

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

K. Karaveli^(1, 2), B. Karasu¹, and H. S. Onal⁽²⁾

⁽¹⁾Anadolu University, Department of Materials Science and Engineering,
26555 Eskisehir, Turkey

⁽²⁾Kaleseramik Canakkale Kalebodur Seramik Sanayi A. S., Wall Tile R&D,
17430 Can, Canakkale, Turkey

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 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 adapting it 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.

1. 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 it is 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, as long as it 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].

2. 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 (STPP) 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 most suitable glazes 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 glaze chosen as a reference: a glossy, white wall tile glaze.

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 α 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).

3. RESULTS AND DISCUSSION

The Seger formulas of the frits studied in the K₂O-MgO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂ 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 were closer to the standard one, it had an undesirable surface quality. High amounts of Al₂O₃ in the frit recipe resulted in an increment in surface tension and caused defective 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.

0.06-0.11	K ₂ O		1.58-1.98	SiO ₂
0.08-0.46	MgO	0.06-0.11	0.17-0.37	B ₂ O ₃
0.50-0.80	CaO			
0.06-0.16	ZnO			

Table 1. Seger formula of the frits studied

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

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

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 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. Al₂O₃ stabilizes the glassy network, increasing mechanical strength. However, it raises melt viscosity, so that it reduces the tendency of the glazes to devitrify [18].

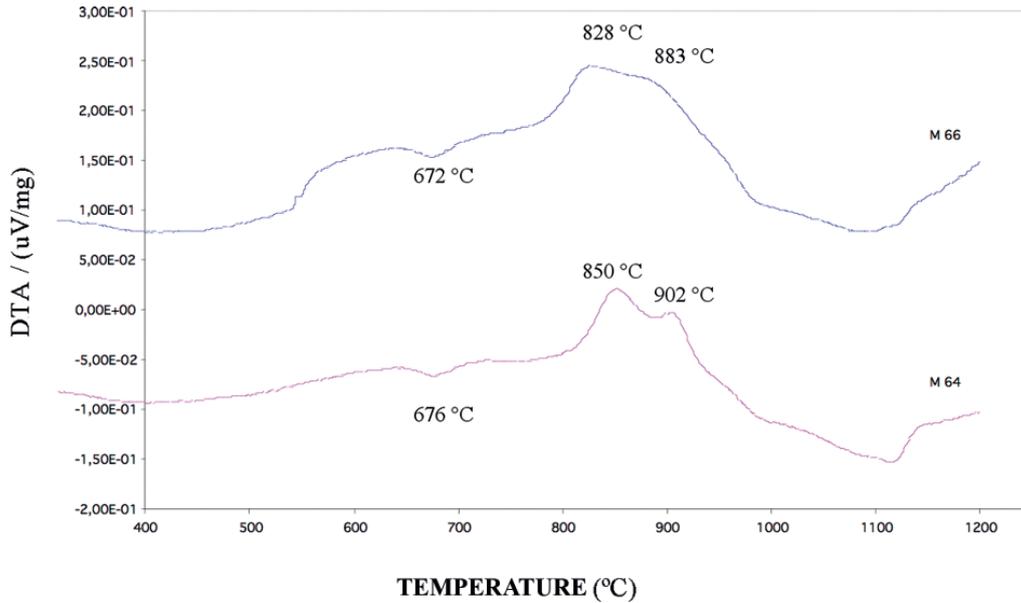


Figure 1. DTA curves of the frits M 64 and M 66.

