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Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production

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Abstract

In the present work, the feasibility to substitute feldspar raw material in a porcelain stoneware body with Panel Cathode Ray Tube (CRT) glass was investigated. A standard batch and a composition, where 35 wt.% Na-feldspar was substituted by CRT glass, were sintered at different temperatures in the range of 1000–1250 °C. The degree of the densification was studied by evaluation of the closed and total porosity, while the sintering rate was estimated by non-isothermal dilatometric measures. The variation of the crystalline phase composition was evaluated by XRD analysis. From the preliminary study other ceramic samples with different percentages of CRT glass (i.e. 2.5, 5 and 10 wt.%) were prepared and fired in industrial kiln. The sintering parameters, the microstructure and the mechanical properties were measured and compared with the standard composition.

Keywords: A. Sintering; B. Porosity; D. Traditional ceramics; CRT glass; Recycling

1. Introduction

The porcelain stoneware tile is a product having high aesthetical qualities and very good technical characteristics are obtained by fast single firing (35–45 min) at about 1200–1250 °C. It is used in larger quantities and in increasing application fields. The Italian production of this typology was 360 million of square meters in 2004 corresponding to 61% of the total tile production [1]. The porcelain stoneware tile shows specific characteristic: extremely low open porosity (WA% < 0.05%), a high abrasion resistance and improved mechanical properties [2–4].

Porcelain stoneware bodies are primarily composed of kaolin and kaolinitic clays, sodium and potassium feldspars and quartz, heat treated to form a mixture of glassy and crystalline phases. The clay-based minerals are the main components (40–55 wt.%). They confer plasticity and workability in green state and furnish the main oxides involved, with fluxes and sintering aids, in the consolidation mechanism during firing. Feldspars and talc are to be considered as fluxing agents which provide, during firing, liquid phase with an adequate viscosity that will constitute the glassy structure of the final product. Quartz helps to balance the viscosity and has a structural function in the finished products. Chemical composition for the typical bodies can be presented graphically as a portion of the (Na_2O, K_2O)–Al_2O_3–SiO_2 plot [5]. Among the above-mentioned raw materials, the feldspar is the most expensive and therefore its replacement would represent a significant reduction in final costs.

During firing the main part of crystalline phases corresponding to the minerals by the green body disappear and are replaced by new amorphous and crystalline phases. Most of these reactions are kinetically governed and since the industrial firing cycle is very short they do not reach thermodynamic equilibrium. Hence, it is very common for the finished porcelain stoneware to contain residual crystalline phases of quartz and feldspars that have not been entirely transformed.

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The plastic clay components disappear completely during firing to form mullite crystalline phase ($3Al_2O_3{\cdot}2SiO_2$).

The cathode ray tube of TV or PC monitor is composed of 85% CRT glass, which is possible to be separate and cleaned by using different suitable techniques. Recycling techniques for metals, plastics, and the other electronic components already exist, while the utilization of end of life (EOL) CRT glass is quite problematic. This is due to the fact that CRTs are normally made of several glass components divided into four typologies (screen or panel, cone or funnel, neck and frit junction), each of them with a different chemical composition and properties [6]. Glasses as cone and neck contain principally lead an other dangerous elements instead panel glass has other heavy metals (Ba, Sr, etc.) that forbid their recycling in the glass industry for the production of containers, domestic glassware and glass fiber. For these reasons, there is an increasing urgency to develop new applications for CRT glass in agreement with Directives 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS), and 2002/96/EC and 2003/108/EC on waste electrical and electronic equipment (WEEE). There is also growing concern about the environmental impact of disposing CRTs in landfill sites due to the presence of hazardous elements in the glass.

In this work, it has been tested the feasibility of panel glass to act as alternative material to replace partially the feldspar in the porcelain stoneware body, as demonstrated by other authors but with different kinds of minerals (nepheline, syenite, feldspatic rocks, zeolites, ...) or cullet glass (soda-lime float and container glass) [7–10]. This opportunity derives from both the CRT glass chemical composition rich in alkali and alkali earth oxides (about 14 and 20 wt.%, respectively) and the feature of porcelain material to develop a high glassy phase amount in the end ceramic product (60–70%). In particular, in the paper, the results on the sintering process and on the technological and mechanical properties (as water absorption, apparent density, linear shrinkage and Young' modulus) are discussed.

