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PRODUCTION OF ZIRCON-FREE OPAQUE WALL TILE FRITS AND THEIR USE IN CERAMIC INDUSTRY

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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 taking glass-ceramic glazes into an account is another option for decreasing the production cost. The glaze compositions belonging to the K_2O - MgO - CaO - ZnO - Al_2O_3 - B_2O_3 - SiO_2 system were studied to prepare newly synthesised wall tile glazes. 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 was to gain opacity by designing a new, alternative glass-ceramic glaze system by optimising the CaO/MgO ratio and adapt them to the industrial working conditions. Glaze preparation, application, and fast single-firing of wall tiles were, first of all, conducted under laboratory conditions and then successful recipes adapted to the relevant industry. The frit crystallization capability and crystallization temperature range were determined by differential thermal analysis (DTA). Characterization of 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 were conducted with a spectrophotometer and a glossmeter, respectively.

Keywords: Zircon, Elimination, Frit, Opacity, Wall tile glaze.

INTRODUCTION

Glass-ceramics are crystalline materials formed through a controlled crystallization of glass during a specific heat treatment. These materials are of growing interest; for example, in case of preparing tile coatings when compared to traditional amorphous glazes [1-12].

Frits based on certain multiple oxides are the main raw materials for glaze compositions used in the manufacture of ceramic products obtained by fast single firing processes. When necessary to hide an undesirable body colour and where aesthetic appeal is an important factor, opaque glazes are preferred. 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 the crystal phase and the matrix, the greater the light scattering and therefore, the

greater the opacity. The diffusing light intensity also depends on the particle size 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 [13-16].

Zircon is a widely used opacifier in ceramic industry. In zircon glazes, the opacity may be achieved by incorporating zircon in a very fine particle size into batches but the cost is increased by finer grinding [13,14]. Moreover, the rapid consumption of zircon sources resulted in the search for a cheaper alternative and led to use glass-ceramic systems.

The potential of glass-ceramic systems as glazes, compared to the traditional ones developing an almost completely glassy phase, is very interesting since they lend the coating a higher softening point and show a better coating capability for relevant substrates and higher chemical and abrasion resistance. For a correct application of glass-ceramic systems on tiles, a scientific background of knowledge is pre-requisite in the glass devitrification phenomenon and phase developments, as in the sintering processes conditioned by the chemical reactions between substrate and coating and by the compatibility with the firing temperature of substrate. In order to design a glass-ceramic composition as tile glaze, certain aspects should be considered. Therefore, glass-ceramic glazes are more easily designed and adjusted in laboratory and only later transferred to industrial practice [17].

MATERIALS AND METHODS

The frits were developed in the K_2O - MgO - CaO - ZnO - Al_2O_3 - B_2O_3 - SiO_2 system. The weighed and thoroughly mixed batches were melted in alumina crucibles in an electrically heated furnace at 1450 °C for 1 h. The melt was then quenched by pouring into cold water to obtain frit. For glaze preparation frit, kaolin, carboxyl methyl cellulose (CMC), sodium tripolyphosphate (STTP) and water were mixed in ball mill for 50 min. The suspensions were applied to green wall tile bodies previously been engobed. The specimens were fired in a laboratory type electric kiln at peak temperatures resembling those employed industrially for this type of product. The glazes being most suitable were selected and fired in industrial working conditions at Kaleseramik San. A.S. The properties of the fired glazes were characterized and determined, as were those of the chosen as reference glazes: glossy, white wall tile one.

Glaze microstructure was examined by SEM (Zeiss EVO 50 at 20 kV), fitted with an EDX. The crystalline phases present in the glazes were identified by XRD (Rigaku Rint 2000 series diffractometer with $Cu K_{\alpha}$ radiation). The colour values L^* , a^* , and b^* of all fired tiles were measured using a Minolta CR-300 series chroma meter. Gloss was determined with glossmeter (Minolta Gloss 268) with a 60° light incident angle on the glaze surface. The frit crystallization capability and crystallization temperature range were determined by DTA (Misura 3.32 ODHT-HSM).

RESULTS AND DISCUSSION

The Seger formulas of the frits studied in the K_2O - MgO - CaO - ZnO - Al_2O_3 - B_2O_3 - SiO_2 system are listed in Table 1. The comparison of the L^* , a^* , b^* and gloss values were made according to those of the standard wall tile with an opaque white glaze taken from Kaleseramik San. A.S (Table 2). Although the colour values of the glaze M 66 was closer to the standard one, it had an undesirable surface quality. High amounts of Al_2O_3 in the frit recipe resulted in an increment in surface tension and caused defected regions. M 66 was the glossiest due to a low silica/alkali ratio. Glaze M 64 had a smooth surface texture with acceptable colour and gloss values.

