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Zircon-free frits suitable for single fast-firing opaque wall tile glazes and their industrial productions

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Abstract

Wall tile glazes with a smooth surface texture, high glossiness, and whiteness are usually based on zirconium containing frits. However, these frits are quite expensive and therefore, there have recently been certain attempts to lower the production cost such as taking suitable glass–ceramic glaze systems into an account. With the present work, the frit-based glaze compositions belonging to the K_2O–MgO–CaO–ZnO–Al_2O_3–B_2O_3–SiO_2 glass–ceramic system were studied to prepare newly synthesized wall tile glazes for industrial single fast-firing. The design of a glass–ceramic glaze for this type of tiles should ensure that the selected frit precursor is technically and commercially compatible with the manufacturing conditions generally used in the production of glazed ceramic wall tiles. The aim of the study is to develop zircon-free, frit-based, glossy opaque glass–ceramic glazes for wall tiles by optimizing the CaO/MgO and adjusting the Al_2O_3/alkali ratios in the starting frit compositions. Frit production, glaze preparation, application, and single fast-firing of wall tiles were, first of all, conducted under laboratory working conditions and then, successful recipes were adapted to the relevant industry. The frit crystallization capability and crystallization temperature range were determined by differential thermal analysis (DTA). Thermal expansion coefficient values of glazes were determined by a dilatometer. Characterization of single fast-fired glass–ceramic glazes was made by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques. Colour and gloss analyses of the final glazes were measured with a spectrophotometer and a gloss meter, respectively.

Keywords: Fast-firing; Glass–ceramic; Zircon-free opaque wall tile glaze

1. Introduction

Glass–ceramics are crystalline materials formed through a controlled crystallization of glass during a specific heat treatment in order to provide a homogeneous microcrystalline structure.[1] Recently, an extensive number of studies was conducted on the glass–ceramic systems of diopside, wollastonite, anorthite, mullite, zircon, cordierite, etc. In these searches it was reported that samples were generally prepared by sintering quenched glass or glass–ceramic powders at several temperatures for varying durations with a controlled heat treatment.[1–3,4–6] In some of these studies nucleating agents such as Cr_2O_3, Fe_2O_3, CaF_2, WO_3, V_2O_5, MoO_3 or TiO_2 were used.[1,3,4,7] Glass–ceramic materials are of growing interest for preparing tile coatings being an alternative to traditional amorphous glazes.[1,3,8–19] To be industrially applicable, a desired devitrification process needs to take place in the glass–ceramic glazes during the single fast-firing cycles typically employed in processing frit-based glazed wall tiles. Developing sufficient crystallization for acceptable glaze opacity is quite complicated in an industrial single fast-firing. Thus, such frits should have a well-selected and controlled chemical composition, so that the kinetic crystallization process, during fast-firing, will take place intensely, leading to a glaze with a high crystalline fraction. Besides crystallization, glaze densification should also occur in such a way as to yield a compact layer, practically free of porosity.[20] In order to design a glass–ceramic composition to be evaluated in the tile glaze production, certain aspects should be considered. Therefore, every glass–ceramic system known so far is not suitable for

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such purposes. Only a limited number of them may fulfil the mentioned requirements such as ZrO_2–CaO–MgO–SiO_2 (ZrCMS)[13,15] and CaO–MgO–Al_2O_3–SiO_2 (CMAS)[12,14] systems. Since there has not yet been sufficient number of studies made on the glass–ceramic systems suitable for wall tile glossy white opaque glazes and the devitrification capability at very fast-firing rates being applied in modern tile industry it is thought that the achievements with the glass–ceramic glazes developed in the K_2O–MgO–CaO–ZnO–Al_2O_3–B_2O_3–SiO_2 system of the present study will make the valuable contributions to both the present literature and the relevant industry.

Frits based upon certain multiple oxides are the main raw materials for certain glaze compositions used in the manufacture of ceramic products obtained by single fast-firing processes. There is a wide variety of frits, which have different characteristics such as opacity, gloss, fusibility, and viscosity.[21,22] Opacity results from the difference between the refractive index of an opacifier and a glassy matrix. Thus, the greater the difference in refractive indices between these two, the higher the light scattering and therefore, the more satisfactory the opacity becomes. The diffusing light intensity also depends on the particle size of crystal phases which as long as is greater than the wavelength of light. The finer the particle size, the greater the surface area, the more numerous the reflecting surfaces and the more often the path of light is broken. This produces a greater reflection and a higher opacity. Another factor influencing the opacity of a material is the amount of opacifying phase present. Increasing the number of crystallites raises the number of reflecting surfaces, which improves the opacity of the material.[23–26]