2. Experimental procedure

2.1. Materials

Cleaned CRT panel glass (washed and without coatings) coming from the dismantling of TV and PC kinescopes was used for this research. The as-received glass, undergo to leaching test, has presented heavy metal released amounts (0.006 and 0.003 ppm for barium and lead, respectively) within the Italian regulation limits (1 and 0.05 ppm, for barium and lead, respectively) according to DM 186/06 All. 3. A traditional porcelain stoneware ceramic body was considered as matrix to obtain ceramic tiles.

For the as-received CRT glass, a dry grinding for 8 h in a slow laboratory ball mill was necessary and the glass powder obtained was sieved at 63 μm. The ceramic raw materials were dried in electrical oven at 110 °C for 24 h.

The chemical composition of the CRT panel glass (G), the raw materials and the batch bodies were performed by inductively coupled plasma (ICP-Varian Liberty 200) for the main elements. The mineralogical analysis was carried out by using a conventional Bragg-Brentano powder diffractometer (PW 3710, Philips Research Laboratories) with Ni-filtered Cu Kα radiation. The patterns have been recorded on the ground samples (<25 μm in size) in the 5–70° 2θ range (step size 0.02° and 1 s counting time for each step). In Table 1 the chemical and mineralogical analysis (wt.% oxide) are reported. C0 is the reference porcelain stoneware body. F-Na is sodium feldspar, K1 and K2 are kaolinitic clays, while S1, S2 and S3 are sands with some feldspars admixtures. Due to its relatively high K_2O percentage, S1 may be partially considered as a flux.

Table 1
Chemical composition (wt.% oxides) and crystalline phases of the raw materials and porcelain stoneware reference body

	G	F-Na	K1	K2	S1	S2	S3
SiO_2	61.2	68.2	58.9	68.2	77.2	84.1	80.9
Al_2O_3	2.6	18.8	27.1	25.6	12.9	8.8	9.8
Fe_2O_3	0.1	0.1	0.9	1.1	0.9	0.2	0.6
TiO_2	–	0.3	1.5	1.5	0.1	0.1	0.1
Na_2O	8.3	10.6	0.4	0.3	0.3	0.2	1.7
K_2O	5.6	0.3	2.0	2.7	6.9	3.8	3.0
CaO	1.1	1.1	0.3	0.2	0.1	0.7	1.5
MgO	0.8	0.2	0.5	0.4	0.1	0.2	0.2
BaO	10.0	–	–	–	–	–	–
SrO	8.8	–	–	–	–	–	–
L.O.I.	–	0.3	8.0	6.2	1.6	1.8	2.0
Phases	–	A,Q	K,Q,I,M	Q,K,I,M	Q,O,M	Q,M	Q,M

Q: quartz; K: kaolinite; I: illite; A: albite; M: mullite; O: orthoclase.

2.2. Ceramic samples preparation

Ceramics mixtures with constant amount of clays and different percentages of panel glass were prepared. In Table 2 the batch compositions are reported and compared with the commercial composition (C0). Each batch composition was prepared by wet-grinding: 100 g of the prepared mixture was suspended in 40 g of industrial water using 0.5 wt.% deflocculating agent and ground by a fast laboratory ball mill for 30 min to obtain a homogeneous slip. In order to prepare suitable press-powder, the slurries were dried at 110 °C, ground again and sieved below 63 μm. Thus obtained powders were humidified with 6 wt.% distilled water and pressed at 30 MPa (400 kg/cm^2) to prepare cylindrical samples (40 mm diameter, 5 mm thickness). C0 and C1 samples were sintered in laboratory furnace at 20 °C/min and 10 °C/min heating and cooling rates, respectively, and 10 min of soaking step at different temperatures. Series of 10 samples of C0, C2, C3 and

Table 2
Batch compositions of the all samples prepared

	G	F-Na	K1	K2	S1	S2	S3
C0	0	35	25	15	8	10	7
C1	35	0	25	15	8	10	7
C2	2.5	33	25	15	7.5	10	7
C3	5	31	25	15	7	10	7
C4	10	27	25	15	6	10	7

C4 compositions were fired in an industrial roller kiln, using 40 min cycle with maximum temperature at 1210 °C.

