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Production of opaque frits with low ZrO_2 and ZnO contents and their industrial uses for fast single-fired wall tile glazes

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Abstract The amounts of zirconium and zinc oxides, which raise the production costs of ceramic glazes, were decreased in fast single-fired wall tile frit compositions and an industrial frit production was conducted. Opacity of the fired frit-based glazes was accomplished by compositional modifications of frits with no other nucleating agent. It was determined that the ratios of $Al_2O_3/\Sigma R_2O$, $Al_2O_3/\Sigma RO$, and Al_2O_3/B_2O_3 have significant effects on decreasing ZrO_2 and ZnO levels in the frit composition. A reduction of 25% in both zirconia and zinc oxide contents of frit batches, with respect to the reference frit (*R*) containing 6–10% ZrO_2 and 6–10% ZnO for a glossy white opaque wall tile glaze, was achieved in the ZD glaze consisting of 4.5–7.5% zirconia and 4.5–7.5% ZnO in its frit composition. It was concluded that zircon was the main crystalline phase of the glaze contributing the opacity. The ZD frit-based glaze has a thermal expansion coefficient value of $61.13 \pm 0.32 \times 10^{-7}\ °C^{-1}$ at 400 °C which well matches to that of the wall tile body. TS EN ISO 10545 standard tests were also applied to the final ZD glaze. It is confirmed that the production cost of a fast single-fired wall tile glaze can be decreased by 15–20% with the successful new frit developed.

Introduction

Multi-oxide containing silicate frits are the predominant materials in the fast single-fire ceramic tile glazes and zircon ($ZrSiO_4$) is the most commonly used opacifier in their compositions [1]. Opaque glazes are employed to cover undesired substrate colors, to overcome body surface defects, and also to supply pleasant and satisfactory esthetic appearances, besides giving sufficient mechanical properties. A surer way to achieve opacity is to add an opacifying agent or opacifier into a starting batch of either frit or glaze itself. The opacity of a fired glaze depends upon the refractive index differences between glassy and crystal phases, concentration of the opacifying agent, particle size distribution of the opacifier, degree of dispersion, glaze thickness, and the character of the boundary zone between crystalline particles and the glassy matrix [2, 3].

The presence of zircon crystals with particle size, approaching the wavelength of incoming light, improves light to scatter and thus, ensures opacification. As well as its high refractive indices, the fine particle size of commercially available zircon enables it to be an excellent opacifier in the ceramic world. However, it has been established that a threshold amount of zircon is required for an adequate opacity in the glaze [4]. Such a high usage level of zircon to make sure the achievement of finer particles of the opacifier imply in an increase in the production cost [5].

Zinc oxide is widely preferred in zirconia containing opaque glazes, thanks to its increasing effect on whiteness and opacity [3]. ZnO dissolved in the glass enhances zircon crystallization of a frit and leads to very stable opaque coatings [1]. Wall tile opaque glazes are prepared by the employment of approximately 95% opaque frit containing zirconia and zinc oxide. However, likewise zirconia, ZnO

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is another expensive component of this type of glazes therefore, it causes high manufacturing costs.

Designing a relatively cheap and alternative opaque frit composition should fulfill many requirements. Besides the adaptation to industrial fast-firing cycles, the production of such a frit in glass-melting furnaces is another important issue in terms of industrial application. The reaction between the molten glass and furnace refractory is inevitable during melting at high temperatures. Opaque frits, from which diopside, anorthite, wollastonite, or mullite formations take place, differs from the one with zirconia content in the view point of alkalinity. These kinds of frit formulations generally include higher amounts of CaO and MgO [6–19]. The presence of transition metal oxides, high level of alkali, and earth-alkali oxides and most importantly alumina in a frit batch lead to serious degradation in many properties [20]. Therefore, their contribution levels are restricted in a zirconia-free frit [16]. Silica refractory's, sometimes termed as acid refractory's, are very well-known for their high-temperature load-bearing capacity and commonly used in industrial glass-melting furnaces, which are resistant to acidic fluids like zirconia containing glass melts. On the other hand, they are readily attacked by the melts consisting of a high proportion of CaO and/or MgO [21]. Therefore, if ZrO_2 is not present in a frit at an optimum level, alkali degradation caused by the melt on the refractories cannot be prevented. Consequently, a proper furnace design is required in the case of industrial zirconia-free frit production. In the ceramic industry, sometimes it is not convenient to design a new furnace for just one single frit composition since the industrial glass melting furnaces are expected to be suitable for the production of various and different kinds of frit with no refractory deterioration and contamination. Therefore, decreasing attempts of zirconia content in a frit, in the view of lowering the production cost, is limited by this fact. So, in the present study ZrO_2 content was duly lowered instead of being totally eliminated. Compositional variations of frits, physical and mechanical properties of the frit-based glazed wall tiles were investigated in order to provide general information needed to find a proper, optimum condition for industrially applicable opaque wall tile glazes with lowered ZrO_2 and ZnO contents.