Glaze opacity may be due either to the nature of the glaze itself or to the presence of opacifying agents in the glaze.[23] Amongst commercial frits, those containing zircon ($ZrSiO_4$) and zirconia (ZrO_2) are of great interest. $ZrSiO_4$ gives rise to opaque frits, which are commonly designated as "white of zirconium.[21,22] These kinds of frit-based glazes, in which opacification and whiteness are because of the zircon devitrification from the frit during tile firing, are generally used in wall tile manufacture.[2] In zircon consisting glazes, the opacity may be achieved by incorporating zircon in a very fine particle size into batches but it must be bearing in mind that the cost is increased by finer grinding.[23,24] Large price swings in the raw materials used to contribute ZrO_2 (as zircon flour) to the frit have driven the search for new frit compositions without ZrO_2, which yield glossy opaque white glazes.[8–10] Moreover, the rapid consumption of zircon sources directed several searches to be made for a cheaper alternative and led to the evaluation of proper glass–ceramic systems. Using them in the production of tile glazes is a promising option for replacing the zircon containing frits, being still in industrial uses, with the zircon-free ones. Environmental issues are other reasons for developing such glass–ceramics. Additionally, the employment of cheap and abundant raw materials as glass batch constituents is also preferred. Bou et al.[2] developed an alternative frit to the zirconium-containing ones and incorporated P_2O_5 into frit batch under laboratory conditions in order to improve the glaze gloss. However, P_2O_5 is a quite expensive raw material for a large industrial production and increases the cost of frit manufacture and also suffers from volatilization depending on its level. Unlike the studies conducted and reported on the important glass–ceramic systems in the literature, the zircon-free frits developed in the K_2O–MgO–CaO–ZnO–Al_2O_3–B_2O_3–SiO_2 glass–ceramic system do not contain any deliberately incorporated nucleating agent into the chemical composition and their glazes easily overcome the crystallisation difficulties during industrial single fast-firing cycles. From that point of view, they are of considerable importance.

Table 1
Composition of the standard (*R*) frit.

Component	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 coming from some raw materials and their amounts are negligible.

2. Experimental procedure

First of all, suitable frit compositions were determined on the basis of industrially produced and used standard frit (R) (Table 1) and prepared. After 70 different frit compositions tried, 25% reduction of both zircon and zinc oxide in frit batches with respect to the R one containing 6–10% ZrO_2 and 6–10% ZnO was achieved with the ZD frit consisting of 4.5–7.5% ZrO_2 and 4.5–7.5% ZnO (Table 2).[27] Such reductions were done by only modifying the frit original chemical composition with no other nucleating agent incorporated for opacification. Then, the studies were focused on the total elimination of ZrO_2. 20 more frits were studied in which ZrO_2 level was decreased step by step and finally the new zirconia-free frit was synthesized in the K_2O–MgO–CaO–ZnO–Al_2O_3–B_2O_3–SiO_2 glass–ceramic system called as DW (Table 3). However, in order to reach satisfactory performance in terms of adaptation into industrial glazed wall tile production further researches were made with a total number of 50 different frits based on DW. Hereby only 4 of them are given and discussed (Table 4).

The weighed and thoroughly mixed batches were melted in alumina crucibles in a laboratory type electrically heated furnace (Protherm PLF 160/7) at 1450 °C for 1 h. The melts were then quenched by pouring into cold water to obtain frits.

Table 2
Composition of the ZD frit.

Component	Content (mol %)
R_2O (Na_2O, K_2O)	5.20
RO (CaO, MgO, ZnO)	26.31
R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3*)	8.28
RO_2 (SiO_2, ZrO_2, TiO_2*)	60.21
Total	100.00

* Fe_2O_3 and TiO_2 are coming from some raw materials and their amounts are negligible.

Table 3
Composition of the DW frit.

Component	Content (mol %)
R_2O (Na_2O, K_2O)	5.96
RO (CaO, MgO, ZnO)	24.28
R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3*)	9.40
RO_2 (SiO_2, TiO_2*)	60.36
Total	100.00

[*] Fe_2O_3 and TiO_2 are coming from some raw materials and their amounts are negligible.

The frit crystallization capability and crystallization temperature ranges were determined by DTA (Netzsch STA 409 PC) on frit samples ground to a grain size of less than 63 μm.