Table 1. Seger formula of the frits studied

0.06-0.11	K_2O		1.58-1.98	SiO_2
0.08-0.46	MgO	0.06-0.11	Al_2O_3	0.17-0.37
0.50-0.80	CaO			
0.06-0.16	ZnO			

Table 2. Colour (L^* , a^* , b^*) and gloss (60°) values of the selected glazes

Glaze	L^*	a^*	b^*	Gloss (60 °)
Standard	92.67	-0.12	2.06	84.8
M 64	90.41	0.23	1.07	82.9
M 66	91.10	-0.29	1.19	87.3

The DTA curves of the investigated frits are plotted in Figure 1. The glass transition temperatures, T_g , of both frits are at around 670 °C. This similarity confirms that the viscosity is not significantly influenced by the compositional variation. The XRD results of the glazes obtained from the frits M 64 and M 66 confirmed that the DTA crystallization peaks belong to diopside and wollastonite (Figure 2). Both frits inhibit exothermic peaks of different magnitudes at different temperatures. The frit M 64 exhibits two intense and sharp crystallization peaks at 850 °C and 902 °C and the frit M 66 depicts two shallow crystallization peaks at 828 °C and 883 °C, respectively. The melting process of the materials started at temperatures above 1150 °C. Although the CaO/MgO ratios were the same, the intensity and temperature of the crystallization peaks were decreased in the frit M 66. This behaviour might be explained by the amount of the glassy phase. According to XRD analysis it exhibits a more glassy behaviour due to the high amounts of alkali and alumina content. Al_2O_3 stabilizes the glassy network, increasing mechanical strength. However, it raises melt viscosity, so that it reduces the tendency of the glazes to devitrify [18].

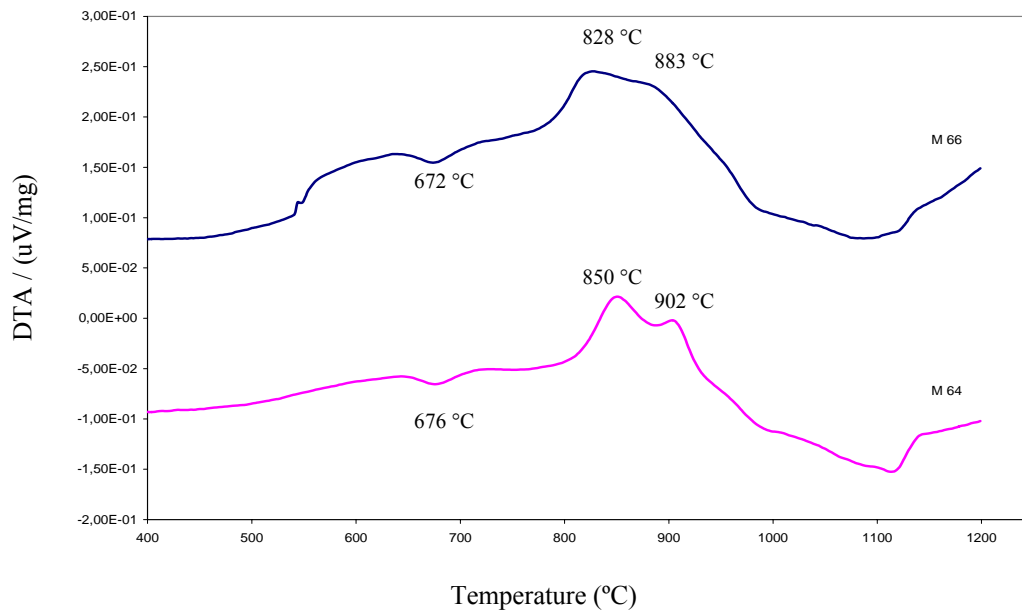


Figure 1. DTA curves of the frits M 64 and M 66.