Experimental

Quartz, kaolin, dolomite, calcite, boric acid, zircon, Na-feldspar, K-nitrate, and zinc oxide were used as frit raw materials. First of all, suitable frit compositions were determined on the basis of industrially used *R* (reference) frit and prepared (Table 1). Compositional details of the studied frits are given in Table 2. After precise weighing and homogeneous mixing, the batches were melted in alumina crucibles at 1,500 °C for 1 h and melts were quenched into water to obtain frits under laboratory working conditions. After the water quenching process, all the melts were found to be in a transparent glassy state. The ZD frit recipe found to be more successful amongst all the other studied ones was then selected and industrially produced over 3 tons.

Table 1 Composition of the starting Z frit

Components	Content (mol%)
R_2O (Na_2O, K_2O)	5.93
RO (CaO, MgO, ZnO)	19.27
R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3)	9.43
RO_2 (SiO_2, ZrO_2, TiO_2)	65.37
Total	100.00

Fe_2O_3 and TiO_2 are from some raw materials and their amounts are negligible

Frits (95 wt%) and 5% kaolin were mixed. Afterwards, 50% water, 0.15% carboxyl methyl cellulose (CMC), and 0.25% sodium tripolyphosphate (STPP) were added to the mixture, which was wet-milled for 50 min in a porcelain mill containing 200 g alumina balls. Then, the glaze slips were applied on previously engobed green wall tiles. Industrial firing was conducted in the fast single-firing furnace with a top temperature 1,140 °C and a total firing cycle of 55 min.

The comparison of the L*, a*, b*, and gloss values of the glazed tiles studied were made with those of the reference (*R*) one covered with an opaque white glaze which is industrially used.

The glass transition (T_g) and the crystallization temperatures of frits were determined by a differential thermal analyzer (DTA, Netzsch STA 409 PC) on the samples ground to less than 63 μm with a heating rate of 10 °C/min up to 1,200 °C.

Frit behavior was studied by a hot stage microscope (Misura ODHT HSM 1600–80) with a heating rate of 10 °C/min up to 1,300 °C. The frit viscosities were calculated employing HSM data in the association with T_g values obtained from DTA.

The coloring parameters L*, a*, and b* of all the fired tiles were measured using a Minolta CR-300 series chromo-meter. Gloss was determined by a gloss-meter (Minolta Gloss 268) with a 60° light incident angle on the glaze surface. L*, a*, b*, and gloss analyses were made three times for every glazed tile samples. Then, the mean values and standard deviations were calculated.

X-ray diffraction (XRD) analyses were conducted by a Rigaku Rint 2000 series difractometer with CuK_α radiation.

Table 2 Compositional details of studied frits (in moles)

Frits	Al_2O_3/SiO_2	Al_2O_3/*ΣR_2O	Al_2O_3/**ΣRO	Al_2O_3/B_2O_3	CaO/MgO	ZrO_2	ZnO
Reference (*R*)	0.06	1.73	0.14	3.25	2.58	x	y
Z	0.04	0.38	0.08	0.38	2.19	$x - 0.032$	$y - 0.94$
ZA	0.04	0.28	0.08	0.28	2.19	$x - 0.013$	$y - 0.94$
ZB	0.06	0.77	0.16	0.77	2.24	$x - 0.013$	$y - 0.94$
ZC	0.06	1.22	0.13	1.22	2.24	$x - 0.013$	$y - 0.24$
ZD	0.06	1.26	0.13	1.26	2.24	$x - 0.010$	$y - 0.24$

* = $Na_2O + K_2O$

** = CaO + MgO + ZnO

XRD patterns were taken from the fired glazed tile surfaces to identify the crystalline phases formed, working at 40 kV and 30 mA, with the scanning velocity of 2°/min. In order to search for the effect of glaze composition on the formation, size, and distribution of the opacifying crystal phases, the samples analyzed with XRD were also subjected to the analyses of a scanning electron microscope (SEM-Zeiss EVO 50 EP at 20 kV) attached to an energy dispersive X-ray analyzer (EDX).