For glaze preparation, in the light of industrial recipes, suitable amounts of frit, kaolin, carboxyl methyl cellulose (CMC), sodium tripolyphosphate (STTP) and water were mixed in a ball mill for 50 min. The suspensions were afterwards applied to pre-engobed green wall tile bodies supplied by Kaleseramik San. A.S. of Turkiye. The glazed specimens were fired in a laboratory type electrically heated single fast-firing kiln (Nabertherm LS 12/13) at peak temperatures resembling those employed industrially for this type of product. The glazes found to be the most suitable ones in desired properties were then selected, prepared, applied and fired under industrial working conditions at Kaleseramik San. A. S. Finally, the properties of industrially single fast-fired glazes were characterized and determined, as were those of the chosen standard: commercially available, zircon containing (6–10%) glossy, white opaque wall tile one for appropriate comparisons.

Samples were heated in a dilatometer (Netzsch DIL 402 PC) at a rate of 10 °C/min up to 600 °C in order to determine thermal expansion coefficient values. The colouring parameters L^*, a^*, and b^* of all the fired tiles were measured by means of a Minolta CR-300 series chromo-meter. Gloss was measured with a gloss meter (Minolta Gloss 268) with a 60° light incident angle on the glaze surface.

XRD analyses were conducted by a Rigaku Rint 2000 series difractometer with Cu Kα radiation. 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. Glaze microstructures were examined by SEM (Zeiss EVO 50 at 20 kV), fitted with an EDX.

Table 5
Colour (L^*, a^*, b^*) and gloss (60°) values of the selected glazes.

Glazes	L^*	a^*	b^*	Gloss (60°)
Standard (R)	92.67	−0.12	2.06	84.8
DW-D	90.41	0.23	1.07	82.9
DW-C	91.10	−0.29	1.19	87.3
DW-A	92.22	−0.17	2.09	85.1

3. Results and discussion

Since the aesthetic characteristics (colour and gloss) of the fired wall tile glazes are the determining factors for designing the frit compositions, the comparisons of the L^*, a^*, b^* and gloss values of developed and produced glazes were, all the time, made with those of the standard opaque wall tile glaze fired under industrial conditions (Table 5) to reach the best composition. The ZD frit with lower ZrO_2 and ZnO contents was successfully synthesized, prepared, melted and its wall tile glaze was produced, applied and single fast-fired at industrial scale. After that, ZrO_2 level in ZD frit composition continuously lowered and total elimination was made by adjusting the CaO/MgO and Al_2O_3/alkali ratios. First satisfactory opacity was achieved with DW glaze and optimum CaO/MgO was determined as 2.15, although the whiteness and gloss values were inadequate. In order to enhance these properties, 50 frit compositions were further studied. Amongst them, DW-A frit has the $Al_2O_3/\Sigma R_2O$ and $Al_2O_3/\Sigma RO$ ratio of 0.70 with higher SiO_2 content ($Al_2O_3/SiO_2 = 0.03$) compared to the DW-B, DW-C and DW-D frits. In DW-B, Al_2O_3/SiO_2 ratio was increased to 0.05 by incorporating more Al_2O_3 to the system. Effect of K_2O and ZnO were evaluated in DW-C frit and final modifications were done in DW-D frit in order to determine the oxide ratios of the satisfactory zirconia-free, glossy white opaque glaze (Table 4).

According to the industrial firings, DW-A glaze has acceptable colour and gloss values. When the $Al_2O_3/\Sigma R_2O$ ratio was increased to 1.26 at the constant CaO/MgO ratio of 2.15 in DW-B, the gloss was increased with primary laboratory trials but a distorted glaze surface texture appeared after industrial firing, so, colour and gloss values could not being measured. This is attributed to the high surface tension of DW-B glaze. 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.[23] The glaze should have a suitable surface

Table 4
Compositional details of studied frits (in moles).

Frits	Al_2O_3/SiO_2	$Al_2O_3/\Sigma R_2O$*	$Al_2O_3/\Sigma RO$**	Al_2O_3/B_2O_3	CaO/MgO	Al_2O_3/ZrO_2
Standard (*R*)	0.06	1.73	0.14	3.25	2.58	1.12
ZD	0.06	1.26	0.13	1.26	2.24	1.42
DW	0.06	1.16	0.10	0.46	2.15	–
DW-A	0.03	0.70	0.07	0.28	2.15	–
DW-B	0.05	1.26	0.13	0.36	2.15	–
DW-C	0.05	1.03	0.10	0.36	2.15	–
DW-D	0.04	0.70	0.07	0.28	2.15	–

[*] $Na_2O + K_2O$.
[**] CaO + MgO + ZnO.

