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Sintering and characterisation of ceramics containing paper sludge, glass cullet and different types of clayey materials

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Abstract

The present paper reports on the sintering behaviour of several ceramics prepared using a previously selected mixture of incinerated paper mill sludge and glass cullet in the ratio 60/40 which was blended with 10, 20, 30 and 40 wt.% of three different natural materials. The three natural products were: a red quartzitic clay, a yellow quartzitic clay and a kaolin. All mixtures were blended by attrition milling and dried; powders were sieved, pressed into specimens and fired for 1 h at temperatures ranging from 1040 to 1140 °C. The resulting materials were characterized by water absorption, shrinkage, crystallographic composition, microstructure and physico-mechanical properties. It was observed that materials containing kaolin display the best overall behaviour independently of the quantity of kaolin introduced. Conversely the optimal sintering temperature, and consequently the best properties of the materials prepared using red or yellow clay were measured on products fired at temperatures above 1080 °C; materials and temperatures are affected by the amount of clay added.

Keywords: A. Sintering; C. Properties; D. Clay; Paper mill sludge; Glass cullet; Kaolin

1. Introduction

In a previous paper [1] we described the production and characterisation of some ceramics containing mixtures of paper sludge (PS) and glass cullet (GC) from recycled colourless bottles; we demonstrated that materials containing 60 wt.% of PS and 40 wt.% of GC have good physico-mechanical properties independently of the type of PS used. Conversely, their shrinkage exceeds the limits established by the standards for tiles production. On the progress of that research [2], we reported results obtained with materials prepared by mixing the above mixture with increasing amounts of natural red clay. It was demonstrated that the addition of 30 wt.% of a natural red clay enables fast firing production of unglazed tiles. More recently, similar trends were observed on ceramics produced changing the GC origin [3]; if GC from waste colourless bottles is replaced by waste energy saving lamps, the best performing composition is the one containing a mixture PS/GC in the ratio 60/40 just like the binary system already studied.

In this regard, it is worth remembering that GC from waste bottles or windows is classified, in the European Waste Catalogue, as a non-dangerous product and it is presently recycled in glass production. Conversely, GC from exhaust energy saving lamps often contains mercury vapours and, before any eventual landfill disposal or recycling, mercury must be removed by a specific washing. This type of GC mainly derives from industrial buildings and represents a little fraction of the total production of GC, but most of existing waste official norms establish that it cannot be recycled in glass production. It follows that, in order to propose some easy and environmental friendly ways for recycling, alternative methods to landfill disposal are now under study.

The present study deals with the production procedure, followed by materials characterisation of some ceramics containing the blend PS/GC = 60/40 which were added of 10, 20, 30 and 40 wt.% of three different natural raw materials namely: a red quartzitic clay (RC), a yellow quartzitic clay (YC) and a high grade kaolin (K). The goal of the study is to

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evaluate the influence of their chemical composition on the performances of the resulting fired materials which were characterized by shrinkage, water absorption and X-ray diffraction, microstructure and mechanical properties.

2. Materials and methods

PS was obtained from an industry which makes paper containing recycled paper. As described previously [1], the sludge was first oven-dried at 150 °C for 24 h and then incinerated at 850 °C for 2 h; the resulting material was ground to coarse powder in a mortar. GC, obtained from exhausted, Hg free, neon lamps, was transformed into a granulated product by the same grinding procedure. Natural clays used to balance the mixtures were: a red commercial product named samone 1 (in the present work called RC); a yellow quartzitic clay and a high grade angolan kaolin (K). The composition of the above materials, obtained by a spectro mass 2000 induced coupled plasma (ICP) mass spectrometer, is reported in Table 1 which also displays lost on ignition (LOI) data obtained after a thermal treatment at 1000 °C for 2 h.

Table 2 displays the composition of the samples prepared, as well as the abbreviations used to define each material.