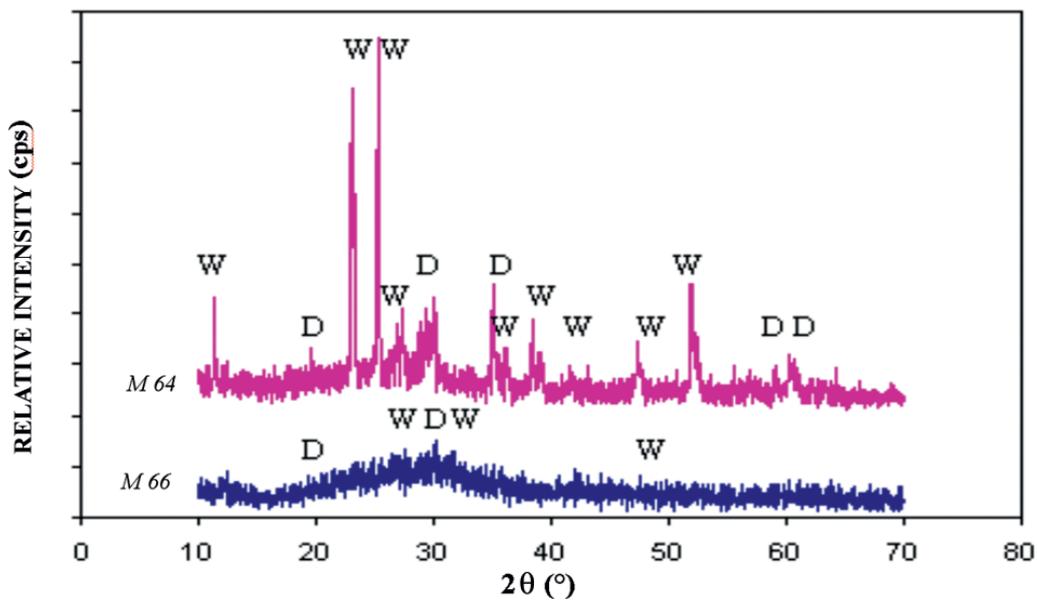


Figure 2. XRD patterns of the glaze M 64 and M 66 (W: Wollastonite, D: Diopside).

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 cross-sectioned ones to diopside (Figures 5-6). The devitrification of these crystals gives rise to a homogeneous microstructure in the glaze M 64. Though the same crystals are observed in both glazes, their morphology and distribution differ. The glaze M 66 presents 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.

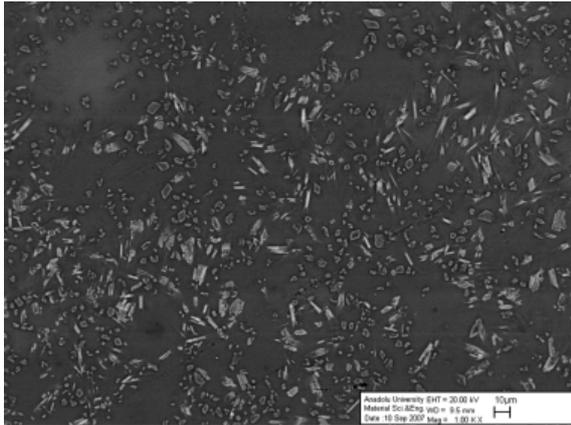


Figure 3. SEM micrograph of the glaze M 64 showing overall diopside and wollastonite crystallization.

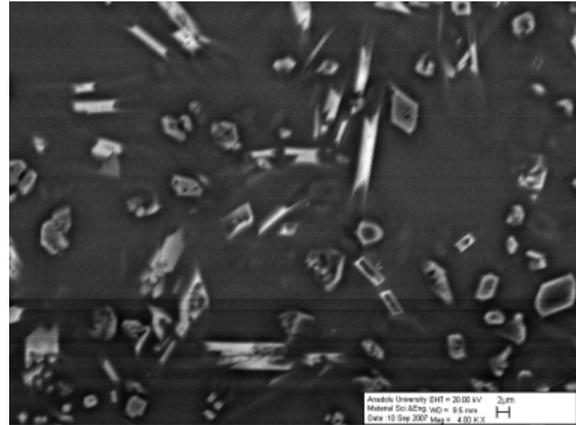


Figure 4. SEM micrograph exhibiting diopside and wollastonite crystallization in the glassy matrix (at higher magnification).

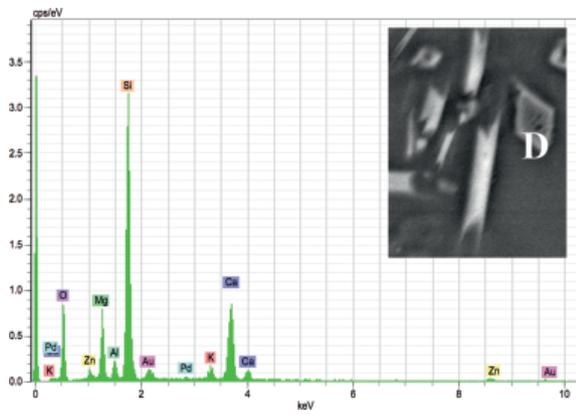


Figure 5. EDX pattern taken from the M 64 glaze inhibiting diopside occurrence.

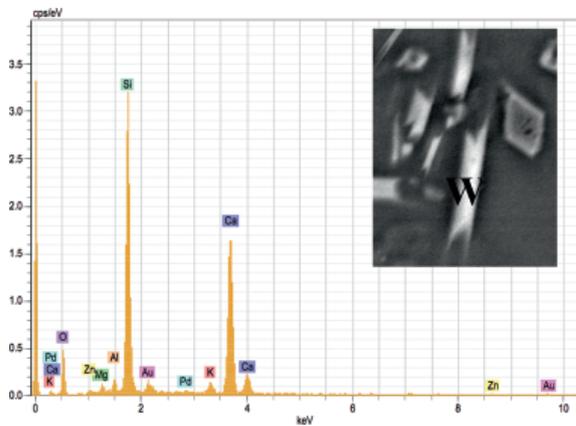


Figure 6. EDX pattern taken from the M 64 glaze presenting wollastonite formation.