tension to minimize crawling of the coating away from the edges or any holes that are present on firing. The formation of occluded bubbles is closely related to, among other factors, the viscosity of the fused glazes, which, in turn, is related to the content of the glassy phase and crystalline particles.[28] K_2O has an important effect on decreasing the surface tension and enhancing the opacity.[29] Therefore, Al_2O_3 and ΣR_2O levels in the DW-B frit recipe were re-modified and industrial firing of its glaze successfully conducted when $Al_2O_3/\Sigma R_2O$ and $Al_2O_3/\Sigma RO$ ratio became 1.03 and 0.10, respectively. Increasing level of K_2O and ZnO in the frit compositions enhanced the surface texture, whiteness, and gloss of the glazes. K_2O belongs to the group of intermediate oxides characterised by low partial values of surface tension and low-temperature viscosity, which occurs on the introduction of K_2O.[29] However, although the surface tension problem was altered by incorporating more K_2O in DW-C, the glaze still suffered from the defects due to the early glaze maturation during single fast-firing. K_2O raises glaze fusibility at low temperatures and restricts its excess usage in single-fired wall tile manufacture.[4] So, K_2O and ZnO levels were re-modified in DW-D glaze. It is very well known fact that the ZnO usage is quite common in glaze industry and its low amounts is adequate for obtaining glossier surfaces. Therefore, $Al_2O_3/\Sigma R_2O$ and $Al_2O_3/\Sigma RO$ ratio was lowered to 0.70 and 0.07, respectively in DW-D glaze and surface characteristics were improved with certain level of ZnO. Amongst the others, DW-D glaze presents a smoother surface texture with acceptable colour and gloss values. Its surface hardness was also measured and determined as 3 according to Mohs scale, which is an accepted value for glazed wall tiles, similar to those of the DW-C, DW-A and standard.

To fully realize the industrial applicability of zirconium-free glazes, the potential of glaze stability was also determined. The selected DW-D glaze, which generates white opacity and displays more satisfactory gloss values when compared with those typically obtained with ZrO_2 containing frit-based wall tile ones was subjected to different firing cycles in industry. When the total firing time was reduced from 55 to 37 min, L^*, a^*, b^* values then became $L^* = 90.83$, $a^* = -0.58$, $b^* = 1.12$ and gloss was measured as 83.7. The final colour and gloss values revealed that this glaze is stable at industrial single fast-firing cycles of 1140 °C with a total time changing from 55 to 37 min.

The thermal expansion coefficients of the wall tile body, R, DW-C and DW-D glazes at 400 °C were measured as 70.2×10^{-7}, 60.5×10^{-7}, 63.2×10^{-7} and 65.8×10^{-7}. These newly developed diopside–wollastonite based glass–ceramic glazes show stability and appear dilatometrically compatible with the tile body. It is, therefore, suggested that they can be considered appropriate for the use as industrially single fast-fired wall tile glazes.

The DTA curves of the reported frits are plotted in Fig. 1. The glass transition temperatures, T_g, of all are at around 670 °C. As a comparison with that of the standard frit (R), 718 °C, it was revealed that thanks to the compositional modifications in frit recipes T_g was lowered. This is also a good sign of easy maturation of their glazes. The frits exhibit exothermic peaks of varying magnitudes at different temperatures. Standard frit exhibited two shallow exothermic peaks at 873 and 953 °C. The former one should belong to the calcium aluminium silicate formation while the latter one to that of zircon whose devitrification was reported to become at about 900–950 °C.[20] The DW-D frit indicates two intense and sharp crystallization peaks at 850 and 902 °C and the DW-A frit depicts them at 869 and 897 °C, respectively. However, crystallization peak temperatures of the DW-C frit with higher ZnO content decreased to 828 and 883 °C. Gradual reduction of crystallization peak temperature of frits with higher alkali oxide contents means that the improvement of crystallization ability is due to lowering the diffusion paths of crystallite constituents.[30] It is observed that, the increment of ZnO in the frit composition lowered the crystallization peak temperatures and the XRD peak intensities

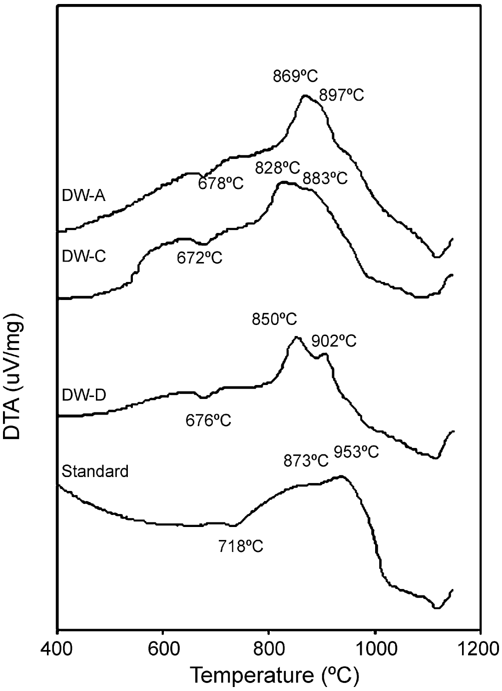

Fig. 1. DTA curves of the standard (R), DW-D, DW-C, and DW-A frits.

