases with glass additions.

Overall, the presence of both types of recycled glasses is able to positively affect the technical and physical properties of the glass added bodies, as a result of a modification of their sintering behaviour.

References

[1] J.M. Hermans, J.G. Peelen, J.R. Bei, Recycling of TV glass: profits or doom? Ceram. Eng. Proc. 2 (2001) 27–37.

[2] N. Menad, Cathode ray tube recycling, Resources Conserv. Recycling 26 (1999) 143–154.

[3] S.C. Cramer, F. Schmidt, R. Clasen, S. Jasen, Recycling of TV-glass: problems and perspectives., Glastech. Ber. Glass Sci. Technol. 68 (C2) (1995) 191–196.

[4] Y. Lingart, Imitation of natural material tiling using waste glass, Glass Technol. 39 (2) (1998) 42–43.

[5] E. Rambaldi, A. Tucci, L. Esposito, Use of recycled materials in the traditional ceramic industry, Ceram. Int. 1–2 (2004) 13–23.

[6] R.V. Manukyan, N.S. Davydova, Use of waste in the ceramic industry, Glass Ceram. 53 (7–8) (1996) 247–248.

[7] I.W. Brown, K.J.D. Mackenzie, Process design for the production of a ceramic-like body from recycled waste glass. Part 1. The effect of fabrication variables on green strength, J. Mater. Sci. 17 (1982) 2164–2170.

[8] C. Carbonchi, P. Danasino, R. Lorici, R. Riveriti, Impiego di fondenti additivati con vetro in un impasto da grès porcellanato, Ceramica Informazione 426 (2003) 580–587.

[9] F. Matteucci, M. Dondi, G. Guarini, Effect of soda–lime glass on sintering and technological properties of porcelain stoneware tiles, Ceram. Int. 28 (2002) 873–880.

[10] A. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, Use of soda–lime scrap-glass as a fluxing agent in a porcelain stoneware mix, J. Eur. Ceram. Soc. 24 (2004) 83–92.

[11] E. Rambaldi, A. Tucci, L. Esposito, Glass recycling in porcelain stoneware tiles: firing behaviour, Process Eng. 81 (3) (2004) 32–36.

[12] A. Karamanov, M. Pelino, M. Slavo, I. Metekovits, Sintered glass-ceramics from incinerator fly ashes. Part II. The influence of particle size and heat-treatment on the properties, J. Eur. Ceram. Soc. 23 (2003) 1609–1615.

[13] A.R. Boccaccini, M. Bücker, P.A. Trusty, M. Romero, J.M. Rincón, Sintering behaviour of compacts made from television tube glasses, Glass Technol. 38 (4) (1997) 128–133.

[14] E.J. Minay, A. Minay, V. Desbois, A.R. Boccaccini, Innovative manufacturing technique for glass matrix composites: extrusion of recycled TV set screen glass reinforced with Al_2O_3 platelets, J. Mater. Process. Technol. 142 (2003) 471–478.

[15] E. Rambaldi, A. Tucci, E. Rastelli, L. Esposito, The use of waste glass as a raw material in porcelain stoneware tiles, in: Proceedings IV Congress VA.RI.REI., 2003, pp. 24–27.

[16] T. Lakatos, G. Johansson, B. Skimmingskold, Viscosity temperature relations in the glass system SiO_2–Al_2O_3–Na_2O–K_2O–CaO–MgO in the composition range of technical glasses, Glass Technol. 13 (1972) 88–95.

[17] F. Cambier, A. Leriche, Vitrification, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Materials Science Technology: A Comprehensive Treatment. Processing of Ceramics—Part II, vol. 17B, VCR Verlagsgesellschaft, Weinheim, 1996 , pp. 123–144 (Chapter 15).

[18] R.M. German, Sintering Theory and Practice, J. Wiley and Sons Inc., 1996 , pp. 225–250 (Chapter 6).

[19] Y.S. Cho, W. Schulze, Crystallization kinetics and properties of nonstechiometric cordierite based thick film dielectrics, J. Am. Ceram. Soc. 82 (11) (1999) 3186–3192.

[20] V.K. Singh, Sintering of calcium illuminate mixes, Br. Ceram. Trans. 98 (4) (1999) 187–191.