2.3. Characterization of samples

The sintering process was studied by dilatometric measurements (Netzsch 402 ED) at heating rate of 20 °C/min in the temperature range of 20–1300 °C. X-ray measurements of the all sintered samples were carried out and quantitative analysis was performed by combined Rietveld-Reference Intensity Ratio (R.I.R.) method. Data have been recorded in the 5–140° 2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-R.I.R. refinements, using GSAS software and EXPGUI as graphical interface [11,12] have been rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized.

The apparent, ρ_a, skeleton, ρ_s, and absolute, ρ_{as}, densities of all sintered samples were determined and the results were used to evaluate total, P_T, closed, P_C, and open P_O porosity:

$$P_T = 100 \times \frac{\rho_{as} - \rho_a}{\rho_{as}} \quad (1)$$

$$P_C = 100 \times \frac{\rho_{as} - \rho_s}{\rho_{as}} \quad (2)$$

$$P_O = 100 \times \frac{\rho_s - \rho_a}{\rho_{as}} \quad (3)$$

ρ_a was estimated by an Envelope Density Analyzer (GeoPyc 1360, Micromeritics) using a dry medium, while ρ_s and ρ_{as} by gas (He) pycnometer (AccyPy1330, Micromeritic) before and after crashing and milling the samples below 26 μm, respectively [13].

Microstructural studies of the samples were conducted by a scanning electron microscopy (SEM, Philips, XL 40) on superficially polished gold-coated specimens. For the industrial fired samples C0, C2, C3, C4 measurements of linear shrinkage (LS%), water absorption (WA%) according to ISO 10545-3, and apparent density were performed. The Young's modulus (E), shear modulus (G) in GPa and Poisson's ratio (ν) were determined by a Lemmens Grindosonic Electronika MK5 Ltd instrument using a non-destructive technique. The elastic modulus values were calculated using dimensions, shape and weight data samples running EMOD software program. This test meets the ASTM 1259 testing method for dynamic elastic modulus [14].

Colorimetric measures by UV–vis spectrophotometer (Perkin Elmer, Lambda 19) using CIELab* (Illuminant D65, Observer 10°) were performed on the fired samples. The L^*, a^*, b^*, ΔE^* parameters have been calculated by the Hunter method [15].

3. Results and discussion

The effect of panel glass addition on the porcelain stoneware was highlighted by completely substitution of the 35% Na-feldspar in the standard body. C0 and C1 compositions were sintered in laboratory furnace at different temperatures and ρ_a, ρ_s, and ρ_{as} were evaluated by pycnometric techniques. The P_T, P_C and P_O were calculated and their evaluated variations are shown in Figs. 1 and 2.

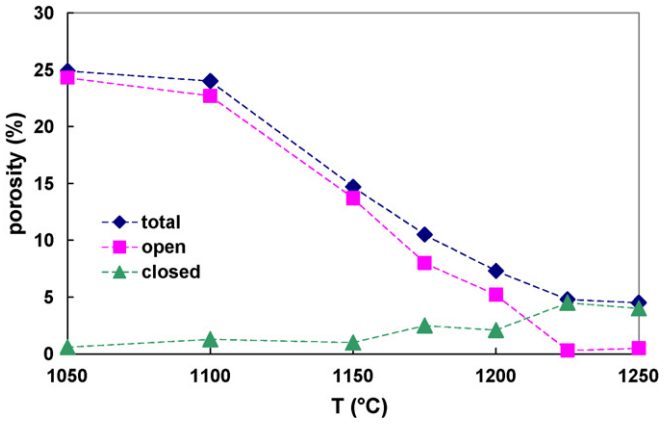

Fig. 1. P_T, P_C, and P_O porosities behaviour vs. temperature for laboratory fired sample (C0).