Blends (70 g of powder for each preparation) were homogenized by attrition milling for 1 h in a homemade instrument. Milling parameters were as follows: high-density nylon container (volume = 750 ml); 500 g of 99 wt.% alumina balls (diameters = 6–8 mm); 150 ml of distilled water; 300 cycles min^{-1}. Slurries were then oven dried for 24 h at 80 °C. After milling, particle size distribution (PSD) was evaluated using a Horiba LA950 laser scattering particle size distribution analyzer: analyses were made in water after a 3 min sonication time. For clarity of comprehension PSD curves are represented with logarithmic abscissa, as it is commonly done for the presentation of this type of results. Dried powders were sieved (200 μm ~70 mesh) and uniaxially pressed at 100 MPa into parallelepipedal specimens (5 mm × 5 mm × 50 mm). Sintering experiments were performed in air, by an electric muffle, at several temperatures in the range 1040–1140 °C with intervals of 20 °C using heating and cooling rates of 20 °C/min and a D-well time of 1 h. Shrinkage on firing was evaluated, by a caliper, along the longest samples dimension (50 mm on green specimens) using the ratio $(h_0 - h_1)/h_0$ (subscripts 0 and 1 refer to the sample dimensions before and after the sintering). Apparent density of sintered materials was determined by the Archimedes method whereas water absorption was determined following the norm EN99; in line with this norm, fired samples were first weighed in air (W_1), then placed in a covered beaker and boiled in water for 2 h. After boiling, samples were cooled in water to room temperature, dried with a cloth and weighed again (W_2). Water absorption was evaluated using the formula: $W(\%) = [(W_2 - W_1)/W_1] \times 100$. Crystal phases of starting powders and those of the fired materials were investigated by X-ray diffraction (XRD). XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu-Kα radiation. Spectra were collected using a step size of 0.02° and a counting time of 15 s per angular abscissa in the range 20–80°. The Philips X'Pert HighScore software was used for phase identification.

Apparent density, strength and Vickers hardness were measured only on specimens fired at 1100 °C. Density was evaluated by the Archimedes method, flexural rupture strength (σ) was evaluated by the 4-point bending test with a crosshead speed of 0.2 mm min^{-1} using a Shimadzu AG10 equipment whereas Vickers hardness (H_v) was determined by a 100 N load with a Zwick indenter on polished surfaces (6 μm diamond paste); data herein reported are all averaged over 10 measurements.

Microstructures were examined, on the as fired materials, by an Assing Stereoscan scanning electron microscope (SEM)

3. Results and discussion

The chemical analysis revealed that, together with an expected high amount of silica, GC contains high quantities of B_2O_3, Al_2O_3, Na_2O and moderate fractions of CaO, P_2O_5, K_2O and MgO. Glass having such composition could have a low softening temperature [4,5].

Table 1
Composition (wt.%) and LOI (%) of Hg free glass cullet (GC), incinerated paper sludge (PS), red clay (RC), yellow clay (YC) and that of Kaolin (K) reported in term of oxides.

Component	SiO_2	Al_2O_3	CaO	MgO	B_2O_3	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5	PbO	Undetermined	LOI
GC	63.40	6.42	3.66	1.03	11.36	5.44	1.65	0.81	1.10	2.01	0.71	1.98	0.28
PS	23.01	17.40	18.48	15.99	<0.01	2.95	1.83	6.70	2.45	4.91	1.05	0.99	2.01
RC	58.34	18.16	3.15	2.00	0.49	1.27	2.83	7.64	1.21	1.45	<0.01	1.54	9.89
YC	59.48	17.46	4.07	2.21	0.21	2.39	2.22	4.72	0.87	1.68	<0.01	1.55	11.2
K	49.8	39.1	0.59	0.49	<0.01	1.08	1.45	0.34	0.51	1.28	<0.01	2.29	12.3

Table 2
Composition of the samples prepared and abbreviations used for materials identification along the paper (RC = red clay; YC = yellow clay; K = Kaolin).