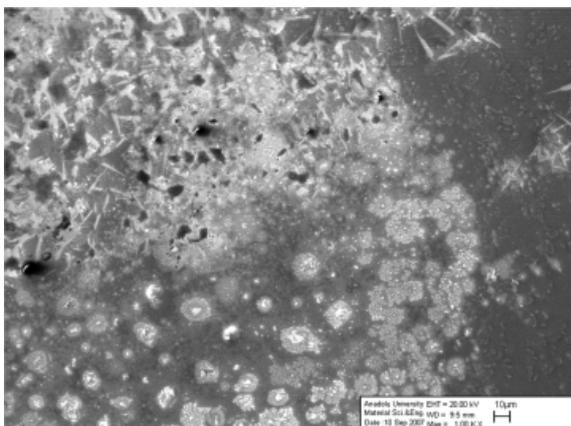


Figure 7. SEM micrograph of the glaze M 64 presenting overall diopside and wollastonite crystallization.

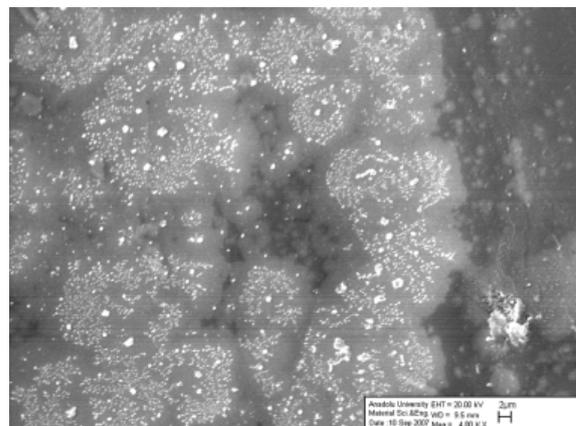


Figure 8. SEM micrograph showing diopside and wollastonite crystallization in the glassy matrix (at higher magnification).

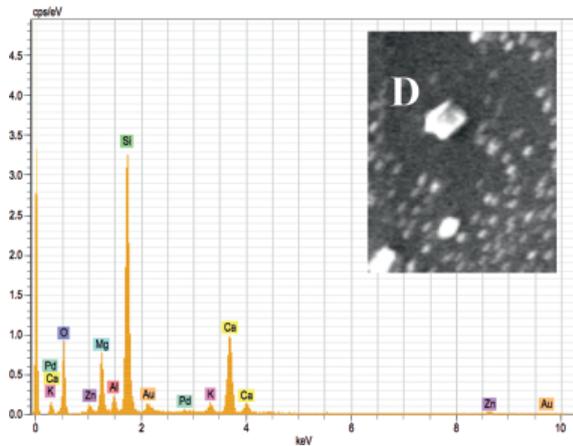


Figure 9. EDX pattern taken from the M 66 glaze exhibiting diopside crystal.

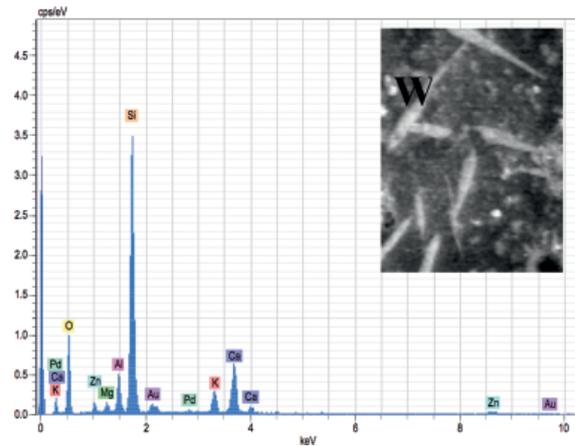


Figure 10. EDX pattern taken from the M 66 glaze showing wollastonite crystal.

4. 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 distort 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.

ACKNOWLEDGEMENT

The Authors would like to thank to TÜB_TAK (Science, Technology and Research Association of Turkey), Supporting Programme of Industrial Research and Development Projects (TEYDEB) for the support to the project numbered 3060236.