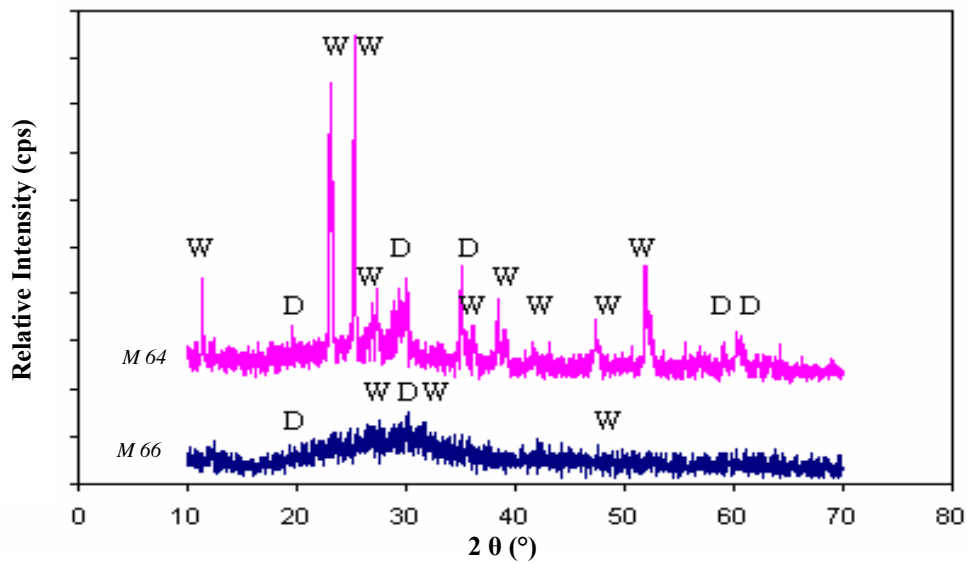


Figure 2. XRD patterns of the glaze M 64 and M 66 (W: Wollastonite, D: Diopside).

The general view of the glaze M 64 and the detailed images of the crystals are depicted in Figures 3 and 4, respectively. The acicular white crystals with different sizes belong to wollastonite and grey flat crosssectioned ones to diopside (Figures 5-6). The devitrification of these crystals gives rise to a homogenous microstructure in the glaze M 64. Though the same crystals are observed in both glazes, their morphology and distribution differ. The glaze M 66 represents a heterogeneous microstructure with needle-shaped wollastonite and isolated diopside crystals immersed in the glassy matrix (Figures 7-8). EDX analyses related to these crystals are presented in Figures 9-10. As the data detailed in Table 2 indicates, the microstructure with heterogeneities in the glaze M 66 did not affect the whiteness. SEM and EDX analyses revealed that the opacity of the glazes were the result of the diopside and wollastonite crystallization under the industrial firing conditions.

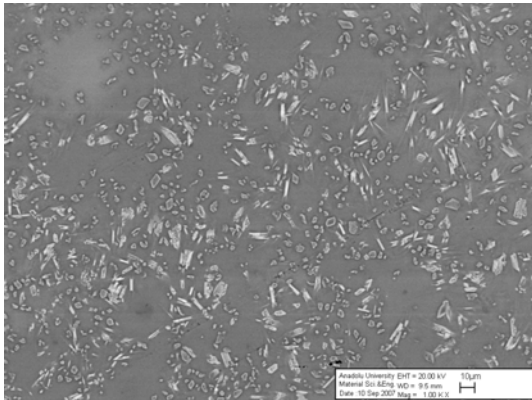


Figure 3. SEM micrograph of the glaze M 64 showing overall diopside and wollastonite crystallization.

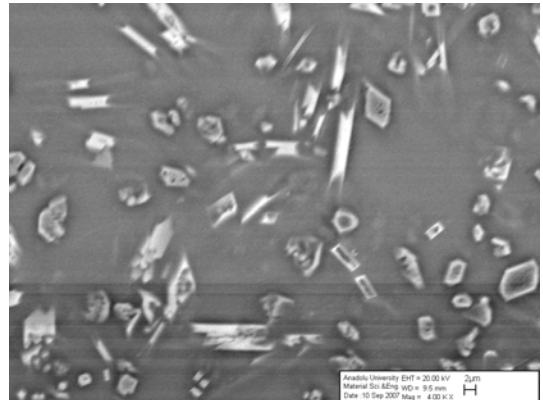


Figure 4. SEM micrograph exhibiting diopside and wollastonite crystallization in the glassy matrix (at higher magnification).

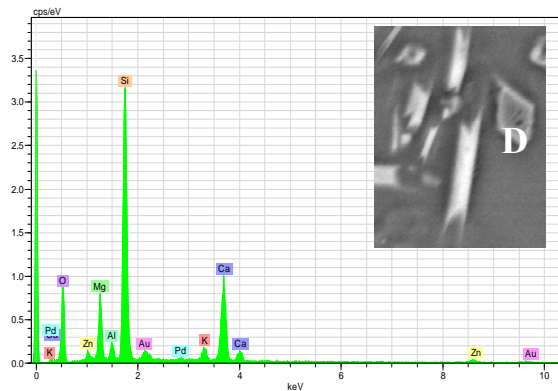


Figure 5. EDX pattern taken from the M 64 glaze inhibiting diopside occurrence.

