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Ceramics International 37 (2011) 1851–1858
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Influence of $CaO–ZrO_2–Al_2O_3–SiO_2$ glass-ceramic frits on the technological properties of porcelain stoneware bodies

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Received 17 September 2010; received in revised form 21 January 2011; accepted 4 February 2011
Available online 9 March 2011

Abstract

In the present work, the effect of the addition to a porcelain stoneware body of glass-ceramic frits belonging to the $CaO–ZrO_2–Al_2O_3–SiO_2$ (CZAS, containing 1, 3, 5, and 10 mol% of Al_2O_3) system as replacement of the ''state of the art'' frit belonging to $CaO–ZrO_2–SiO_2$ system (CZS) was evaluated. The firing process was performed in a furnace able to complete the thermal cycle in 50 min, in order to simulate the industrial process.

Technological properties such as water absorption, firing shrinkage, flexural strength, and thermal expansion behaviour were measured. Aesthetical properties were also evaluated. X-ray diffraction and scanning electron microscopy studies were also carried out to analyse the microstructure and the phase compositions of the studied samples.

It was found that the sample containing the CZAS frit with 5 mol% of Al_2O_3 shows, in general, the best combination of properties in term of mechanical, physical and aesthetical properties.

Keywords: A. Sintering; B. Microstructure-final; C. Glass-ceramics; D. Traditional ceramics

1. Introduction

This study reports the results concerning the effects of the addition to porcelain stoneware body [1–4] of different glass-ceramic frits belonging to the $CaO–ZrO_2–Al_2O_3–SiO_2$ system containing different amount of alumina. As reported in [5], the studied glasses originate from the $CaO–ZrO_2–SiO_2$ (CZS) system; the frit belonging to this system is largely used as ceramic frit [6,7]. In particular several frits are introduced in the raw materials used for the production of ''porcelainized stoneware tiles'' in order to improve some technological properties [8]. Since this frit contains ZrO_2, it shows high chemical durability, low coefficient of thermal expansion and, during heat treatment, it easily devitrifies producing interesting crystalline phases [9–11].

When this frit is added to a traditional ceramic mix, it tends to react with the alumina contained in the clays, inducing the crystallization of different crystalline phases. This reactivity can affect the mechanical properties of the final ceramic product [12]. In order to strongly limit this reactivity, different amounts of alumina 1, 3, 5, and 10 mol% have been added to the base glass, CZS, obtaining new frits belonging to the $CaO–Al_2O_3–ZrO_2–SiO_2$ (CZAS) innovative quaternary system.

In a previous paper only the glass-ceramic frits were studied [13]. It is important to underline that the $CaO–ZrO_2–SiO_2$ base-frits during heat treatment form two main crystalline phases, wollastonite and a calcium zirconium silicate ($2CaO·4SiO_2·ZrO_2$) [10], while the frits belonging to the $CaO–ZrO_2–Al_2O_3–SiO_2$ system form as main phases anorthite and the same $2CaO·4SiO_2·ZrO_2$ phase [13].

Specimens of porcelain stoneware body with a 10 wt% addition of frits belonging to CZAS systems, to replace the ''state of the art'' CZS frit, were produced. Many technological properties, such as firing shrinkage, coefficient of thermal expansion, water absorption, apparent density, modulus of rupture and the Hunter parameters (white index, L^*, a^*, b^*) were investigated. Besides, the effect played by these glass-ceramic frits on sintering, phase transformation and microstructures of porcelain stoneware body was also studied and reported.

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.03.010

2. Experimental procedure

The nominal chemical compositions (wt%) of the studied frits are reported in Table 1.

The glasses were prepared by industrial grade raw materials ($CaCO_3$, Al_2O_3, $ZrSiO_4$, SiO_2) in an alumina crucible inside a super kanthal electric furnace (Nannetti, Faenza, Italy) at about 1550 °C, with 1 h soaking time. The melted batches were quenched in water in order to obtain frits. The characterization of the frits was reported in a previous paper [13].

500 g of frit was wet-milled for 45 min in a laboratory mill using 500 g Alubit® spheres of different diameter as a milling media, in order to obtain fine glass powders.

The body composition of the studied mixtures is reported in Tables 2 and 3.

The samples were prepared at the laboratory scale simulating the industrial tile manufacturing process. The first step consisted in mixing and wet grinding the raw materials (see Table 2) in porcelain jar with dense alumina grinding media for 20 min in a planetary mill (the fraction below 270 mesh, after sieving, was less than 1%). The forming step was preceded by drying the suspension at 105 ± 5 °C overnight and by deagglomerating the powder (by hammer mill, 0.75 mm grid) and humidifying it with 6% water. The specimens were formed by uniaxial pressing at a pressure of 40 MPa. They were then dried in an electric oven at 105 ± 5 °C overnight. The firing step was carried out by heating the samples in an electric roller kiln (Nannetti, ER 15) at a maximum temperature of 1220 °C with a thermal cycle of 51 min cold-to-cold. These latter firing conditions can be considered equivalent to the state of the art of the firing step in an industrial tile manufacturing process.