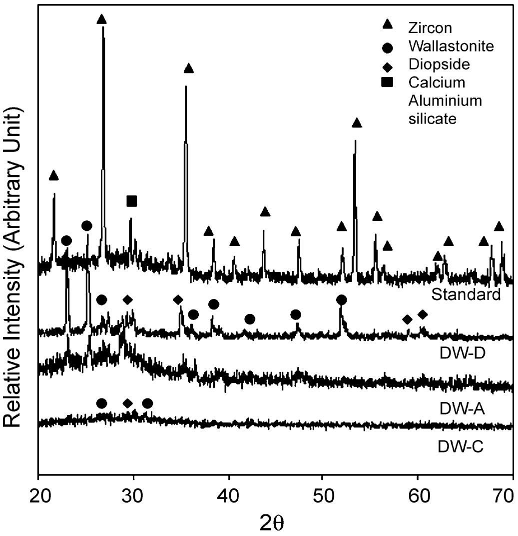

Fig. 2. XRD patterns of the standard (R), DW-D, DW-C, and DW-A glazes.

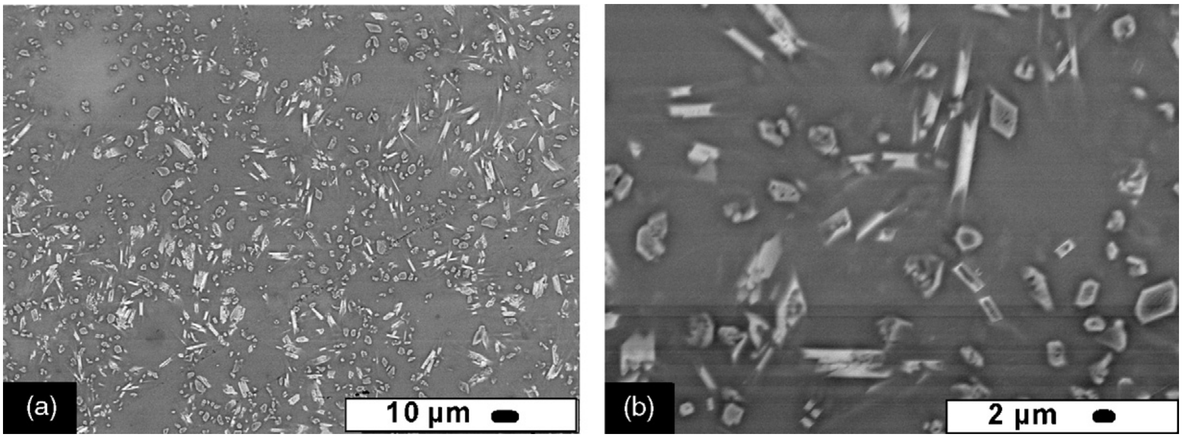

Fig. 3. SEM micrographs of the DW-D glaze showing overall diopside and wollastonite crystals and their distribution.