The reference C0 composition shows the follow sintering behaviour: the densification starts after 1100 °C (i.e. in the melting range of sodium feldspar); in the range of 1175–1225 °C total porosity decreases from 12 to 8% and, as a results, starts the transformation of open into closed porosity; at 1250 °C the porosity becomes practically only closed with value of about 4.5%. This trend is typical for the traditional ceramic materials [16].

At the same time C1 composition shows an unusual densification behaviour. The sintering process of C1 starts before than C0 and the open porosity at 1150 °C is practically eliminated. The formation of closed porosity however stars at 1100 °C when open porosity still has a too high value of 14%. Then P_C amount increases with the temperature reaching 18% at 1200 °C; as a result, the total porosity is always very high.

The abnormal sintering behaviour of C1 was confirmed by non-isothermal dilatometric experiments. Fig. 3 shows the obtained sintering plots of C0 and C1, while Fig. 4 demonstrates the corresponding sintering rate (i.e. the

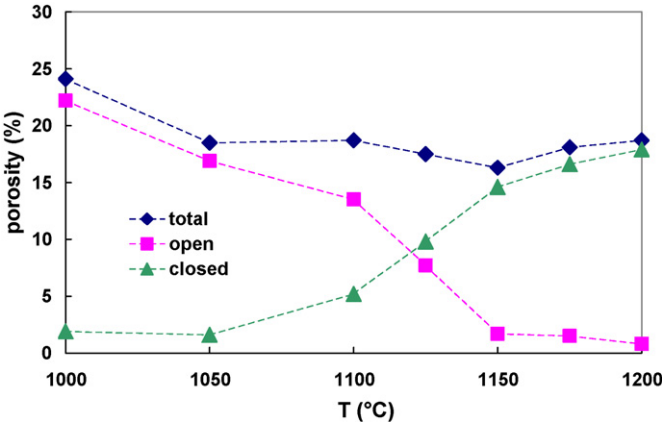

Fig. 2. P_T, P_C, and P_O porosities behaviour vs. temperature for laboratory fired sample (C1).

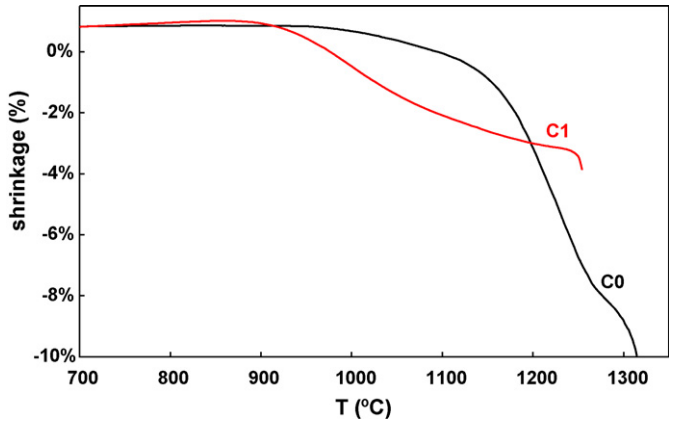

Fig. 3. Dilatometric sintering curves of C0 and C1 compositions.

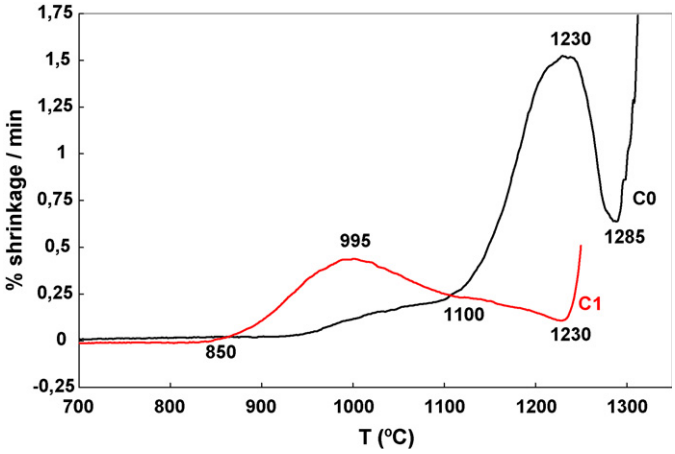

Fig. 4. Sintering rate curves of C0 and C1 compositions.