Material name	RC1	RC2	RC3	RC4	YC1	YC2	YC3	YC4	K1	K2	K3	K4
Clay quantity (wt.%)	10	20	30	40	10	20	30	40	10	20	30	40
Incinerated PS (wt.%)	54	48	42	36	54	48	42	36	54	48	42	36
GC (wt.%)	36	32	28	24	36	32	28	24	36	32	28	24

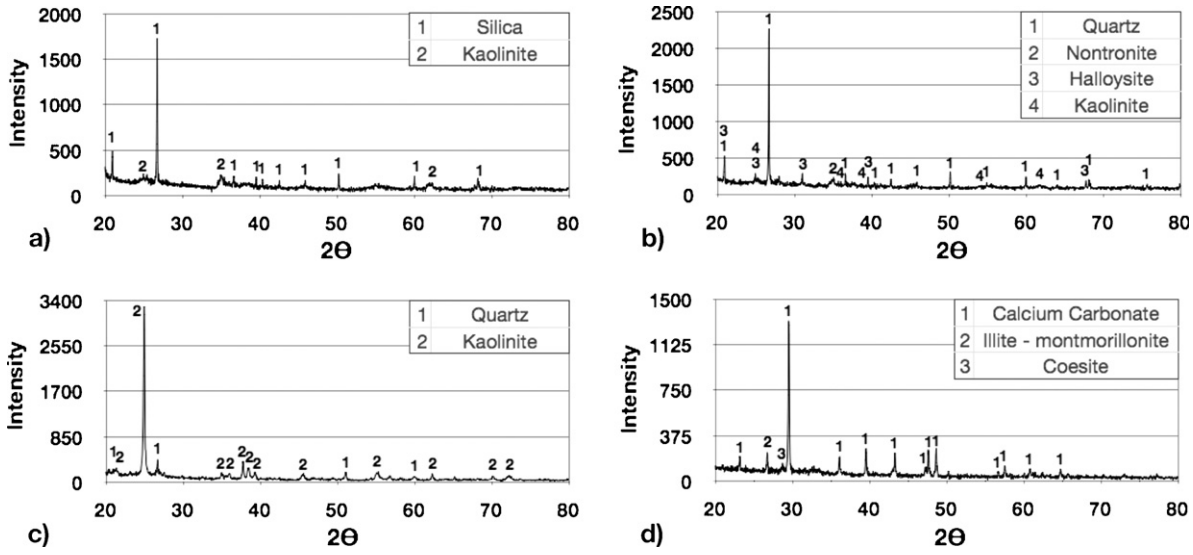

Fig. 1. X-ray diffraction patterns of the starting materials: (a) RC, (b) YC, (c) K and (d) PS.

RC and YC have similar chemical compositions, the main difference being the amount of iron oxide which, in RC, is twice that of YC. The analysis of kaolin revealed the presence of great quantities of SiO_2, Al_2O_3, and minor fractions of other components, in line with literature data [6,7].

PS contains high quantities of SiO_2, Al_2O_3, CaO, MgO, and moderate amounts Fe_2O_3 and P_2O_5, Na_2O, K_2O, TiO_2; most of these components have white colour and are added to the paper as whitening agents alone or in relative blends.

Unlike the chemical analysis, the X-rays diffraction investigation revealed sensible differences between the crystal phases of RC and YC. In fact, the presence of quartz (PDF 01-086-1629), nontronite (PDF00-029-1497), hallosyte (PDF 00-003-0184) and kaolinite (PDF 00-029-1488) in RC was identified, but only silica (PDF 01-085-0794) and kaolinite (PDF 00-029-1488) in YC. On the other hand, kaolinite (PDF 01-083-0971) and a small quantity of free quartz (PDF01-078-1253) were revealed in K whereas incinerated PS contains a great amount of calcium carbonate (PDF 01-085-1108) and small amounts of illite-montmorillonite (PDF 00-035-0652) and coesite (PDF 01-076-1805). As expected, no crystal structures were detected in GC. The above results are documented in Fig. 1 which displays the four X-ray diffraction patterns.

Fig. 2 shows the PSD curves, determined after the milling procedure, relative to powders blends prepared using RC and K. Curves extracted from mixtures containing YC are not reported since they showed the same trends as those obtained on mixtures containing RC. It can be observed that all curves show the presence of three peaks: one with the maximum below 1 μm, another with the maximum between 1 and 10 μm and the third with the maximum between 10 and 100 μm. Compositions made with clays show that peaks intensity is function of powders composition. It can be observed that, as it is increased the quantity of clay, also the amount of small particles is increased at the expense of large aggregates (peak between 10 and 100 μm) which are minimized in compositions RC4 and YC4. Powders blends containing kaolin do not show great changes of PSD curves shape as the amount of K is increased: their trend seems to be independent of composition, but affected by casual events. The different PSD between compositions containing clays and those containing kaolin is