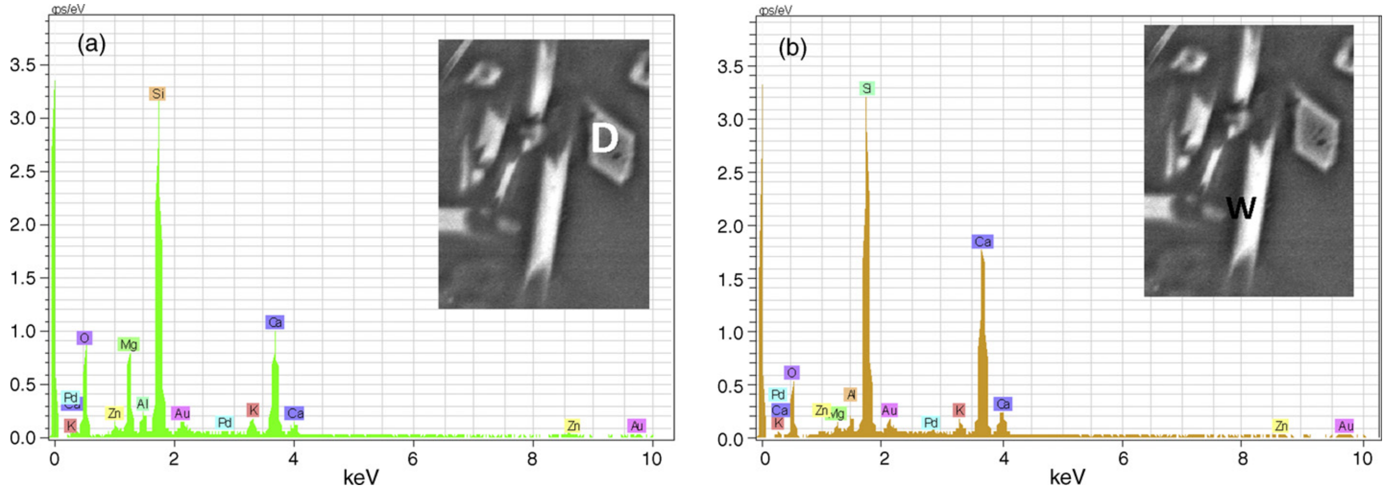

Fig. 4. EDX patterns taken from the DW-D glaze inhibiting diopside (D) (a) and wollastonite (W) occurrences (b).

of precipitated diopside and wollastonite decreased after single fast-firing at 1140 °C for 55 min (Fig. 2). Generally, based on the glass composition, wollastonite and diopside occurrences start after 800 and 850 °C, respectively.[2,20] Although the CaO/MgO ratios were the same in all the reported frit compositions here, the intensity and temperature of the crystallization were declined in the DW-C frit. According to XRD analysis, DW-C glaze exhibits a more glassy behaviour (Fig. 2) which might be explained by higher amount of the glassy phase. Beside certain alkali oxide and boric oxide presence, high level of ZnO in glaze composition may lead to the dissolution of diopside and wollastonite into the residual glass phase, enhancement of which

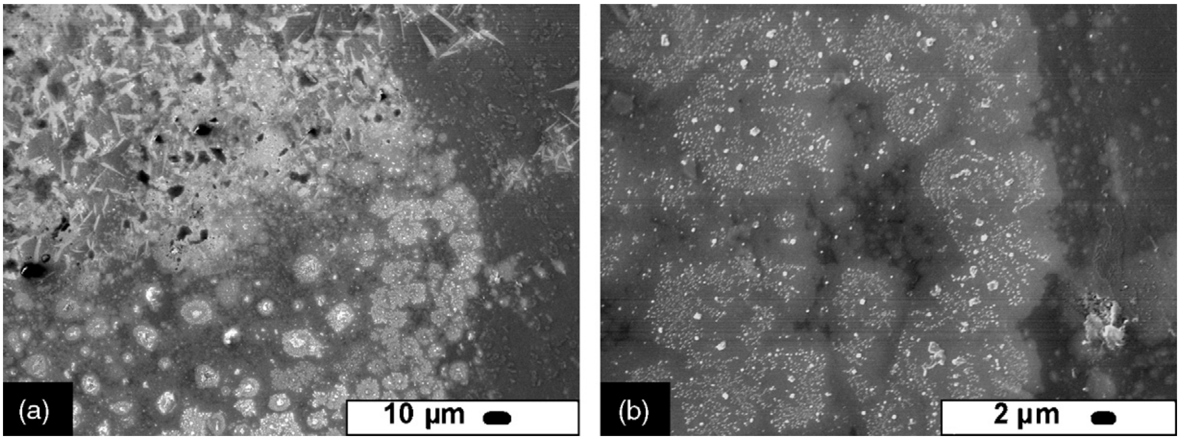

Fig. 5. SEM micrographs of the DW-C glaze representing overall diopside and wollastonite crystallizations and their distribution.