shrinkage derivatives). The traces of C0 highlight ~1% linear shrinkage, $\Delta L/L_0$, in the range 1000–1100 °C (caused by the phase transformations of methakaolinite [17,18], beginning of the sintering at 1100 °C and maximum densification rate at 1230 °C. Then, due to the load of the dilatometer push-rod on the sample, the increase of the amount of liquid phase and the decrease of its viscosity, at 1285 °C and at $\Delta L/L_0$ of about 8% starts the deformation of the sample.

Because of the relatively low viscosity of parent CRT glass, particularly enriched in alkali and alkali-earth oxides [19], the shrinkage in C1 starts at about 850 °C and $\Delta L/L_0$ of 1% is reached at 980 °C. Then, however, due to the intensive formation of closed pores, the shrink rate significantly decreases. At 1230 °C and at 3.5% $\Delta L/L_0$ starts the deformation of the sample. These results permits to say that using great amount of panel glass as fluxing agent a reduction on firing sintering temperature and sintering range is observed.

The formation of more closed porosity in C1 than in C0, is related to the presence of aboundand low viscosity glassy phase derived mainly from the panel glass. This glass trappes the gas (CO_2) developed, around 900–1000 °C, by the decomposition of the carbonates present inside the raw materials (sands, ~1%).

In order to confirms this hypothesis, an analysis of gassy phase trapped inside the body pores of C1 ceramic sintered at 1150 °C was performed. Series of three samples were crushed under vacuum at room temperature and the gas phases were evaluated by Mass spectrometer. The results: N_2: 70.7 ± 1.5%, CO_2: 21.2 ± 0.2%, O_2: 6.6 ± 0.9% and Ar: 0.9 ± 0.05 confirmed that the gas composition is similar to the air atmosphere in N_2 and Ar percentages, while the presence of CO_2 is related to the carbonates decomposition [16].

Table 3
Crystalline phase composition by quantitative Rietveld-R.I.R (%) for all samples

Phases	C0[a]	C1[a]	C0[b]	C2[b]	C3[b]	C4[b]
Quartz	17.6	10.7	22.7	21.0	19.8	18.5
Mullite	8.2	–	4.8	5.3	4.2	2.6
Albite	2.8	12.8	3.6	3.0	4.7	6.1
Ba-Orthoclase	–	16.3	–	–	–	–
Glassy	71.4	60.1	68.9	70.6	71.3	72.7

[a] Samples fired in laboratory furnace.
[b] Samples fired in industrial knil.

The XRD analysis of the C0 and C1 samples (sintered at 1250 and 1200 °C, respectively) highlight that the 35% CRT glass addition also modifies the phases composition of the fired samples. The results, presented in Table 3, show that C0 sample, sintered at 1250 °C, is composed of 71.4% glassy phase and quartz, mullite, albite (i.e. typical phase composition for a porcelain stoneware materials [2]), while in C1 sample the great amount of CRT panel glass provokes both a more effective melting of quartz (10.7% in C1 instead of 20.4% in C0) and the disappearance or dissolution of mullite in the ceramic material. In accordance with other authors [20] the formation of a new crystalline phase (16.3% Ba-orthoclase (ICDD #100182), derived from the reaction between the kaolinitc clays and the Ba-rich glass, was observed.

From this preliminary study was concluded that, due to intensive closed pore formation, the total replacement of feldspar with CRT panel glass is inappropriate for industrial application.

For this reason other compositions, where 2.5, 5 and 10 wt.% Na-F and S1 (K-F sand) were substituted by panel glass, were investigated. Table 4 reports the chemical analysis of C0, C2, C3 and C4 compositions and highlights that the ceramics with panel glass contain SiO_2, Al_2O_3, Na_2O and K_2O wt.%, similar to C0 std body together with small amounts (less than 1 wt.%) of SrO and BaO derived from waste glass.