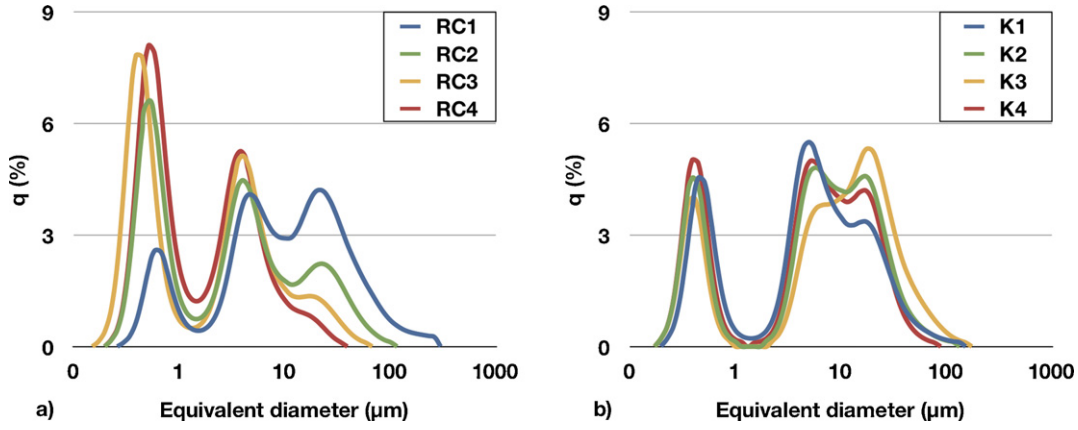

Fig. 2. Particle size distribution of the milled powders: (a) RC series and (b) K series. Curves are represented with logarithmic abscissa.

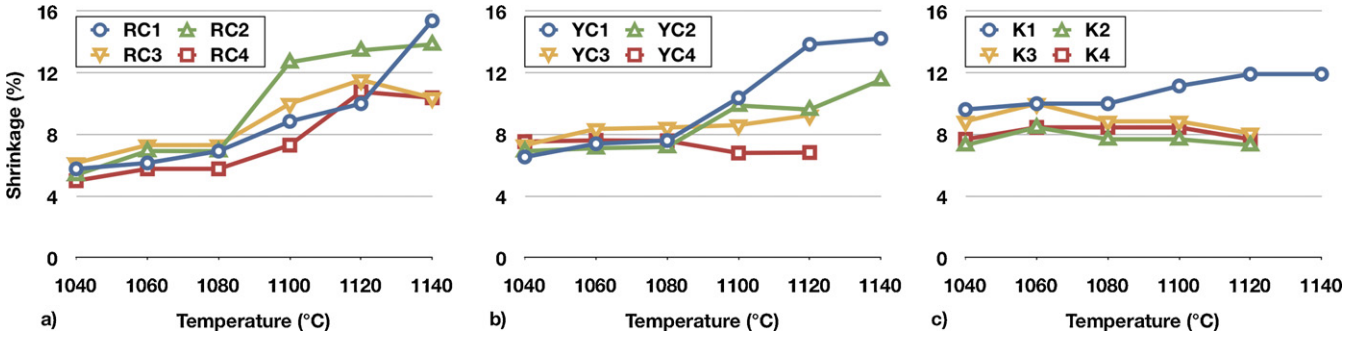

Fig. 3. Shrinkage (%), as a function of firing temperature, of the samples containing RC (a), YC (b) and K (c).

reasonably due to the different dimension of clays and kaolin particles. It is known, in fact, that kaolins have particles of greater size with respect to clays; consequently, the milling process is much more efficient on the former than on the latter.

Water absorption, directly related to the open porosity, and linear shrinkage are physical parameters used for drawing the sintering curves which lead to optimization of firing cycles and, in turn, to the production of materials with required properties. Fig. 3 reports shrinkage trend as a function of temperature for all materials.