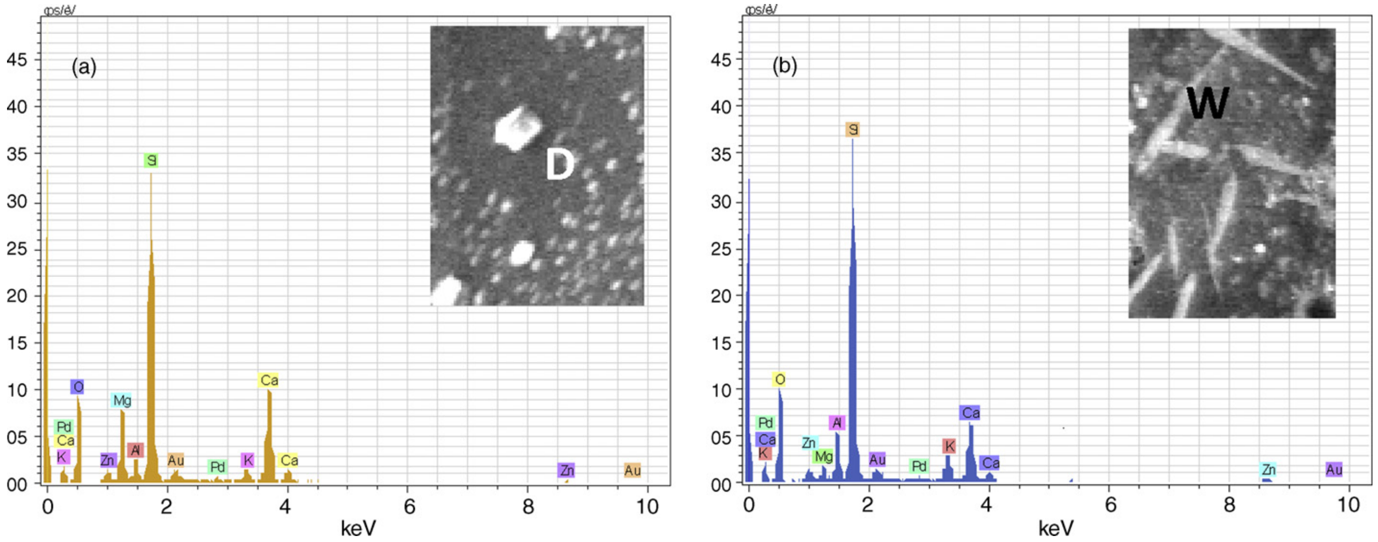

Fig. 6. EDX patterns taken from the DW-C glaze showing diopside (D) (a) and wollastonite (W) formations (b).

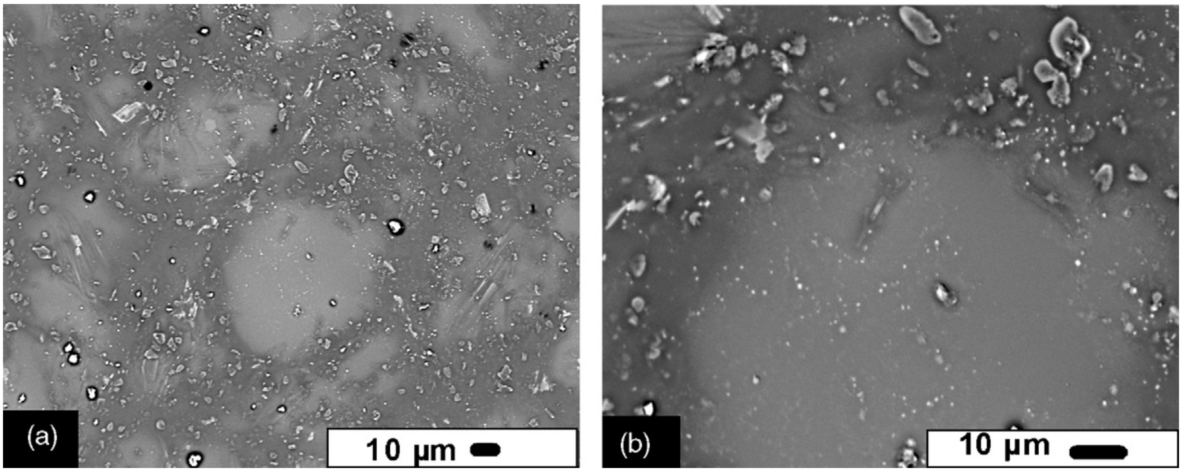

Fig. 7. SEM micrographs of the DW-A glaze exhibiting overall diopside and wollastonite crystals and their distribution.