Glaze samples, engobe, and wall tile body were heated in a dilatometer (Netzsch DIL 402 PC) at a rate of 10 °C/min up to 600 °C in order to determine their thermal expansion coefficient values (α). Dilatometer analyses were made three times for every glaze, engobe, and wall tile body samples. Then, the mean values and standard deviations were calculated. All the fired glazed tile samples were undertaken to certain standard tests of thermal shock resistance, autoclave, Harcourt, chemical durability, stain resistance, and Mohs hardness (TS EN ISO 10545). Five glazed and fired tiles with the dimensions of 15 × 15 cm were heated to 145 °C and remained for 20 min in a stove and after, their glazed surfaces immersed in cold water. This procedure was repeated 10 times and following, the solution of 1% dilute methylene blue was brushed onto the glazed surfaces. Standard autoclave test was also carried out at 5 atm pressure to identify the crack resistance of the glazes with the assistance of aqueous methylene blue solution brushed onto the glazed tiles. The sample surfaces were checked out to see whether any cracking occurred. Chemical resistance test was conducted onto the glazed tile surfaces with hydrochloric acid, potassium hydroxide, low and highly concentrated solutions of house chemicals, pool salt and citric acid. Green colored material in oil and iodine and olive oil were used for stain resistance test.

Results and discussion

Table 3 Color (L*, a*, b*) and gloss (60°) values of some studied glazes

Glazes	L*	a*	b*	Gloss (60°)
Reference (*R*)	92.67 ± 0.43	−0.12 ± 0.25	2.06 ± 0.42	95.0 ± 0.64
Z	89.46 ± 0.44	−0.29 ± 0.28	3.70 ± 0.46	65.3 ± 0.67
ZA	89.16 ± 0.49	0.17 ± 0.28	3.23 ± 0.48	90.7 ± 0.63
ZB	87.70 ± 0.46	0.30 ± 0.30	3.84 ± 0.44	–
ZC	89.48 ± 0.43	0.01 ± 0.26	3.01 ± 0.42	80.2 ± 0.66
ZD	92.19 ± 0.44	−0.34 ± 0.26	2.05 ± 0.43	95.0 ± 0.65

Color (L*, a*, b*) and gloss (60°) values of some studied glazes are represented in Table 3. Thanks to the compositional modifications in the frit recipes, ZrO_2, and ZnO contents were lowered with no other nucleating agent. Reducing them in the composition was accomplished by optimizing the frit recipes. All the frit-based glazes studied were matured at 1,140 °C for a total time of 55 min in a fast single-firing industrial furnace.