It can be seen that all compositions prepared using RC display a flat trend up to 1080 °C, then their shrinkage increases. More in detail, RC1 shows a continuous shrinkage increase between 1080 and 1140 °C, whereas RC2, RC3 and RC4 reveal quite high shrinkage between 1080 and 1100 °C, but for higher temperatures they do not show great variations.

Materials prepared using YC too display a flat trend up to 1080 °C and also YC1 (as for RC1) shows a continuous shrinkage increase between 1080 and 1140 °C. Conversely, YC2, YC3 and YC4 show a flat shrinkage trend at all the temperatures; YC4, in particular, melts between 1120 and 1140 °C so that it was not possible to measure its shrinkage at the highest tested temperature. Materials prepared using K display a flat trend in the examined range, K1 being the one showing largest variations. It must be pointed that compositions K2, K3 and K4 melts between 1120 and 1140 °C: their shrinkage was therefore not measured after firing at 1140 °C. It can be also observed that compositions RC3, RC4, YC3, YC4, K2, K3 and K4 display shrinkage values below 10% at all the temperatures tested and therefore could be considered suitable for the industrial production of some typologies of commercial tiles [7]. Of course, before any industrial application, behaviour and data must be confirmed under industrial production conditions that are: products shape and dimensions, forming pressure and sintering parameters.

Fig. 4 reports water absorption vs. firing temperature of the materials produced. As it was observed about shrinkage, all materials containing RC display high variation between 1080 and 1100 °C. Detailing: RC1 shows a continuous reduction of water absorption in the whole range examined. RC2, RC3 and RC4 show a great change between 1080 and 1100 °C, but, for higher temperatures, great changes were not revealed. Also, the behaviour of materials containing YC depends on the amount of clay added: YC1 shows a continuous decrease of water absorption as a function of the temperature; water absorption of YC2 is noticeable up to 1100, but, for higher temperatures, it remains rather constant; YC3 and YC4, on the other hand, show almost a flat trend in the whole range examined. It must be pointed out that YC3 and YC4 show a non-negligible increase of water absorption after firing at 1120 and 1140 °C with respect to materials fired at lower temperatures. Such behaviour depends on the presence of open small bubbles caused by the formation of a great amount of liquid phase on sintering. The trend observed on materials containing K is rather similar to the one previously described, although absolute values are sensibly lower. Compositions K3 and K4 display a flat trend in the whole temperature range; in this case, no open bubbles were observed and consequently no increase of water absorption was measured after firing at 1120 or 1140 °C. K1 displays a continuous decrease up to 1120 °C, then reduction is stopped;

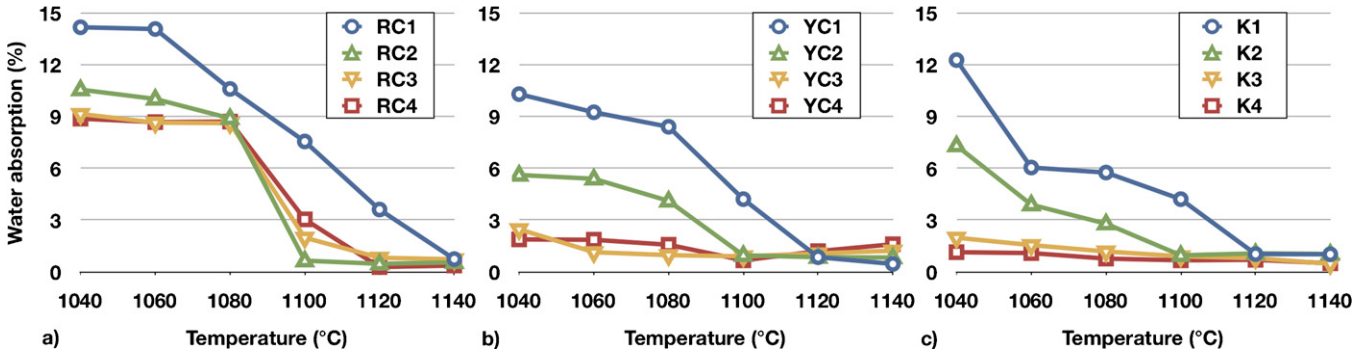

Fig. 4. Water absorption (%) versus sintering temperature of the samples prepared with RC (a), YC (b) and K (c).