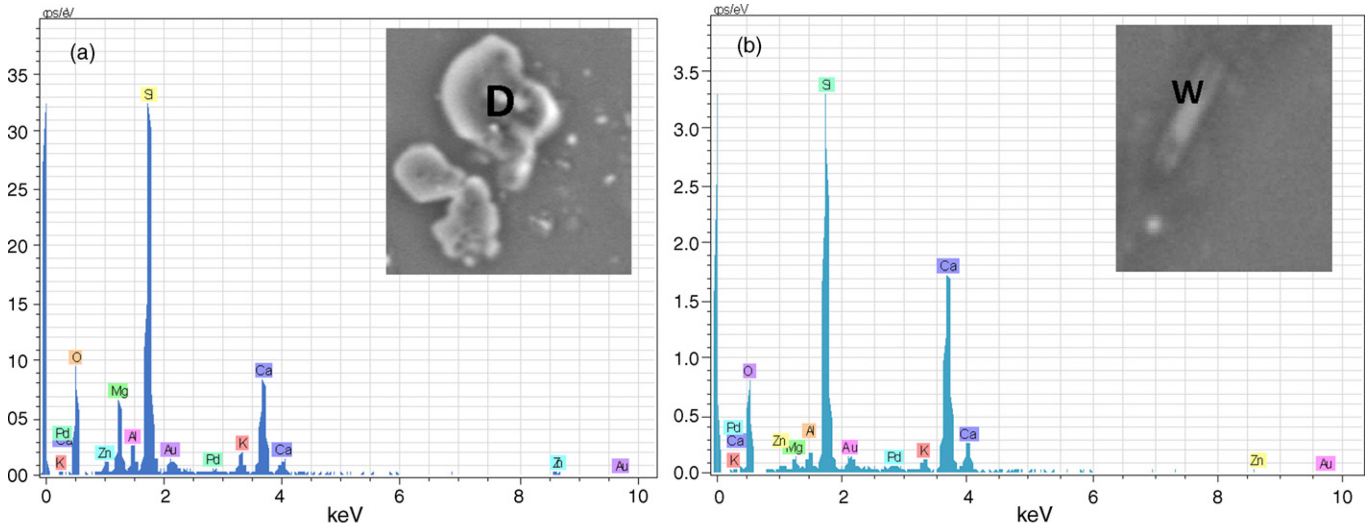

Fig. 8. EDX pattern taken from the DW-A glaze showing diopside (a) and wollastonite presence (b).

gives rise to a better glossy opaque glaze and surface texture, during firing. Similar behaviour of ZnO was reported in the literature in glass–ceramic floor and porcelain tile glazes.[29,31]

The standard glaze has predominantly zircon and secondly calcium aluminium silicate crystals after single fast-firing (Fig. 2).[27] The XRD results of the glazes obtained from the DW-D, DW-C, and DW-A frits agreed with the DTA data confirming both diopside and wollastonite crystallizations.

The general micro structural views of the DW-D glaze and the crystals formed are depicted in Fig. 3. The acicular white crystals with different sizes belong to wollastonite and grey flat cross sectional ones to diopside (Fig. 4). The devitrification of these crystals results in a homogenous microstructure in the DW-D glaze. Though the same crystals are observed in all the glazes, their morphology and distribution differ. For instance, the DW-C glaze represents a heterogeneous microstructure with needle-shaped wollastonite and isolated diopside crystals immersed in the glassy matrix (Fig. 5). EDX analyses related to these crystals are presented in Fig. 6. As the data detailed in Table 5 indicates, the heterogeneous microstructure of the DW-C glaze did not affect the whiteness. Fig. 7 represents the microstructures of the DW-A glaze. Irregular-shaped diopside and rod-like wollastonite are heterogeneously distributed, as seen in the DW-C glaze, in the glassy matrix (Fig. 8). SEM and EDX analyses revealed that the opacity of these glazes was supplied by the diopside and wollastonite crystallization under the industrial firing conditions.

4. Conclusions

Single fast-fired glass–ceramic opaque wall tile glazes without zirconium content were developed. In the studied K_2O–MgO–CaO–ZnO–Al_2O_3–B_2O_3–SiO_2 glass–ceramic system, diopside and wollastonite are easily forming predominant crystalline phases without a need of nucleating agent incorporation. They contribute to the opacity of the final glazes whereas the opacity is usually and predominantly gained by zircon in the zirconium containing opaque wall tile glaze industrially produced. The elimination of zircon from frit batches was successfully made by the optimization of CaO/MgO, and the adjustment of Al_2O_3/alkali ratios. The amount of the crystalline phases and glassy matrix were related with alkali oxide and ZnO levels. When the amounts of glassy phase increases, the gloss of the glaze is naturally improved. High proportions of alumina in the studied system distort the surface quality due to its increasing effect on the surface tension. Achieving opacity with diopside and wollastonite crystallization, instead of zircon, offers a decrease of 55–60% in the production cost of this newly developed frits suitable for the production of industrial single fast-fired opaque wall tile glazes with satisfactory other final properties.

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