At the stage of compositional arrangement, ZrO_2 (x mole) and ZnO (y mole) contents in the *R* glaze were, first of all, decreased as presented in Table 2. Although the *Z* glaze surface was smooth, it's L* and gloss values were lower with respect to those of the *R* one (Table 3). When ZrO_2 was lowered ($x - 0.013$ mole) and ZnO level was kept constant, the ZA glaze exhibited a considerably higher gloss value and the whiteness did not significantly change but pinhole problem appeared. Air trapped in closed pores must diffuse to the surface where it can be eliminated. Bubbles rapidly form on heating when gas dissolves in the frit or molten glaze or gas that is a decomposition product produces bubbles [22]. Pinholes are among the main glaze defects commonly faced with. If the glaze is a kind sealing over at a quite lower temperature then, there will be insufficient time for gases to escape [23]. Pinhole problem can be explained by the migration of small gaseous bubbles due to dissociation of carbonates, from the interior of the glaze layer toward its surface forming small craters, which do not have time enough to be filled by viscous flow of melted glaze accordingly, more or less perceptible pinholes remained after cooling [24]. Therefore, pre-sintering reactions such as decomposition of inorganic components and particulate carbon should be completed before the final stage of sintering and in a fast single-firing process, the sintering of the glaze must be synchronized with the sintering of the underlying body. Smoothing of the surface depends on viscous flow after surface bubbles break [22]. In terms of gloss, whiteness and surface quality of the opaque glazes, increasing boric oxide in the composition has a positive effect. B_2O_3 in the glazes reduces the softening and maturation temperatures, lowers surface tension, and improves the mechanical and thermal properties [25]. Since all the samples were fired under the same conditions in the present study, it is thought that the pinhole formation tendency is caused by earlier glaze maturation, which is a consequence of the presence R_2O oxides and B_2O_3 at a high level. In order to get rid of these pinholes, both Al_2O_3 content and CaO/MgO ratio were increased in the ZB glaze composition. However, surface defects were experienced and gloss value could not been measured. This is thought to be due to the high surface tension of the ZB glaze. Such a distorted surface texture may be attributed to higher Al_2O_3 level compared to that of the ZA glaze. As is known, Al_2O_3 is capable of modifying the viscosity during glass melting. On the other hand, it increases the surface tension and causes defects on the glaze surface [3, 26, 27]. ZnO content decreased as $y - 0.24$ mole (20%) in the ZC composition without changing the Al_2O_3/SiO_2 ratio. Such a modification gave rise to a smooth glaze surface with higher L* and gloss values with respect to the ZA one. Final compositional optimizations were done in terms of color and gloss and the ZD glaze was achieved. In that glaze ZrO_2 level was diminished by $x - 0.01$ mol (21%) by keeping the Al_2O_3/SiO_2 and CaO/MgO ratios constant compared to that of the *R* glaze. Al_2O_3 is involved in the adhesion stability of the glaze to the body. When its content is too low, such stability may be decreased, impeding the formation of a glass layer with uniform thickness on the glazed surface. When it is too high, the chemical resistance of the glass layer may unpreferably be reduced [26].

Lowering ZnO content in a zirconia containing opaque glaze diminishes the whiteness because ZnO contributes to the enhancement of color development and increases the brightness as well as improving the glaze surface quality [1, 3, 26]. These indispensable contributions of ZnO in opaque glazes were fulfilled with the presence of B_2O_3 and Al_2O_3 in the current study. A reduction of 25% of both zirconia and zinc oxides in frit batches with respect to the reference frit (*R*) containing 6–10% ZrO_2 and 6–10% ZnO for glossy white opaque wall tile glaze was achieved in the ZD glaze consisting of 4.5–7.5% zirconia and 4.5–7.5% ZnO in its frit composition. The ZD glaze was found to be the most opaque and glossy one with desired surface properties when compared to the other low zirconia and ZnO containing glazes after the laboratory studies. Consequently, its frit was produced in the industrial frit melting furnace.

The hot stage microscope analyses conducted on the *R* and ZD frits are presented in Table 4. Their shrinkage and viscosity graphs are depicted in Fig. 1. While ZrO_2 and ZnO contents were lowered as 21 and 20%, respectively in the frit composition, the $\sum R_2O$, $\sum RO$ and B_2O_3 levels were increased. It is a very well-known fact that alkali and earth-alkali oxides are capable of lowering the softening point and viscosity [25, 28]. Such an effect was clearly experienced with the softening points decreasing in the ZD frit.

Common linear shrinkage behavior was observed in both frits as seen in Fig. 1. At a higher temperature, with which sintering starts, the curves flatten with no distinct change in linear shrinkage until the softening temperature

Table 4 Hot stage microscope analyses of the *R* and ZD frits

Temperature (°C)	*R*	ZD
Sintering	855	855
Softening	1,056	1,047
Sphere	1,140	1,135
Half sphere	1,170	1,190
Fusion	1,184	1,210