While the sintering study was carried out on the disc shaped specimens, the flexural strength study was conducted on rectangular bars. The unfired bars had dimensions of 10 mm × 100 mm × 6 mm and the unfired discs were 40 mm in diameter and 5 mm thick. Both kind of specimens were characterized testing the firing shrinkage by measuring the diameter of disks before and after sintering (ASTM C326) using the formula $(L_g \times L_f/L_g) \times 100$, where L_g and L_f were the measured length of green and fired samples, respectively. The coefficient of thermal expansion (CTE) between room temperature and 400 °C of the sintered specimens was measured using a NETZSCH automatic contact dilatometer at a heating rate of 10 °C/min. The sintering degree of the samples was indirectly tested by measuring the water absorption of the fired discs by a water displacement method (WA% ISO 10545 part 3) and the apparent density by using the Archimedes's method in Hg. The mechanical properties of the specimens (rectangular bars) were evaluated by measuring the modulus of rupture by a three-point bending test based on the standard ISO 10545 – part 4; four samples were tested for each composition. The aesthetical appearance of the tiles can be crucial for their impact on the market and was quantified by measuring their whiteness by means of the Hunter parameters. The aesthetic properties and the white index with Taube method were characterized by using CIE-Lab colourimetry (ISO 10545–16, equipment ColorEye XTH, Xrite). This method allowed to investigate the dependence of the samples whiteness on the frit compositions.

The crystalline phases composition present in the fired samples was qualitatively identified by XRD method performed both on the surface of the bulk samples and on the samples reduced in powder form after extensive grinding. Quantitative phase composition XRD analysis was also performed on the ground samples (from 5 to 140 2θ degree, 6 s each 0.02 2θ step size), adding 10 wt% of Al_2O_3 (standard NIST, SRM676) as internal standard and following a RIR-Rietveld procedure, using GSAS software and EXPGUI as the graphical interface [14–16]. The microstructure of the samples was analysed by scanning electron microscopy (SEM, Philips XL 40) with energy dispersion spectroscopy (Oxford) investigating both the surface of the specimens in ''as-fired'' conditions (no post firing mechanical polishing was carried out) and the cross section in polished conditions. The polishing procedure of the cross sections consisted in mounting the samples in resin; the specimens were then mechanically ground with SiC abrasive papers and polished with diamond slurry down to 0.5 μm. The samples were gold-coated with a 10 nm layer by sputtering before SEM observation.

Table 1
Nominal chemical composition of frits (wt%).

Frits	CaO	SiO_2	ZrO_2	Al_2O_3
CZS	30.00	54.97	15.03	0.00
CZS1Al	29.52	54.10	14.79	1.59
CZS3Al	28.63	52.45	14.34	4.58
CZS5Al	27.77	50.89	13.92	7.42
CZS10Al	25.85	47.37	12.96	13.81

Table 2
Body composition of studied ceramics samples (wt%).

Raw materials	BG0Al	BG1Al	BG3Al	BG5Al	BG10Al
Illitic–kaolinitic clay	18	18	18	18	18
Kaolin	10	10	10	10	10
Feldspathic sand	10	10	10	10	10
Nefeline	45	45	45	45	45
$ZrSiO_4$	5	5	5	5	5
Calcite	2	2	2	2	2
Frit	10 (CZS)	10 (CZS1Al)	10 (CZS3Al)	10 (CZS5Al)	10 (CZS10Al)

Table 3
Nominal chemical composition of studied ceramics bodies (wt%).

Oxides	BG0Al	BG1Al	BG3Al	BG5Al	BG10Al
SiO_2	58.51	58.42	58.26	58.10	57.75
Al_2O_3	20.01	20.17	20.47	20.76	21.39
Fe_2O_3	0.22	0.22	0.22	0.22	0.22
TiO_2	0.24	0.24	0.24	0.24	0.24
MgO	0.10	0.10	0.10	0.10	0.10
CaO	4.35	4.30	4.21	4.13	3.93
Na_2O	4.50	4.50	4.50	4.50	4.50
K_2O	3.48	3.48	3.48	3.48	3.48
ZrO2	4.70	4.68	4.63	4.59	4.50