REFERENCES

- [1] Alizadeh, P. and Marghussian, V. K. The effect of compositional changes on the crystallization behaviour and mechanical properties of diopside-wollastonite glass-ceramics in the SiO_2 -CaO-MgO (Na_2O) system. J. Eur. Ceram. Soc., 20, 765-773 (2000).
- [2] Barbieri, L., Bondioli, F., Lancellotti, I., Leonelli, C., and Montrosi, M. The anorthite-diopside system: structural and devitrification study. Part II: Crystallinity analysis by the Rietveld-RIR method. J. Am. Ceram. Soc., 88 [11] 3131-3136 (2005).
- [3] Karasu, B. and Kaya, G. Glass-ceramic glazes in the CaO-MgO- Al_2O_3 - SiO_2 (CMAS) system for porcelain tiles. Proceedings of Austceram & The 3rd International Conference on Advanced Materials Processing, 103-304, Melbourne Australia (2004).
- [4] Kaya, G. and Karasu, B. ZrO_2 -CaO-MgO- SiO_2 (ZrCMS) system glass-ceramic glazes suitable for porcelain tiles. Proceedings of Austceram & The 3rd International Conference on Advanced Materials Processing, 301-302, Melbourne Australia (2004).

- [5] Karasu, B., Kaya, G. and Taykurt, M. The effects of borax wastes on the final properties and microstructure of fast fired $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) glass-ceramic system porcelain tile glazes. Abstract Book of the 9th International Ceramic Processing Science Symposium, Coral Springs, Florida, ICPSS-044-2006, 24 (2006).
- [6] Karasu, B., Kaya, G. and Taykurt, M. The use of borax wastes in the fast fired $\text{ZrO}_2\text{-CaO-MgO-SiO}_2$ (ZrCMS) glass-ceramic system porcelain tile glazes. Abstract Book of the 9th International Ceramic Processing Science Symposium, Coral Springs, Florida, ICPSS-045-2006, 25 (2006).
- [7] Karasu, B., Kaya, G. and Ozdemir, O. Use of borax solid wastes in diopside based glass-ceramic floor tile glazes. Proceedings of Sohn International Symposium on Advanced Processing of Metals and Materials: Principles, Technologies and Industrial Practice, San Diego, America, 529-534 (2006).
- [8] Karasu, B., Kaya, G., Taykurt, M., Çakır, A., and Kavas, T. Effects of borax solid wastes on the final properties of fast-fired porcelain glass-ceramic glazes. III. International Boron Symposium, Ankara, 91-95 (in Turkish) (2006).
- [9] Karaveli, K., Karasu, B. and Onal, H. S. Decreasing of zircon content in opaque wall tile frits. Proceeding Book of the X. Conference and Exhibition of the European Ceramic Society, Berlin, Germany, (in print) (2007).
- [10] Kaya, G., Karasu, B. and Cakir, A., Characterization of diopside-based glass-ceramic porcelain tile glazes containing borax solid wastes. Proceeding Book of the X. Conference and Exhibition of the European Ceramic Society, Berlin, Germany, (in print) (2007).
- [11] Kaya, G., Karasu, B., and Ozdemir, O. The development of diopside based glass-ceramic glazes suitable for fast fired floor tiles. 6th National Ceramic Congress with International Participation, Sakarya, Turkish Ceramic Society, 473-478, (in Turkish) (2006).
- [12] Karaveli, K., Karasu, B. and Onal, H. S. Production of zircon-free opaque frit and frit-based single fast firing wall tile glaze and characterization. Proceeding Books of the VI. Ceramic, Glass, Enamel, Glaze and Pigment Seminar with International Participation (SERES 2007), 26-28 November 2007 (in Turkish) (in print) (2007).
- [13] Taylor, J. R. and Bull, A. C. Ceramics glaze technology. London: Pergamon Press, 111 (1980).
- [14] Fraser, H. Glazes for the craft potter. London: A&C Black, Am. Ceram. Soc., 53-55 (1998).
- [15] Noble, B. D., Parker, J. M., James, P. F., and Hand, R. J. Opacification of $\text{ZnO-B}_2\text{O}_3\text{-ZrO}_2$ glasses. Glass Technol., 45, 101-104 (2004).
- [16] Santos, C. R., Fontana, T. L. B., Uggioni, E., Riella, H. G., and Bernardin, A. M. Achieving opacity in ceramic tiles: Microstructural and spectrophotometric analysis. Castellón: Qualicer 2004 (2004).
- [17] Leonelli, C., Manfredini, T., and Siligardi, C. New tile glaze families based on glass ceramic systems. Int. Cer. J., April, 31-35, (2002).
- [18] Sorlí, S., Tena, M. A., Mestre, A., Llusar, M., and Monrós, G. Effect of the major devitrifying phase on ceramic glaze microstructure and mechanical properties. Castellón: Qualicer 2004 (2004).