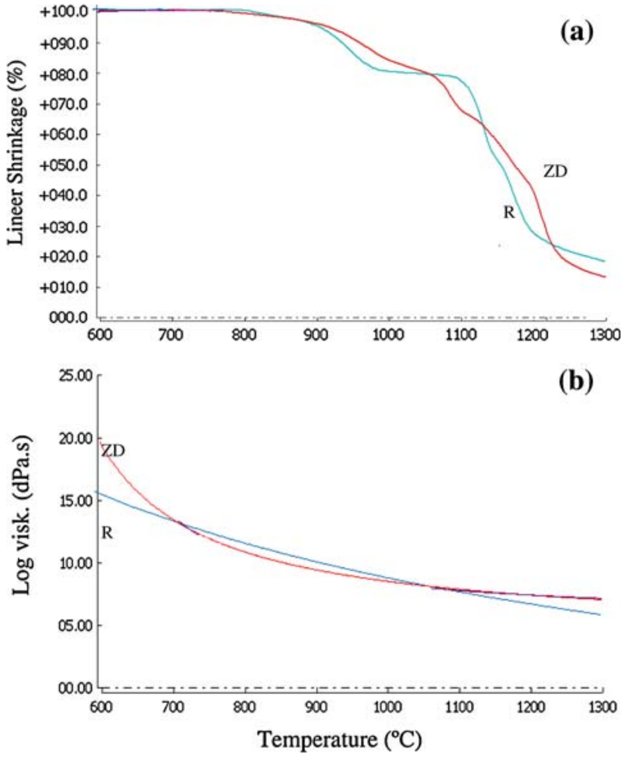

Fig. 1 Linear shrinkage (**a**) and viscosity (**b**) graphs of the R and ZD frits

is reached. During heating, the sintering tendency of the specimens is interrupted when crystallization occurs. At much higher temperatures, densification carries on with the linear shrinkage decreasing. The Al_2O_3/alkali and Al_2O_3/B_2O_3 ratios of ZD frit are lower than those of *R*. The increase in alkali and B_2O_3 contents in the composition leads to lower viscosity. Alkali and earth-alkali oxides considered as glass network modifiers do not remarkably influence the glass behavior during devitrification. These oxides usually weaken the glass structure, inducing a viscosity decrease with an association of decreases in glass transition, crystallization, and melting temperatures. As viscosity is lowered, all the diffusive processes strictly connected to crystallization are favored [17, 29, 30]. It was observed that the viscosity of the ZD frit is lower than that of *R* one at 700–1,000 °C and there is not a distinct change after that temperature. However, the viscosity of the ZD frit decreases continuously with increasing temperature.

With respect to that of *R* one, the higher viscosity level of the ZD frit at higher temperatures is attributed to the increased MgO content. The CaO/MgO ratio of the *R* frit was decreased from 2.58 to 2.24 mol in the ZD frit formulation by incorporating more MgO to the system. Both MgO and ZnO are well-known network modifiers with their high field-strength, producing a more ordered, glassy structure with respect to other network modifying oxides. They are colloquially called stabilizer in industrial frit formulations. The macroscopic effect is an increased glass viscosity with respect to other bivalent oxides, e.g., CaO and BaO [29].

The glass transition (T_g) and the exothermal peak temperature (T_p) of the industrially produced *R* and ZD frits are shown in Fig. 2. Their T_g values were measured as 718 and 713 °C, respectively. The former one exhibited two shallow exothermic peaks at 873 and 953 °C while the ZD demonstrated an intense exothermic peak at 951 °C. Although these frits have a similar thermal behavior in terms of T_g, it was determined that they have different crystallization peak intensities due to the compositional changes. The crystallization peak temperatures, T_p, decrease and the intensity of crystallization peaks increase as a function of the amount of the crystal phase formed in the ZD frit.

Zircon crystallization generally occurs at 900–950 °C according to the literature [6, 17, 31–33]. Therefore, the peaks appeared at 873 and 953 °C in the *R* frit are attributed to calcium aluminum silicate and zircon crystallizations, respectively. In the case of ZD with lower ZrO_2 and ZnO, only zircon formation takes place as a result of the compositional modifications made in its frit recipe. Studied frits, apart from the ZD being the best one in many aspects, were melted under laboratory conditions and then glazes based upon them were fired in the industrial furnace. Figure 3 represents the good comparisons of XRD patterns of the studied glazes and the effect of ZrO_2 and ZnO decreases in frit recipes.

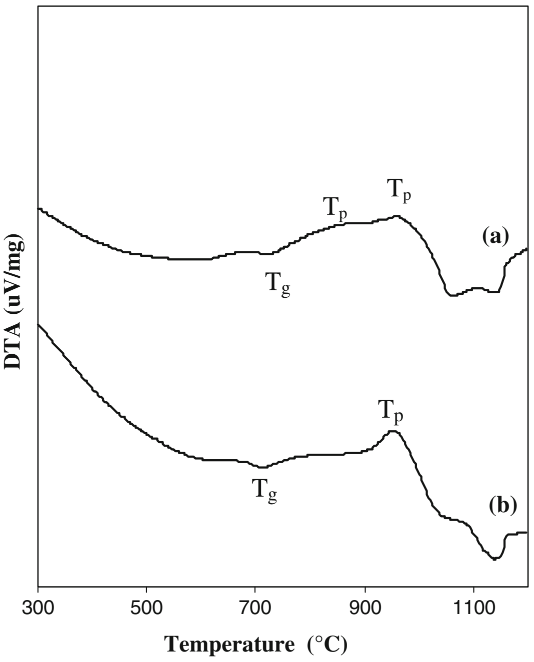

Fig. 2 DTA curves of the reference *R* (a) and ZD frit (b) with a heating rate of 10°C/min