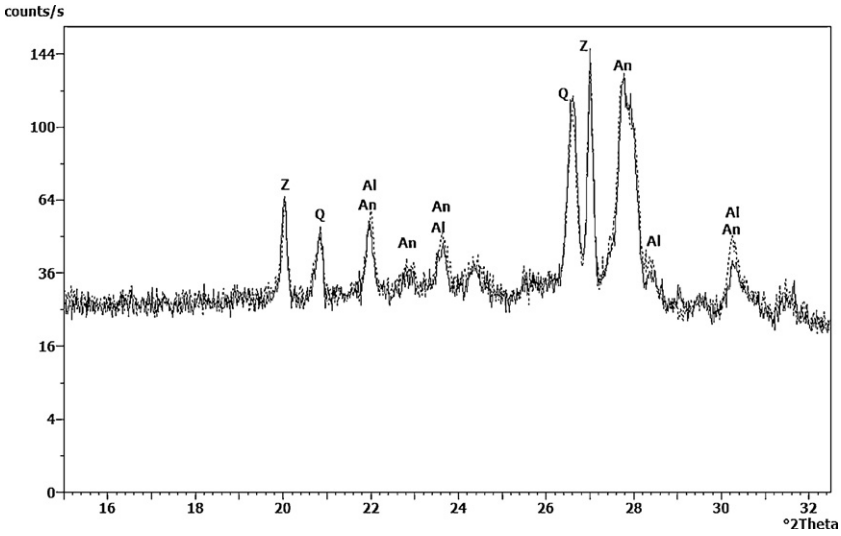


Fig. 1. XRD pattern surface of BG0Al and BG10Al: Z = zircon; Q = quartz; An = anorthite; Al = albite.

3. Results and discussion

3.1. Mineralogical analysis

Glass-ceramic frits induce some changes in amount and chemistry of the crystalline phases in the new porcelain stoneware. Anyway, some general trends may be outlined, in particular: qualitative analysis performed through XRD patterns made on the surface of the BG0Al and BG10Al bulk samples (Fig. 1) does not show any changes in terms of crystalline phases, depending on the different amount of added alumina, since all samples display as main phases zircon, quartz, anorthite, albite and a relevant glassy phase (only two samples are reported in Fig. 1). Some changes are shown in the XRD patterns obtained on the powdered samples after a grinding of the bulk samples. Since all samples show the same behaviour, only the features of sample BG10Al were reported (Fig. 2). The powdered sample shows a lower amount of albite, anorthite and zircon than bulk samples and quartz becomes the main phase. This behaviour is due to a temperature gradient, going from the surface to the core of the material that occur during the heating of the samples. As already demonstrated by other authors, the surfaces of porcelainized stoneware tiles show a higher amount of glassy phase than inside the body: quartz is the main phase because it is an unreacted raw material and not a newly formed crystalline phase [17]. The quantitative analysis by Rietveld method on the ground samples revealed, instead, interesting variations between the low-amount and high-amount alumina samples. The effect of the vitreous precursor containing different amount of alumina can be noticed (Table 4): increasing the alumina content does not significantly change the amount of zircon, while the glassy phase increases and quartz decreases especially in the BG0Al, BG1Al and BG3Al samples. The latter three samples have more or less the same amount of anorthite and $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ crystalline phases induced by the heat treatment. It is important to underline that the frit CZS1Al containing very low amount of alumina had devetrification

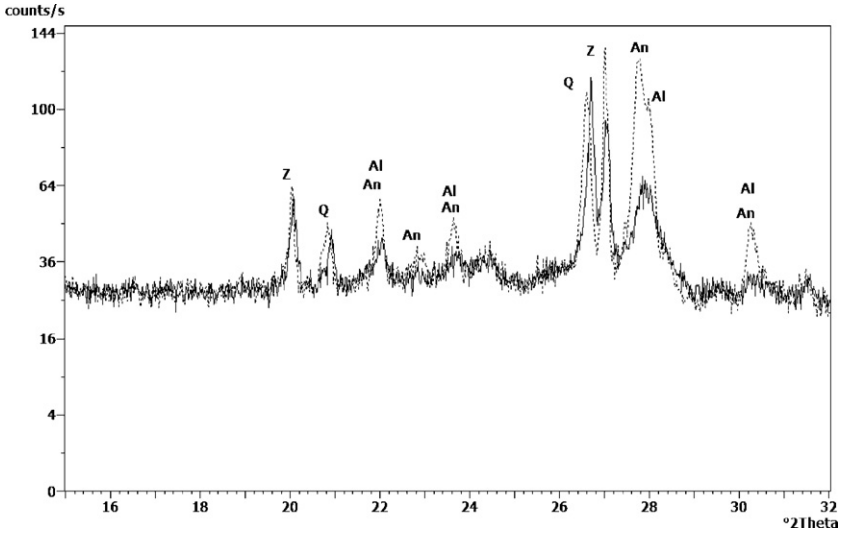


Fig. 2. XRD pattern of BG10Al: dot line = surface; bold line = powder.

Table 4
Qualitative and quantitative analysis of crystalline phases.