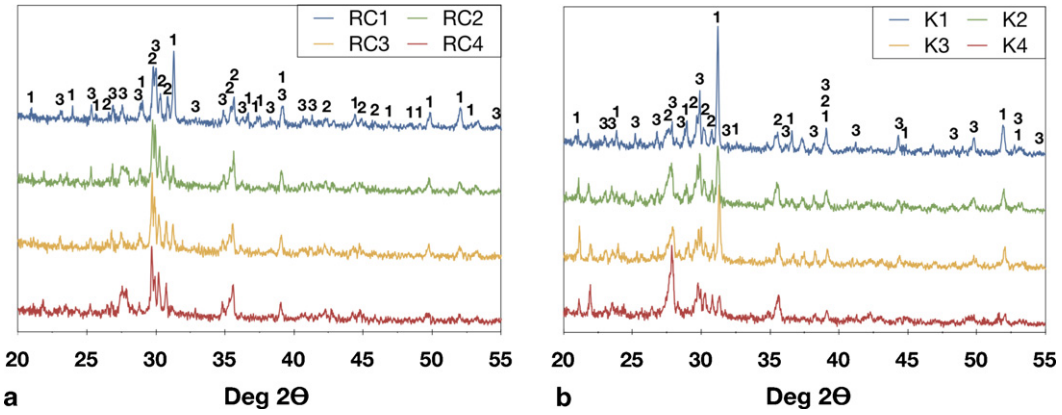

Fig. 5. X-ray diffraction patterns (20–55°) acquired on the free surface of samples made with RC (a) and K (b) set of materials fired at 1100 °C. Phases of RC set of materials are: (1) akermanite–gehlenite, (2) augite, (3) wollastonite; phases of K compositions are: (1) akermanite, (2) diopside, (3) wollastonite.

water absorption of K2 remains constant for firing temperatures equal or higher than 1100 °C. It must be observed that the low absolute values measured on composition K3 and K4 also depends on their very low open porosity. The evolution of linear shrinkage and water absorption of the materials prepared in the present study fits well, in agreement with the trend which was first described by Kingery [6], with the sintering behaviour of ceramics affected by the formation of a ''transitory liquid'' phase which improves densification of the green body.

One should also keep in mind that water absorption, shrinkage and then bending strength values are interdependent, so that the lower water absorption corresponds to the greater linear shrinkage and then high bending strength. In this respect, it is worth pointing out that water absorption values below 10% meet the official Italian requirements for the production of red stoneware and ''monoporosa'' therefore it can be concluded that, if other parameters are not considered, many compositions prepared in the present research are in line with the norm, provided that products could be fired at their optimal sintering temperature.

Fig. 5 shows the X-ray diffraction patterns of the samples made with RC and K fired at 1100 °C; this temperature was selected in order to test materials with low residual porosity, a completely developed crystalline structure and a limited quantity of vitreous phase as a result of a firing cycle sufficiently far from their softening temperature. Patterns acquired on samples made with YC are not reported for brevity since they showed same peaks and same phases as those made with RC.

It can be observed that samples prepared using RC, showed the presence of akermanite–gehlenite (1) (Powders Diffraction File no. 01-079-2423), augite (2) (PDF 00-024-0201 and wollastonite (3) (PDF 00-027-0088). Conversely specimens made with kaolin showed akermanite (1) (PDF 01-079-2424), diopside (2) (PDF 01-081-0487) and wollastonite (3) (PDF 01-076-0186); such phases are present independently of materials composition: i.e. the addition of a greater or smaller amount of clay or kaolin only modifies their relative fraction. In particular, it can be observed that an increased addition of clay or kaolin also increases the amount of wollastonite and augite (RC and YC) or wollanstonite and diopside (K) at expense of akermanite–gehelenite (RC and YC) or akermanite in K containing materials. The presence of mullite, although expected, was not revealed by the software used for phase identification probably due to the low sintering temperatures used in all our experiments. In fact other authors demonstrated [8–10] that mullite could be clearly detected in materials fired at temperature higher than 1200 °C.