When following Fig. 3, it is quite obvious that the Z glaze depicts only wollastonite crystallization. However, when ZrO_2 and ZnO contents of the frits started to decrease with compositional modifications the only phase contributing to the opacity becomes zircon. Its peak intensity in the ZA glaze is higher due to its excess B_2O_3 content lowering viscosity and facilitating zircon formation. While ZrO_2 and ZnO were reduced, B_2O_3 was optimized. On the contrary to alumina, alkali metal oxides (Na_2O, K_2O, etc.), and B_2O_3 increase the glaze fluidity [17, 25]. Although the ZD frit has a similar Al_2O_3/SiO_2 ratio (0.06) compared to the reference one, its low Al_2O_3/B_2O_3 ratio (1.26) resulted in high XRD zircon crystallization peak intensity to appear after industrial firing of its glaze (Fig. 3). The ZD glaze presents more glassy behavior due to the high B_2O_3 content and has an enhanced amount of zircon after fast-firing. The XRD results of the glazes obtained from the ZD and R frits confirmed the DTA data showing the calcium aluminum silicate and zircon crystallizations.

Previous studies have shown that zircon forms during heating, rather than cooling [34, 35]. The amount of zircon or zirconium oxide formed initially is dependent on the SiO_2/ZrO_2 ratio of the frit. High levels of SiO_2 and Al_2O_3 help to increase the opacity in glazes with zircon but both also lead to increased glaze viscosity. A molecular SiO_2/Al_2O_3 ratio of 10/1 with the SiO_2 level being 2.5–3.5 mol usually forms the basis of satisfactory zircon-opaque glazes [3]. Glazes with lower silica contents have a tendency,

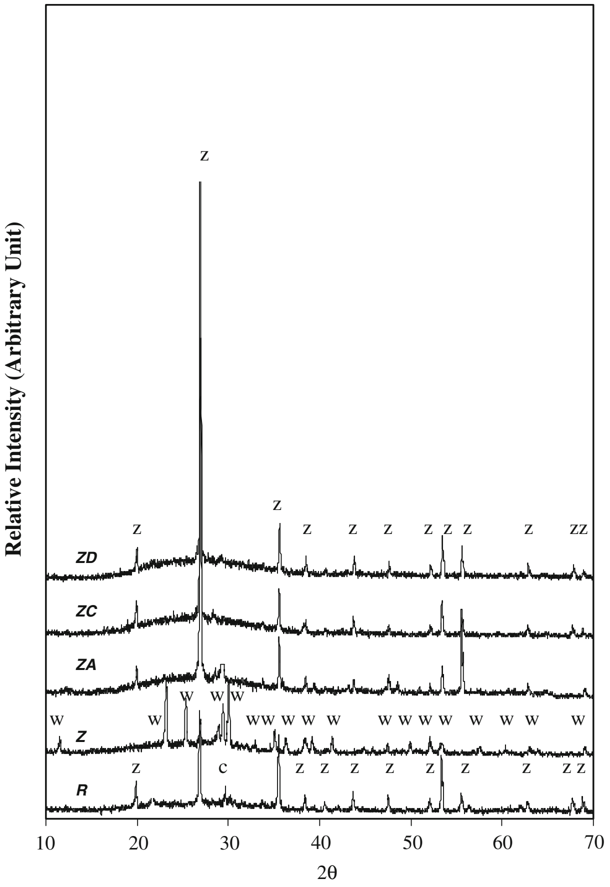

Fig. 3 XRD patterns of some studied glazes industrially fast-fired at 1,140 °C for 55 min (c: calcium aluminum silicate [$CaAl_2SiO_6$], w: wollastonite [$CaSiO_3$] and z: zircon [$ZrSiO_4$])

Table 5 Thermal expansion coefficients (α) values of the wall tile body, engobe, R and ZD glazes

	Thermal expansion coefficient ($\times 10^{-7}$ °C^{-1})
Body	69.63 ± 0.60
Engobe	68.33 ± 0.45
R	61.00 ± 0.46
ZD	61.13 ± 0.32

initially, to exhibit zirconium oxide formation, unlike higher silica ones possessing zircon crystals appeared during heating. In either case, zircon is the final major opacifying component of the glaze [34, 35].