Samples	Qualitative surface	Qualitative powders	Quantitative powders
BG0	Z (100)	Q (100)	Q 6.2 (1)%
	Q (72)	Z (72)	Z 3.9 (1)%
	A (86,58)	A (31)	An 11.4 (8)
	Glass phase	Glass phase	Al 6.3 (8)%
			CZS 1.1 (2)%
			Amorphous 71.2 (9)%
			$\chi^2 = 0.86$
			Rwp = 7.35% Rp = 5.67%
BG1Al	Z (100)	Q (100)	Q 4.7 (2)%
	Q (81)	Z (76)	Z 3.6 (1)%
	A (72,55)	A (37)	An 11.0(7)%
	Glass phase	Glass phase	Al 5.7 (8)%
			CZS 1.2 (2)
			Amorphous 73.8 (9)%
			$\chi^2 = 0.90$
			Rwp = 7.48% Rp = 5.76%
BG3Al	Z (100)	Q (100)	Q 4.2 (2)%
	Q (80)	Z (96)	Z 3.7 (1)%
	A (90,64)	A (35)	An 9.5(5)%
	Glass phase	Glass phase	Al 5.9 (6)%
			CZS 1.2 (4)
			Amorphous 75.5 (9)%
			$\chi^2 = 0.91$
			Rwp = 7.50% Rp = 5.83%
BG5Al	Z (100)	Q (100)	Q 5.3 (2)%
	Q (94)	Z (85)	Z 4.1 (1)%
	A (78,55)	A (40)	An 13.2(6)%
	Glass phase	Glass phase	Al 4.8 (6)%
			Amorphous 72.4 (9)%
			$\chi^2 = 0.86$
			Rwp = 7.25% Rp = 5.58%
BG10Al	Z (100)	Q (100)	Q 7.7 (2)%
	A (98,66)	Z (77)	Z 5.5 (1)%
	Q (80)	A (40)	An 18.1(6)%
	Glass phase	Glass phase	Al 12.7 (7)%
			Amorphous 55.2 (9)%
			$\chi^2 = 0.89$
			Rwp = 7.39% Rp = 5.69%

Q = quartz; Z = zircon; An = anorthite; Al = albite; CZS = $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$.

behaviour similar to CZS glasses [11]. As a matter of fact, during the heat treatment, both frits separate a calcium silicate ($CaO{\cdot}SiO_2$) wollastonite as main crystalline phase and a ternary crystalline phase $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$. In this study, in the samples BG0Al and BG1AL which contain CZS and CSZ 1Al frits respectively, no wollastonite crystals but only the anorthite crystalline phase is formed. Latter phenomenon is due to the reaction of clays, that during the heat treatment react with the frit grains, but it will be better explained in Section 3.2. Moreover, it is important to consider that the body mix contains small amount of calcite (2 wt%), which can react with clays forming anorthite as well [18]. Thus, summing up, two main concurrent phenomena can lead to the formation of anorthite in the samples to which the frits with a low amount of alumina were added: firstly, clays can react with surface of the frit grains; secondly, clays can react with calcite as well [19].

As reported in [13] CZS5Al and CSZ10Al glass-ceramic samples, containing higher amount of alumina, usually form anorthite, even if small amounts of $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ are already present in the glass-ceramic samples. In the studied samples, BG5Al and BG10Al, the anorthite phase increases, the zirconia-rich phase (CZS) instead disappears and in the BG10Al, the glassy phase strongly decreases compared to BG5Al sample. The frit with highest alumina content strongly influences the samples increasing crystallinity, the relative amount of the crystalline phases is also changed since anorthite quantitative amount is higher than in the others studied samples. In fact, BG5Al and BG10Al display the higher amount of anorthite phase. This behaviour is probably due to the molar ratio among $CaO{:}Al_2O_3{:}SiO_2$, which becomes more and more closer to the stoichiometric one of crystalline anorthite. It is quite known that glasses, whose composition becomes similar to the stoichiometric composition of certain crystalline species, are likely to devitrify those same species [20]. Besides, if we focus our attention on the crystallization temperature (Tp) of both frits, CZS10Al frit shows two crystallization temperatures, one at 1016 °C and the other at 1120 °C, while CZS5Al frit at 1033 °C and 1131 °C, respectively: first of all, their behaviour implies that CZS10Al frit tends to crystallize more easily in the sample while undergoing the firing process; moreover, the reactivity of the frit with clay becomes a minor event compared to their tendency to crystallize anorthite.

The quantitative analysis (Table 4) of BG5Al and BG10Al can be compared to the other samples and some further considerations could be made:

(1) BG10Al and BG5Al respectively contain the higher amount of anorthite, 18% and 13.2% while only BG10Al sample shows the highest content of albite (12.7%).
(2) The amount of vitreous phase is similar in all samples, BG5Al included, while BG10Al shows by far the lowest content (55%).
(3) BG0Al and BG5Al present, more or less, similar amount of glass phase, but different crystalline phases. As a matter of fact BG5Al presents higher amount of anorthite (13.2%) than BG0Al (11.4%) but no zircon-phase.

Thus, it is possible to underline that the frits interact in two main different way into the body mixture, leading to different microstructures that change the properties of the fired gres bodies as reported in the next section.

3.2. Microstructure

The microstructure of the surface of the samples is shown in Fig. 3. All bodies present qualitatively similar microstructures which are dense and vitrified. A very low porosity is also visible. The presence of a glass phase on the surface of the sample can fill the pores leading to a smoother and more cleanable surface.