It can be concluded that the crystal structure of the fired materials at 1100 °C is mainly determined by nature, chemical composition and crystal phases of the recycled materials (PS and GC) and minimally by the chemistry of the natural materials used. In fact, augite and diopside belongs to the same mineral group of pyroxenes type compounds and have similar monoclinic crystal structure. A parallel comparison is possible between akermanite and akermanite–gehelenite.

The presence of vitreous phase was observed in all the samples fired at 1100 °C or above by the SEM analysis and it is documented by Fig. 6(a–f) which shows micrographies of the fired (1100 °C) surfaces of compositions RC1, RC4, YC1, YC4, K1 and K4. It is worthy pointing out that it was preferred to report only images acquired on extreme compositions for each set of materials in order to limit redundant documentation.

The presence of prismatic elongated structures, probably due to well developed diopside, akermanite or augite crystals [11], can be observed in compositions RC4, K4 and YC4; the latter being the composition showing crystals of highest shape ratio, probably due to the presence of a high content of liquid phase during sintering as it is possible to observe by the SEM image which highlights large vitreous zones.

Table 3 reports apparent density, hardness and bending rupture strength of the materials fired at 1100 °C. For each composition, strength and hardness variability is limited being always below 10% of the average value and seem to be not affected by materials composition. However, it can be observed that all the properties follow water absorption values, i.e., as water absorption decreases, density, hardness and strength are