The results were also used to theoretically verify the effect of the CRT glass introduction on several important technological parameters in the ceramic body formulation: (1) total amount of alkali ($Na_2O + K_2O$); (2) alkali ratio (Na_2O/K_2O); (3) total amount of cromophore oxides ($Fe_2O_3 + TiO_2$); (4) ratio SiO_2/Al_2O_3. The addition of waste glass increases the alkaline oxide quantity in the body (6.14–7.10%). The ratio sodium-potassium oxide decreases (1.87–1.72%), confirmed from the increase of the potassium oxide amount with respect to the standard mixture. The amount of cromophore oxides (TiO_2, Fe_2O_3) increases as a function of the glass introduced, but within an industrial tolerance (1.27–1.29%). The SiO_2/Al_2O_3 ratio increases as a function of the CRT glass amount added (3.49–3.72%).

Table 4
Chemical composition of the prepared bodies (wt.% oxides)

	C0	C1	C2	C3	C4
SiO_2	69.07	64.55	69.80	70.53	72.20
Al_2O_3	19.78	15.24	19.67	19.56	19.33
Fe_2O_3	0.55	0.52	0.55	0.55	0.55
TiO_2	0.73	0.72	0.73	0.74	0.75
Na_2O	4.00	4.33	4.13	4.26	4.51
K_2O	2.14	3.64	2.26	2.38	2.62
CaO	0. 67	0.76	0.70	0.72	0.77
MgO	0.29	0.65	0.32	0.35	0.41
P_2O_5	0.06	0.02	0.05	0.05	0.05
BaO	0.00	3.11	0.25	0.50	0.89
SrO	0.00	3.29	0.24	0.47	0.94
CoO	0.00	0.01	0.00	0.00	0.00
ZrO_2	0.00	0.63	0.05	0.01	0.18
ZnO	0.00	0.07	0.01	0.01	0.02
PbO	0.00	0.01	0.00	0.00	0.00
NiO	0.00	0.01	0.001	0.00	0.00
L.O.I.	3.50	3.40	3.50	3.50	3.50

The results of the sintering parameters, mechanical properties and P_T, P_C, P_O porosities for industrial fired samples, are summarised in Table 5.

The LS% and WA% values, as the function of the screen glass amount into the body, are in agreement with the apparent density values obtained by using the mercury immersion technique (Archimedes' method). It is observed that 2.5 wt.% of CRT glass leads to higher LS% value than the reference body, the introduction of 5 wt.% may be considered as a good result, while 10 wt.% addition causes a decrease of the shrinkage.

The water absorption is strictly related to the morphology materials and is proportional to the open porosity. The calculated P_O values permit to observe the positive effect of the CRT glass addition, since all compositions present lower P_O values than C0. The apparent density values indicate an enhancement of the densification process with the increase of glass amount into the body, in agreement with the total porosity data obtained (Eq. (1)). From these results it is evident that the glass presence in the body contributes to the sintering kinetic, in particular the increase of firing shrinkage and the decrease of the open porosity.

Table 5
Sintering parameters, mechanical properties and calculated total (P_T), open (P_O) and closed (P_C) porosities for the industrial fired samples C0, C2, C3, C4

	Sample (wt.% CRT glass)			
	C0 (0.0)	C2 (2.5)	C3 (5.0)	C4 (10.0)
LS (%)	7.67	7.85	7.60	7.34
WA (%)	0.017	0.002	0.003	0.006
Dap (g/cm^3)	2.38	2.40	2.40	2.39
Young' modulus (GPa)	70.64	72.60	71.78	68.65
Shear modulus (GPa)	29.5	30.22	29.7	28.45
Poison ratio, μ	0.19	0.20	0.20	0.21
P_T	6.02	4.92	4.99	5.36
P_C	4.67	4.28	4.26	4.51
P_O	1.35	0.64	0.73	0.85

The three compositions have similar mechanical characteristics, typical for the porcelain stoneware production [2]. C2 and C3 show better sintering degree and mechanical properties with respect to the standard one (i.e. decreasing of both open and closed porosity). In the same time, C4 shows lower mechanical properties than C0, lower open and similar closed porosity. The slight decrease of the properties of C4 probably is due to the higher amount of vitreous phase formed and to the increase of closed porosity. This assumption has been confirmed by the XRD and SEM results.