The porosity seems to increase with the alumina content into the frits and this effect is particularly evident in the BG10Al sample. Investigating the samples more in detail, at higher magnification, all of them display several crystalline phases

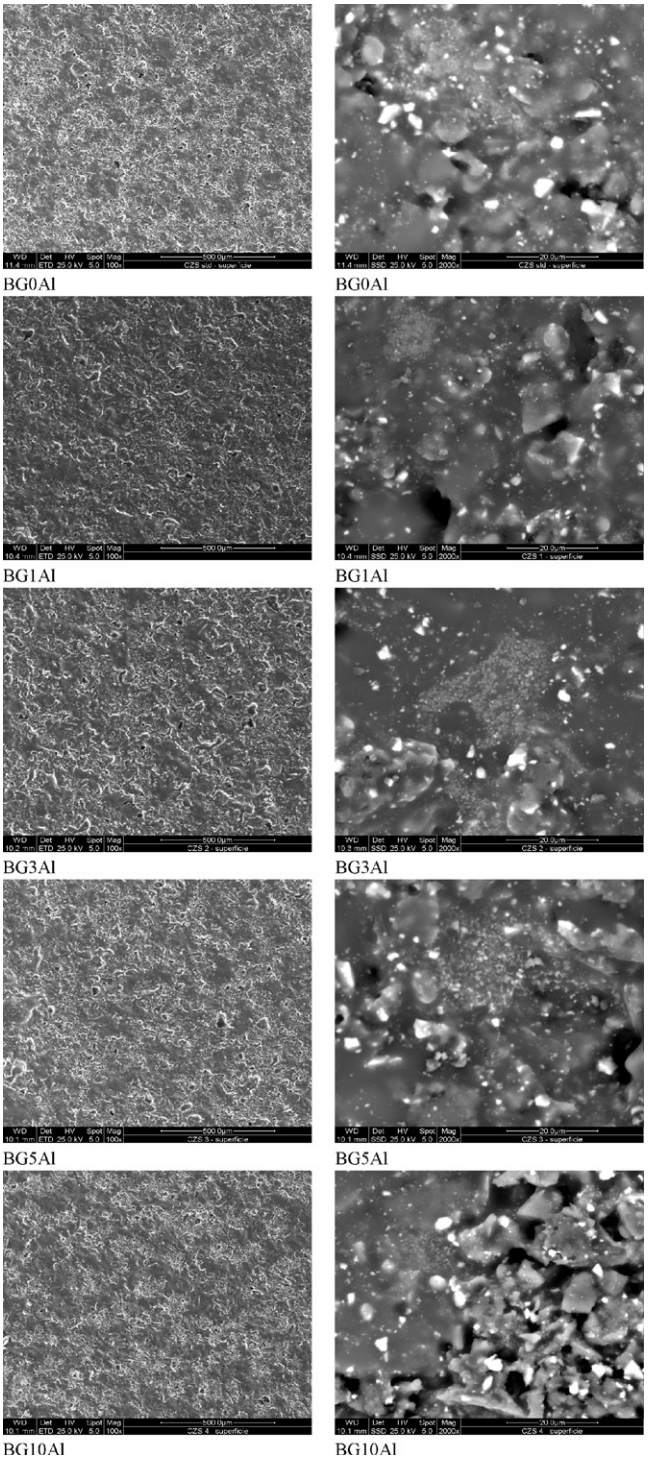


Fig. 3. SEM microstructure of surfaces at different magnification. See magnification bar.

immersed in a glassy matrix. The samples appear quite heterogeneous, the crystalline phases having different size and morphology. The sample BG10Al contains a lower amount of glassy phase than the other samples containing alumina, as already reported in the XRD results (Table 4). Several SEM observations were also done on the polished cross section of the samples, in order to understand the reactivity of the frits with the other components of the bodies (Fig. 4). At lower magnification, the samples BG0Al, BG1Al and BG3Al show a very similar microstructure. Thanks to the backscattered electrons images, it is possible to observe small bright crystals immersed into darker crystalline and glassy phases, while the samples containing frits with higher amount of alumina do not show any white crystals. Moreover, the porosity seems to increase in the BG3Al and BG5Al samples, which is in agreement with the values of linear shrinkage reported in Table 5. A SEM/EDS study was performed at a higher magnification (Fig. 4) on the grain of unreacted frits present in the samples in order to understand their interaction during firing with the other components of the body mixture.

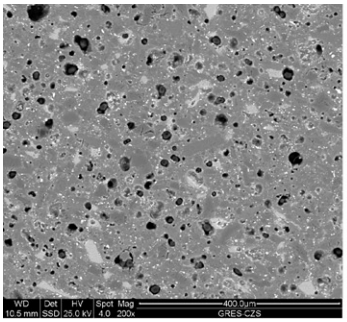
In the BG0Al sample, the small white crystals reported above were identified as grains of CZS frit by using EDS technique. It is interesting to observe that the frit grains present a sort of ‘‘gradient microstructure’’ since the surface of the grains display crystals of different chemistry compared to their inner part and moreover, an interface between frit-grains and the surrounding sample is quite evident.