Table 5 shows α values of the wall tile body, engobe, *R*, and ZD glazes between 20 and 400 °C. According to the TS EN ISO 10545 Standards, the difference between the *R* and ZD glazes are acceptable [36]. The dilatometer test results indicated that α of the ZD glaze is lower than those of the engobe and the body. If the three layers were not constrained by their interfacial adhesion, the glaze would contract less than the engobe and the body. The action of sealing them together forces them to be equal in dimension. Thus, the glaze will be compressed by engobe. The engobe will be stressed in tension by the glaze, but will be compressed by the body. In most cases, these effects will cancel out. The substrate will be permanently stressed in tension. At moderate differences, this condition can be tolerated, as the greater thickness of the body relative to the glaze and engobe will serve to spread the stress enough that the body can withstand it [23].

The glaze properties depend upon the microstructure. Thus, in order to relate the properties with the microstructure, it is necessary to characterize the final glaze. In order to end up with a low-porosity in crystallized materials, the sintering must be largely completed before the crystallization [17]. Figure 4 represents the SEM microstructures of the ZD and *R* glazes. Both of them exhibited similar micro structural views. Figure 5 shows the zircon occurrence in the *R* glaze. The acicular crystals originated from the starting frit of the *R* and ZD glaze consist of zircon (Fig. 6). These crystals are generally dispersed in the glassy matrix and they are approximately 2 μm or smaller in size. Generally, zircon crystals have a tendency to become acicular, and their elongation sizes may lead to a loss of opacity [4].

Some properties of the newly developed ZD glaze were determined by certain standard tests [36] (Table 6). The ZD glaze gave the similar results to those of the reference

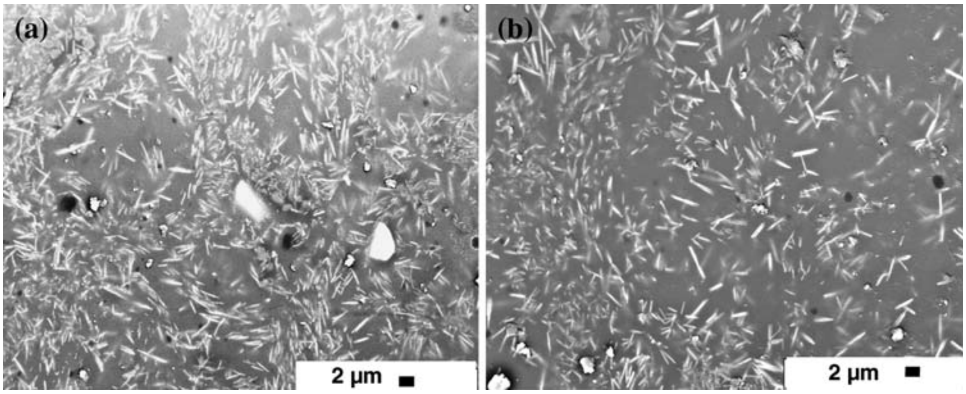

Fig. 4 SEM micrographs of the *R* glaze (**a**) and ZD glaze (**b**)

R in the autoclave test. In the Harcourt test, five samples were used and glaze-cracks were not observed at the standard test temperatures, 105–110 °C.