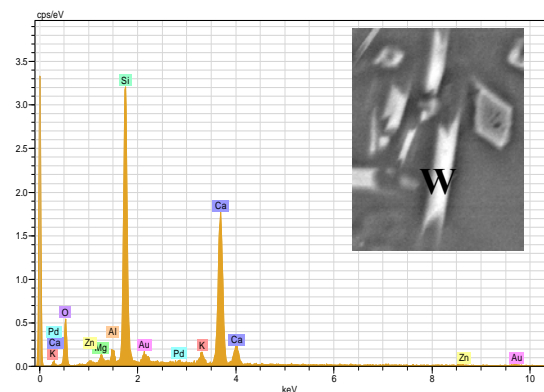


Figure 6. EDX pattern taken from the M 64 glaze presenting wollastonite formation.

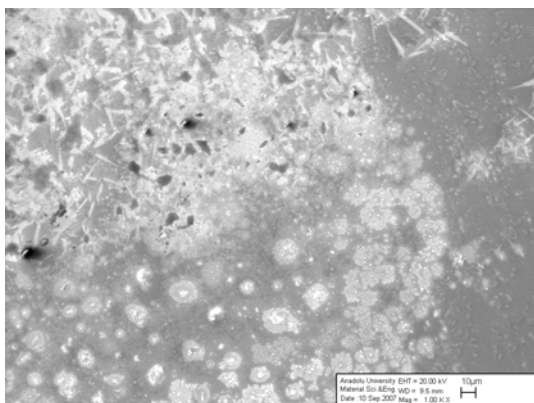


Figure 7. SEM micrograph of the glaze M 64 representing overall diopside and wollastonite crystallization.

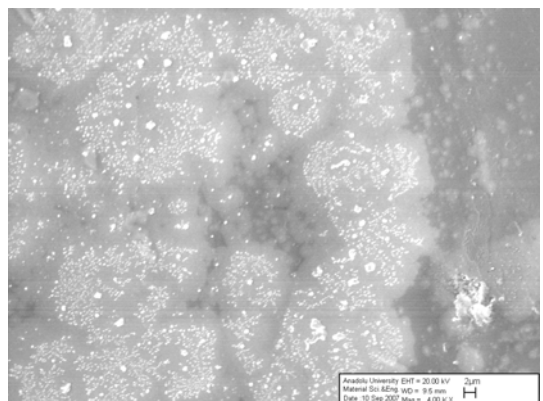


Figure 8. SEM micrograph showing diopside and wollastonite crystallization in the glassy matrix (at higher magnification).

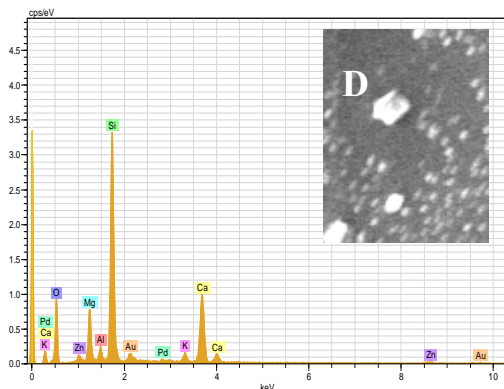


Figure 9. EDX pattern taken from the M 66 glaze exhibiting diopside crystal.

CONCLUSIONS

Fast fired glass-ceramic glazes were developed. The suitability of their frits to be used under industrial working conditions is an ongoing research. In the studied glass-ceramic system, diopside and wollastonite were the predominant crystalline phases which contribute to the opacity. The amount of these phases and glassy matrix were related with the alumina and alkali/silica content. When the glassy phase increases, the gloss of the glaze increases. High proportions of aluminium in the K_2O - MgO - CaO - ZnO - Al_2O_3 - B_2O_3 - SiO_2 system distorts the surface quality as a result of high surface tension. Achieving opacity with diopside and wollastonite crystallization instead of zircon decreased the production cost of this newly developed wall tile frits.

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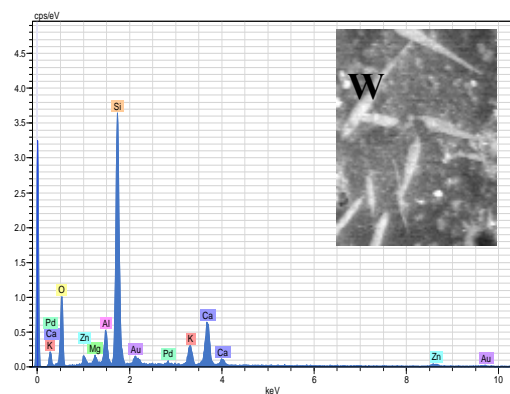


Figure 10. EDX pattern taken from the M 66 glaze showing wollastonite crystal.

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