This effect is due to the diffusion of aluminium ions from the surrounding clays (illitic–kaolinitic clays and kaolin) to the frit grains. This behaviour has been found in the samples were the added frits do not contain alumina, or a very few amount of it (BG0Al and BG1Al). The EDS analysis reveals, in fact, that the surface is richer in alumina, while the bulk contains only the three oxides CaO, ZrO_2 and SiO_2. Also Pontikes et al. [21] revealed areas richer in Al at the intergranular rim between glass and ceramic matrix, as a possible indication of crystalline phases development. This result confirms that during heat treatment, the clays react with the surface of the grains leading to the formation of a new crystalline phase, anorthite, while the bulk of the grain, richer in CaO, ZrO_2 and SiO_2, is where the $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ phase forms. As reported in some papers [22,23] this latter phase is the main crystalline system, together with wollastonite, induced by CZS devitrification. A similar behaviour is also observed in the sample BG1Al [13].

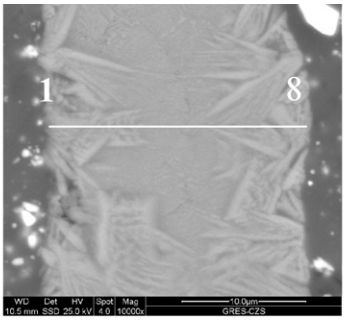
In the sample BG3Al, a different microstructure is observed in the frit grains. In this case, the grains show a homogeneous crystallization, with no ‘‘gradient microstructure’’. The alumina already present in the frit, probably delays the diffusion of the aluminium ions from the external clay matrix. SEM observation reveals two different crystalline phases, also in this case, anorthite and $CaO4SiO_2ZrO_2$, which are the main phases of CZAS glass-ceramic system, as reported in a previous paper [13]. This is a clear evidence that increasing the amount of alumina into the frit and the reactivity of the glass with the clays of the body mixture lead to an increase of anorthite into the sample.

In fact, in the samples BG5Al and BG10Al, glass-ceramic frit grains present mainly the anorthite phase, even if small crystals of $CaO{\cdot}4SiO_2{\cdot}ZrO_2$ are also visible in the SEM image. This ternary phase is not detectable by XRD technique since its amount is lower than standard laboratory XRD detection limit.

This behaviour is in good agreement with what previously found and discussed. In fact, both in BG5Al and in BG10Al, the frit grains do not display anymore a ‘‘chemical gradient’’ microstructure from the surfaces to their cores, but they are

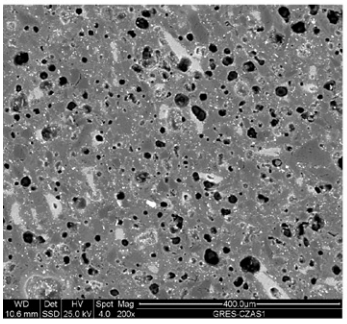


BG0Al

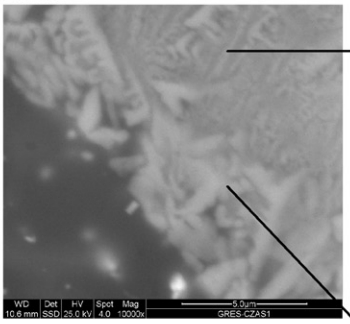


BG0Al

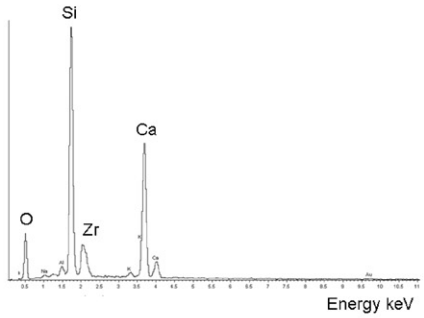
Wt%	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	ZrO_2
Point 1	2.7	10.8	58.8	3.12	11.8	12.8
Point 2	0.8	1.8	55.3	0	25.0	16.1
Point 3	0	0	55.8	0	29.0	14.3
Point 4	0	0	56.1	0	28.6	13.5
Point 5	0	0	54.4	0	28.8	15.2
Point 6	0	0	55.4	0	28.4	14.7
Point 7	1.1	1.8	55.6	0	28.1	12.6
Point 8	3.6	12.1	60.6	3.9	11.6	8.1