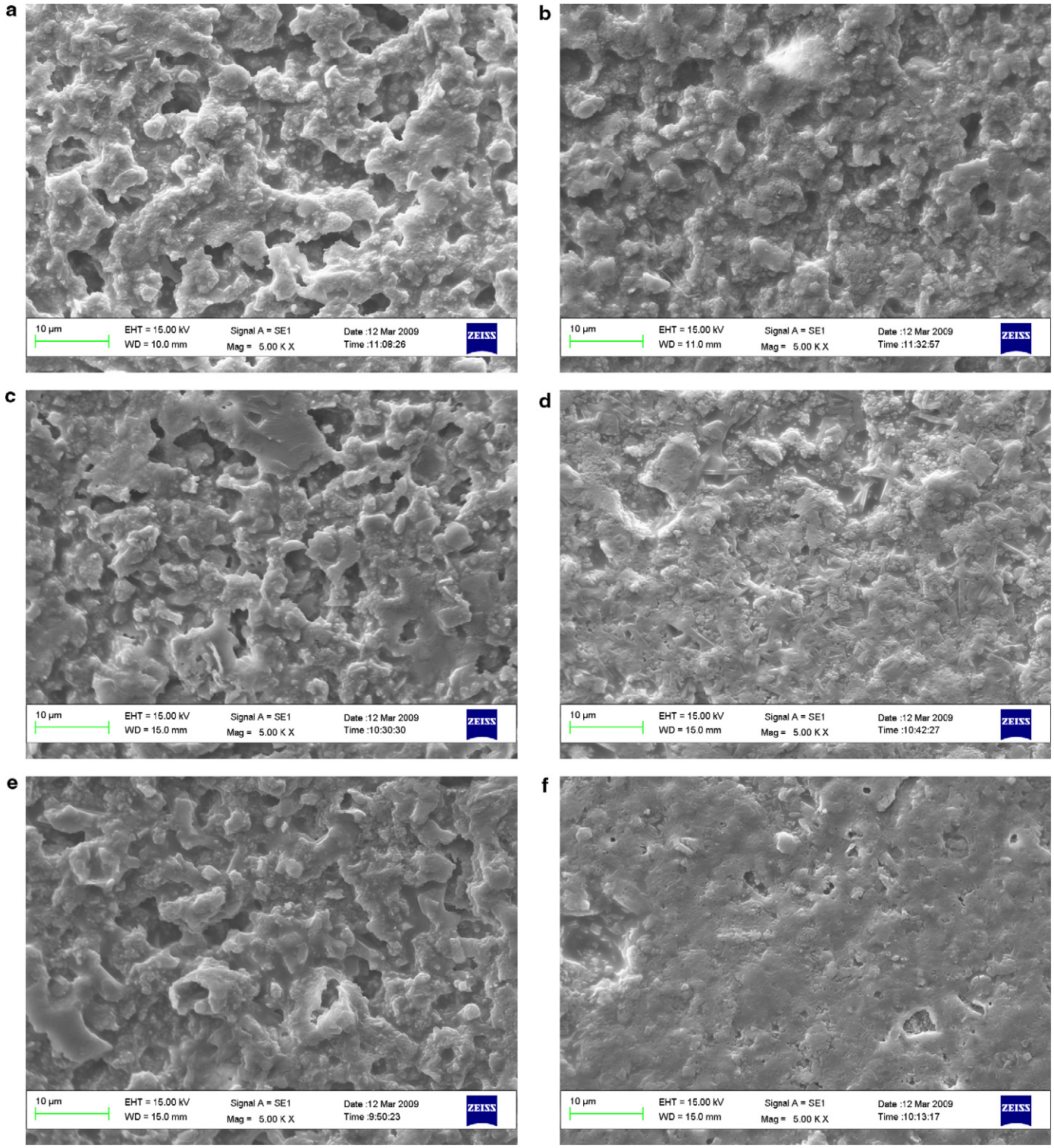

Fig. 6. SEM micrographies (5000x) of the as fired (1100 °C) surface of samples with composition RC1, RC4, YC1, YC4, K1 and K4. In detail: (a) RC1, (b) RC4, (c) YC1, (d) YC4, (e) K1 and (f) K4.

improved. It can be also observed that the presence of different phases seems to have little influence on materials hardness and strength. K1 and K4 samples have similar strength at 1100 °C, but water absorption of K1 is higher than that of K4. K4 contains much more vitreous phases than K2 as it is fired much closer to its softening temperature than K4. This statement is also supported by Fig. 6(e and f). The higher amount of crystalline phase probably compensates the higher porosity.

As an additional information, it is interesting pointing out that Italian official norms for the industrial production of earthenware or red monoporosa, set, as lower strength

Table 3
Averaged values of apparent density (ρ), flexural rupture strength (σ) and Vickers hardness (H_v) of materials fired at 1100 °C; variability is also displayed.

Material's name	ρ [g/cm^3]	σ [MPa]	H_v [GPa]
RC1	2.37	30 ± 2	2.8 ± 0.5
RC2	2.37	42 ± 3	4.4 ± 0.3
RC3	2.41	40 ± 4	4.3 ± 0.2
RC4	2.36	38 ± 2	4.0 ± 0.3
YC1	2.37	37 ± 4	3.5 ± 0.4
YC2	2.23	39 ± 4	4.9 ± 0.3
YC3	2.20	41 ± 3	4.5 ± 0.2
YC4	1.81	39 ± 4	4.6 ± 0.3
K1	2.09	38 ± 3	4.1 ± 0.2
K2	2.13	41 ± 2	5.1 ± 0.4
K3	2.17	43 ± 4	4.8 ± 0.2
K4	2.20	39 ± 3	4.9 ± 0.3

limits, 12 MPa for wall tiles and 25 MPa for floor tiles [7]. Table 3 displays that all the compositions fired at 1100 °C reach at higher level.

4. Conclusions

The present research deals with production and characterization of ceramics prepared using a previously selected mixture of incinerated paper mill sludge and glass cullet from energy saving lamps which was blended with 10, 20, 30 and 40 wt.% of a red clay, a yellow clay and a high grade kaolin.

The sintering experiments demonstrated that:

- Compositions containing 30 and 40% of RC, 30 and 40% of YC, 20, 30 and 40% of K display shrinkage values below 10% at all the temperatures tested.
- The crystal structure of the fired materials is mainly caused by nature, chemical composition and crystal phases of the recycled materials (PS and GC) and minimally by the characteristics of the natural materials added.
- A certain quantity of vitreous phase has been revealed in all the materials fired at 1100 °C or above by the SEM analysis.
- Materials fired at 1100 °C showed averaged strength values in line with the Italian official norms for the industrial production of earthenware or red monoporosa.
- Rather similar behaviour was observed between materials prepared using different quantities cheap clays or high grade kaolin.

Experiments are now in progress in order to test fast firing of best performing compositions and possibility of glazing in order to evaluate the possible industrial production of ceramics using GC and PS as raw materials.

Acknowledgment

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