Conclusions

Zirconia and zinc oxides in frit batches are expensive components. However, thanks to their contributions to ceramic glazes, they are in common use. With the present study their contents in a conventional fast single-fired wall tile glaze was lowered by 25% each. Reduction was done by modifying the frit chemical composition with no other nucleating agent incorporated for the opacification. The ZD frit with lower ZrO_2 and ZnO contents was successfully prepared and a wall tile glaze was produced with it, applied and fast single-fired at an industrial scale. The results of the

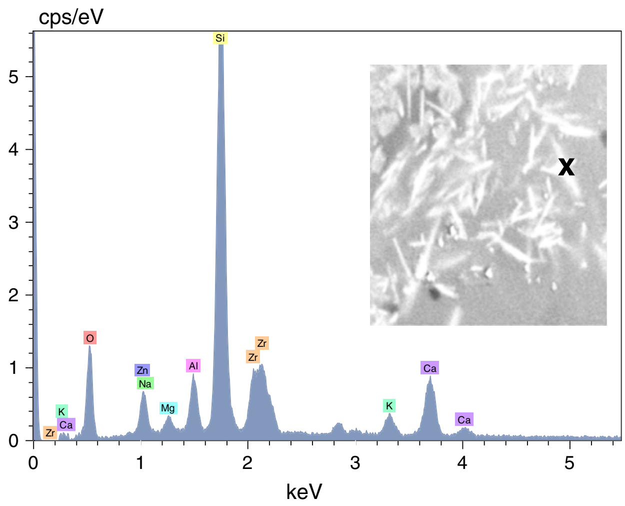

Fig. 5 EDX result showing the zircon occurrence in the *R* glaze

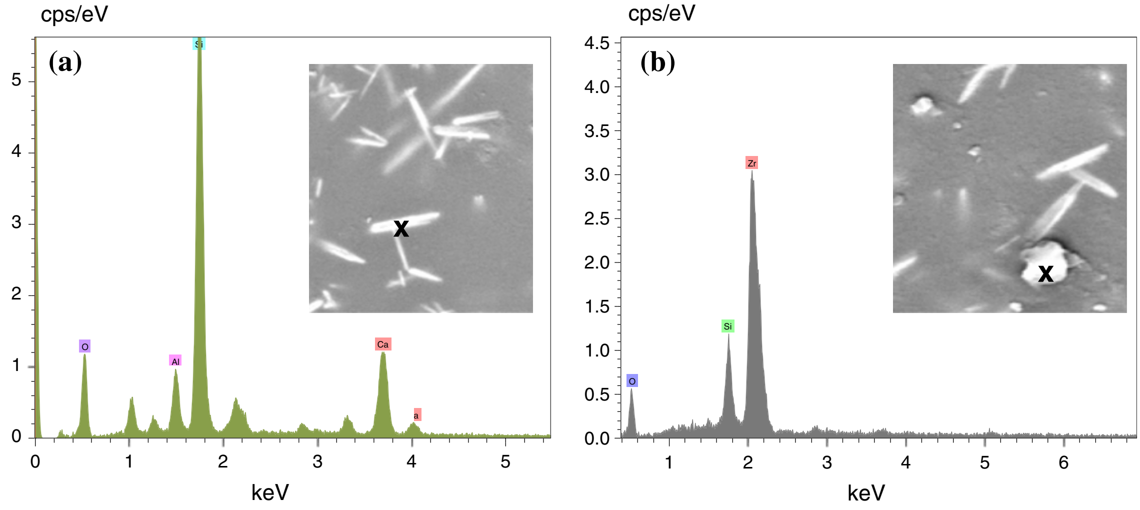

Fig. 6 EDX results exhibiting the zircon occurrence in the ZD glaze in acicular (**a**) and irregular shape (**b**)

Table 6 Some properties of the ZD glaze determined by certain standard tests (TS EN ISO 10545)

Test	Results of the *R* glaze	Results of the ZD glaze
Thermal shock resistance	No cracking	No cracking
Crazing resistance	No cracking	No cracking
Chemical resistance		
House chemicals	GA (No visible difference)	GA (No visible difference)
Pool salts	GA (No visible difference)	GA (No visible difference)
Acids and alkalis		
Low concentration (L)	GLA (No visible difference)	GLA (No visible difference)
High concentration (H)	GHA (No visible difference)	GHA (No visible difference)
Stain resistance		
Green stain		
Olive oil	Class 5 (Cleaned with water)	Class 5 (Cleaned with water)
Iodine solution		
Scratching resistance (Mohs)	3	3

final product were satisfactory in terms of color, gloss, surface texture, and met the requirements of standard tests for glazed wall tiles. The $Al_2O_3/\Sigma R_2O$, $Al_2O_3/\Sigma RO$ and Al_2O_3/B_2O_3 ratios have significant effects on decreasing ZrO_2 and ZnO levels. The newly developed ZD glaze was produced with a decrease of 15–20% in the production cost.

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