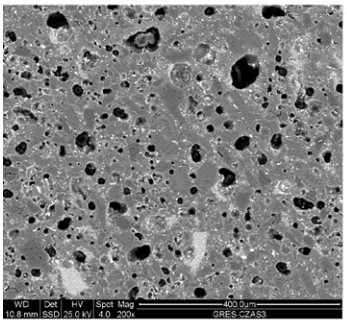


BG1Al

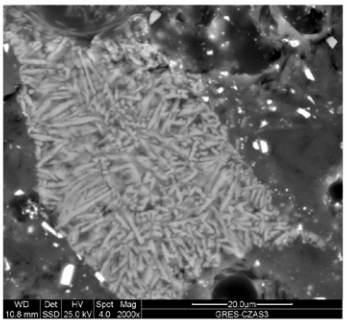


BG1Al

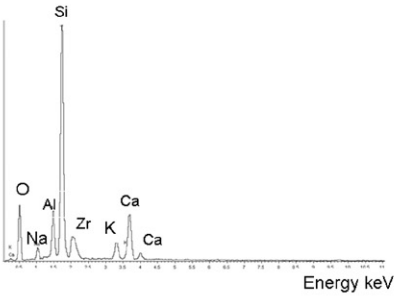


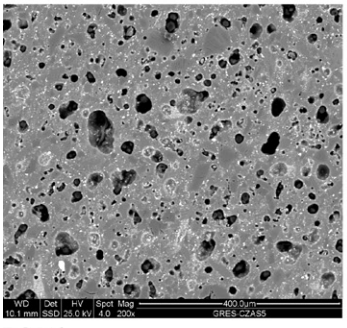


BG3AL

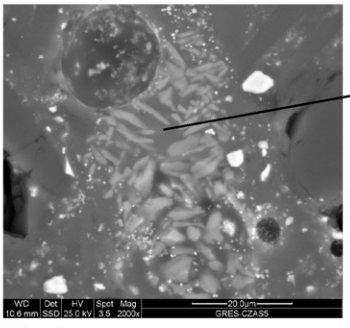


BG3AL

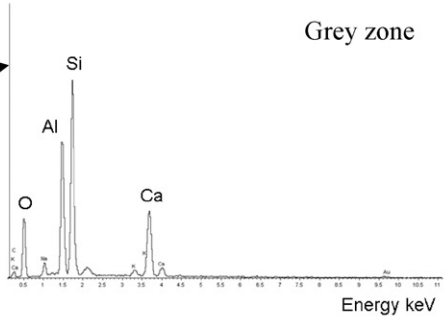


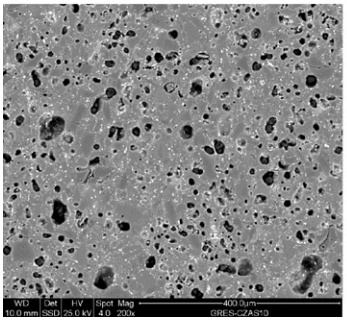


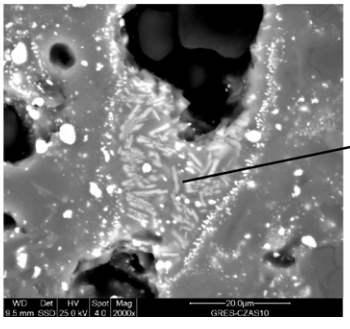
BG5Al



BG5Al







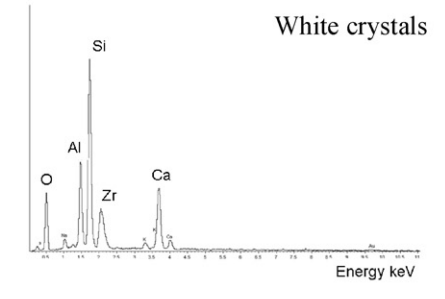


Fig. 4. SEM microstructure of cross section polished samples and the EDS analysis (wt%).

Table 5
Technological properties of studied samples.

	BG0Al	BG1Al	BG3Al	BG5Al	BG10Al
Linear shrinkage (%)	5.1 ± 0.1	4.6 ± 0.1	3.8 ± 0.1	3.5 ± 0.1	4.1 ± 0.1
WA%	<0.01	<0.01	<0.01	0.01	0.02
Modulus of rupture (N/mm^2)	55.5	51.1	51.3	63.3	59.1
CTE ($10^{-6}/°C^{-1}$)	7.2 ± 0.1	7.3 ± 0.1	7.1 ± 0.1	7.2 ± 0.1	7.1 ± 0.1
L^*	87.7 ± 0.1	86.9 ± 0.1	88 ± 0.1.1	87.6 ± 0.1	87.3 ± 0.1
a^*	0.1 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.1
b^*	6.7 ± 0.1	6.3 ± 0.1	6.4 ± 0.1	6.5 ± 0.1	6.7 ± 0.1
WI	40.6 ± 0.1	40.6 ± 0.1	42.9 ± 0.1	41.2 ± 0.1	39.9 ± 0.1
AE*	Ref	0.81 ± 0.1	0.93 ± 0.1	0.43 ± 0.1	0.45 ± 0.1

much more homogenous all along their thickness, where a crystalline phase, caused by devitrification of the grains during firing, is embedded in a vitreous matrix and clearly visible. The lack of the ''gradient'' microstructure is likely due to the significantly reduced reactivity of the clays with the surface of the frit grains, caused by the already mentioned spontaneous devitrification process of the frit.