Table 3 summarizes the crystalline phase data, obtained by Ritveld -R.I.R. method. The quantitative analysis confirmed that the industrial fired reference sample (C0) contains mainly glassy phase, together with quartz, mullite and some residual Na-feldspar (albite). The addition of panel glass (up to 10 wt.%) does not change the crystalline phases present, but increases the amount of the vitreous phase due to more intensive dissolution of the quartz, similar behaviour to that reported in literature for soda lime glass [9,10,21]. In particular, the glass presence up to 5 wt.% does not obstruct the formation of mullite; for upper amounts an evident decrease is observed. This fact also may be connected with the less mechanical performance of C4 composition.

Fig. 5 shows SEM micrographs of surface polished C0, C3, C4 industrial fired samples. It is noticeable that, according to XRD and Rietveld-R.I.R. analysis, the addition up to 10 wt.% of CRT glass does not change the crystalline phases present and consequently the microstructure.

In the ceramic industry, the CIELab* method is the most utilized to determine the whiteness and the color of the tiles by measuring the three parameters L^* (brightness) from absolute white $L = 100$ to absolute black $L = 0$, a^* (red–green), b^* (yellow–blue) elaborated from the visible spectra [15]. The derived ΔE^* parameter indicates the shift respect to the standard. ΔE^* values lower than 1 are considered within the industrial tolerance.

From the results obtained on unglazed samples (Table 6), a decrease in L^* was observed as a function of the CRT panel glass content, while is evident an increase in the a^* and b^* Hunter parameters. Similar results relative only to L^* parameter were found by other authors using soda lime glass [9]; in this specific case the cause of darkening probably derived to the presence of Ni and Co (used to the screen functionality) in the chemical composition of the panel glass [22]. On the other hand, the a^* (red) and b^* (yellow) increased values derive from the introduction of more amounts of cromophore elements (Fe and Ti) present into CRT glass composition [22].

Table 6
CIELab* parameters calculated by Hunter method for the industrial fired unglazed C0, C2, C3, C4 samples

% CRT glass	L^*	a^*	b^*	ΔE^*
C0	72.82	2.18	10.90	–
C2	72.30	2.35	12.07	1.29
C3	71.60	2.41	12.35	1.90
C4	69.50	2.35	12.57	3.72