As a matter of fact, the CZAS frit seems to modify the equilibrium between the co-existing glass and the crystalline phases in the porcelain stoneware bodies. The most relevant contribution of Al_2O_3 addition into the frit is promoting a higher crystallization of the gres bodies for amount higher than 5%, since the amount of glassy phase decreases and the amount of plagioclase (anorthite) increases.

3.3. Technological characterization

The incorporation of new glass-ceramic precursor (containing different amount of alumina) in the porcelain stoneware body compared to the no-alumina added sample BG0Al slightly influence the firing behaviour of the porcelain stoneware tiles (Table 5). The water absorption (WA%), CTE and the colour components are mainly similar to BG0Al, while modulus of rupture presents higher values for BG5Al and BG10Al. As reported in the *microstructure* section, the samples which present higher amount of alumina (5 and 10 mol%) show higher amount of anorthite. It is well known that the mechanical properties of the samples depend on several microstructural parameters in particular from kind, ratio and size of crystalline phases, amount and chemical composition of vitreous phase, porosity, interfaces glass/crystal, etc. [23]. SEM observations made on the studied samples reveal that increasing the alumina content into the frit, the microstructure of the final product becomes more homogeneous, since the gradient structure of frit grains tends to disappear with increasing alumina, even if the ratio between crystalline phase/vitreous phase increases in BG10Al. The beneficial effect of anorthite was found also by Taskiran et al. [24] who studied a new porcelainised stoneware material based on anorthite whose technological properties were significantly better than the properties of the conventional porcelainised stoneware, and concluding that it was due to the high content of anorthite into the final product.

Firing shrinkage slowly decreases with the increase of the amount of alumina into the frits: BG5Al presents the lowest value of linear shrinkage%. During the heat treatment feldspars form a glassy phase and this viscous phase can improve the linear shrinkage. Moreover, generally increasing the alumina content in a glass leads to an increase in viscosity at low temperature, but at temperature higher than 1100 °C this behaviour can change. In fact in a work of Solvang et al. [25] the viscosity–temperature relationship of different CaO–Al_2O_3–SiO_2 compositions was reported and a cross over (from high to low viscosity) was reported for the studied series. They explained that the cross over between the viscosity curves may suggest an inverse compositional dependency of viscosity in the high and low viscous range. In our samples the CZS10Al and CZS5Al frits, at high temperature (>1100 °C) having a lower viscosity than CZS3Al, CZS1Al, can react with the surrounding raw materials (feldspars, dehydroxylated clays) separating crystalline phases as anorthite and albite. The linear shrinkage of BG10Al sample is lower than the sample BG5Al and this effect is due to this crystallization process that in BG10Al is more relevant, as reported in Table 5. BG10Al sample displays a lower viscosity than BG5Al: this characteristic improves the crystallization process of the sample, which form higher amount of crystalline phases than BG5Al sample, and shows the higher linear shrinkage%.

Observing all the results reported in Table 5, it is possible to conclude that BG5Al shows, in general, the best combination of properties in terms of mechanical, physical and aesthetical properties because the linear shrinkage decreases, the water absorption is low (0.01%), the modulus of rupture is 14% higher than BG0Al while the coefficient of linear expansion (CTE) and the aesthetical properties in terms of Hunter parameter, white index and AE are quite similar to those of BG0Al sample. Further amount of alumina into the frit (BG10Al) does not further increase the technological properties, because linear shrinkage starts to increase and the modulus of rupture to decrease, further demonstrating that the 5% addition of Al_2O_3 to CZS frit (sample BG5Al) represents the optimal amount to achieve the best combination of properties.

4. Conclusions

The studied glasses originate from the CaO–ZrO_2–SiO_2 (CZS) system; the frit belonging to this system is largely used as ceramic frits. When this frit is added to a traditional ceramic mix, it tends to react with the alumina contained in the clays,

inducing the crystallization of different crystalline phases. This reactivity can affect the mechanical properties of the final ceramic product. In order to strongly limit this reactivity, different amounts of alumina 1, 3, 5, and 10 mol% have been added to the base glass, CZS, obtaining new frits belonging to the $CaO–Al_2O_3–ZrO_2–SiO_2$ (CZAS) innovative quaternary system.

Observing all the results it is possible to conclude that the sample containing the CZAS frit with 5 mol% of Al_2O_3 shows, in general, the best combination of properties in term of mechanical, physical and aesthetical properties. Further amount of alumina into the CZAS frit (10 mol%) does not further increase the technological properties, while the samples containing the CZAS frits with lesser content of alumina (1 and 3 mol%) show similar properties of the sample containing the CZS-frit (no-alumina addition).

Moreover, last but not least, BG5Al, is cheaper than the base CZS-frit since a part of ZrO_2 was replaced by alumina. The raw materials used for the frit preparation are quartz, calcite, zircon and alumina. Among these raw materials zircon is the more expensive. It is important to underline that the melting temperature of the all mixes are the same, 1550 °C, as already reported in the paper.

Acknowledgment

The authors are grateful for the constructive comments of the anonymous reviewer.

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