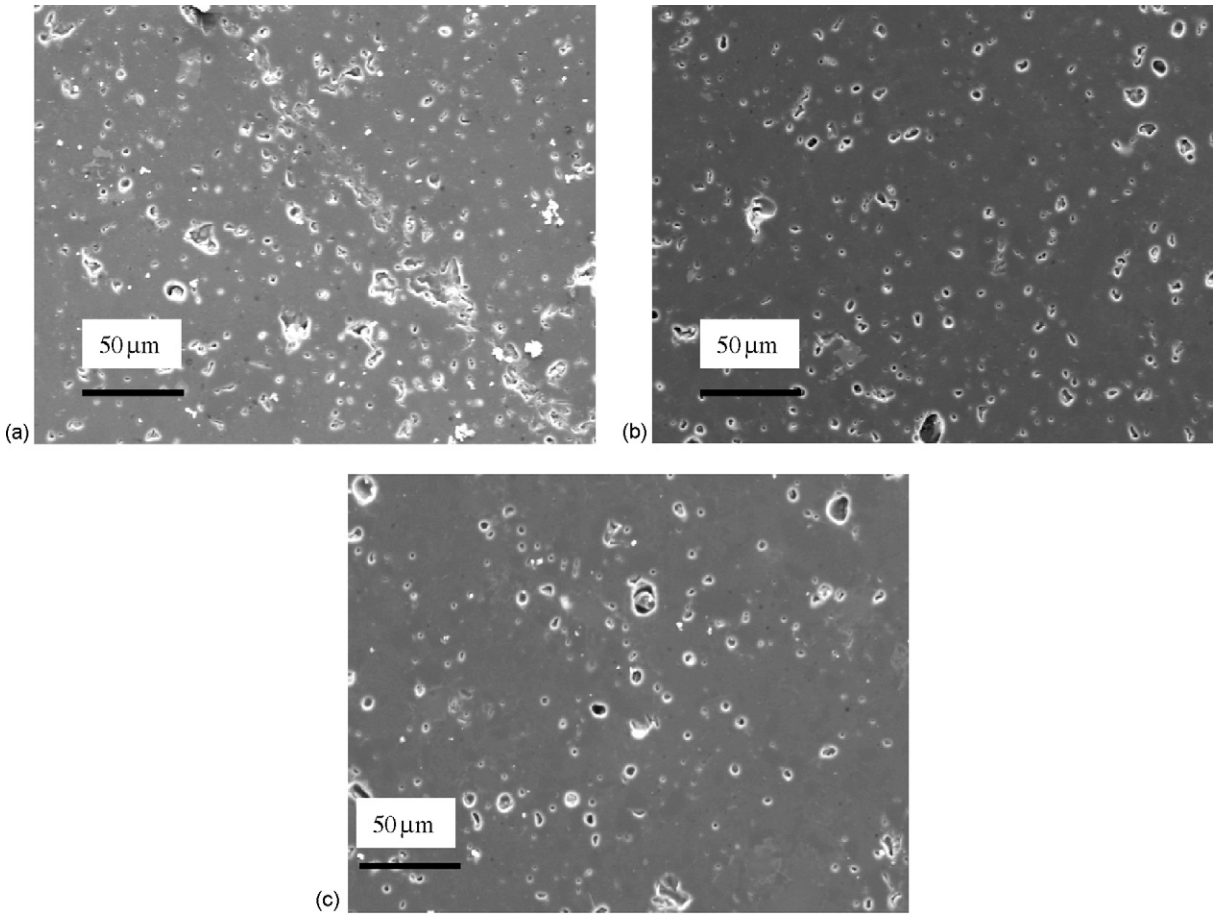

Fig. 5. SEM microphotograph (350×) for (a) C0, (b) C3, (c) C4 industrial fired samples.

On the basis of these results CRT panel glass addition causes a slight change of color with respect to the base body ($\Delta E^* < 2$ up to 5 wt.% addition; $\Delta E^* < 4$ for 10 wt.%). For this reason, in order to deepen the study, other measures on glazed (using a white commercial glaze) samples containing CRT glass were performed. The results obtained highlighted that the presence of panel glass does not affect the aesthetical properties of the end products ($\Delta E^* < 0.50$ up to 5 wt.% CRT glass) and $\Delta E^* = 1.36$ for 10 wt.% CRT glass).These results confirmed that up to 5 wt.% CRT glass addition does not influence the final colour of glazed porcelain stoneware tiles, because the $\Delta E^* < 1$ (industrial tolerance).

4. Conclusions

These results suggest that the ceramic sector might represent a suitable alternative to recycle this kind of waste glass as fluxing agent in the porcelain stoneware body. The addition of low viscosity panel glass has shown a positive effect on the quartz dissolution and on the formation of liquid phase, which give the possibility to reduce the amount of feldspar in the mass. Used in small amounts (up to 5 wt.%), it can replace conventional flux agents improving the densification process (linear shrinkage, water absorption, apparent density) and the mechanical properties (Young' modulus). During firing CRT screen glass gets better sintering kinetic with some positive effects: lower final open and total porosity and higher apparent density. CRT glass added up to 10 wt.% does not change the crystalline phases present and consequently the microstructure.

On the other hands higher amounts (35 wt.%) provoke negative effects because the glass reacts with porcelain stoneware raw materials modifying their microstructure (a new crystalline phase, barian orthoclase, appears).

Acknowledgements

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