OPAQUE GLAZES WITH VARYING MATTNESS FOR GLAZED PORCELAIN TILE

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1. INTRODUCTION

Glazes are fundamental materials which provide physical advantages and aesthetic appearance to ceramic bodies. Glossiness and mattness are important properties of appearance which depend on diffuse and specular reflection of light from glazed surfaces [1]. These reflections are mainly controlled by surface topography, which is influenced by microstructure and microstructural changes. The starting compositions, particle size of raw materials, firing schedule and vitrification/devitrification have a great influence on final microstructure.

2. MATERIAL AND METHODS

This study aims to obtain high opacity glazes with varying mattness in a glaze system containing anorthite, zircon, quartz and amorphous phases. For this purpose, a systematic approach was taken into account for controlling qualitative amounts of these phases. This was achieved by systematically changing the contents of raw materials (wollastonite, kaolin, frit, feldspar and zircon) with constant amounts of quartz, clay and ZnO by using experimental design software. In Figure 1, compositional points of raw materials are shown where zircon was changed between 0-15 wt%; frit + feldspar combined at constant weight ratio of 1/3 was changed between 13-48 wt%; and kaolin + wollastonite combined at equal molar ratio of CaO and kaolinite (with considerable amount of kaolinite from clay) was changed between 20-40 wt%. Glazes (1710 gr/L) were applied on a green body (L* value of the fired body is 55) without an engobe layer and samples fired at 1190 °C. The resultant phases were characterized by XRD and SEM together with opacity and glossiness measurements of the glazes.

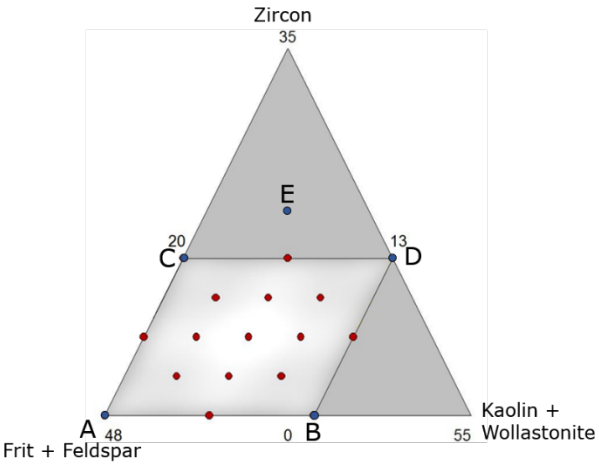

Figure 1. *Compositional points of glazes.*

3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of compositions A to D. The XRD patterns of compositions A and B show peaks attributed to the quartz and anorthite as crystalline phases, and a large hump between 15-30° 2θ is due to the amorphous phase. In composition B, the anorthite to quartz peak intensity ratio is increased and the amorphous region is decreased, indicating increased anorthite crystallization. The same alteration is seen in composition C and D with respect to anorthite and amorphous phase presence. Additional zircon peaks are also visible on these compositions containing zircon.

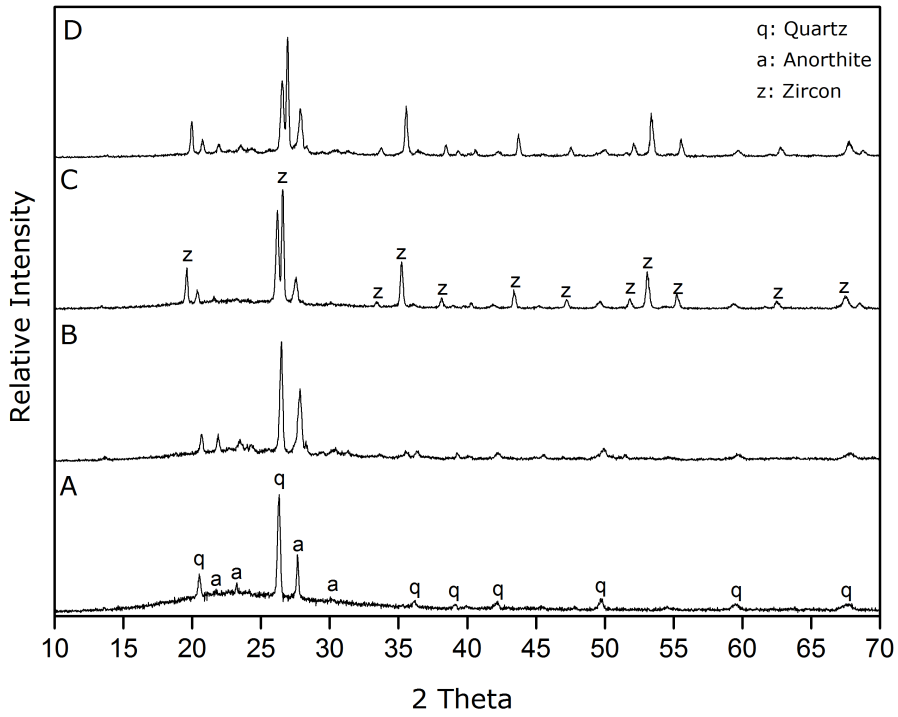

Figure 2. *XRD patterns of A, B, C and D compositions.*

In the SEM micrographs of composition A (Figure 3A), small amounts of quartz and anorthite are present in a large volume of the amorphous phase. In composition B, on the other hand, the amount of anorthite crystals (very fine features in Figure 3B) is increased. This is substantially in agreement with XRD spectra.

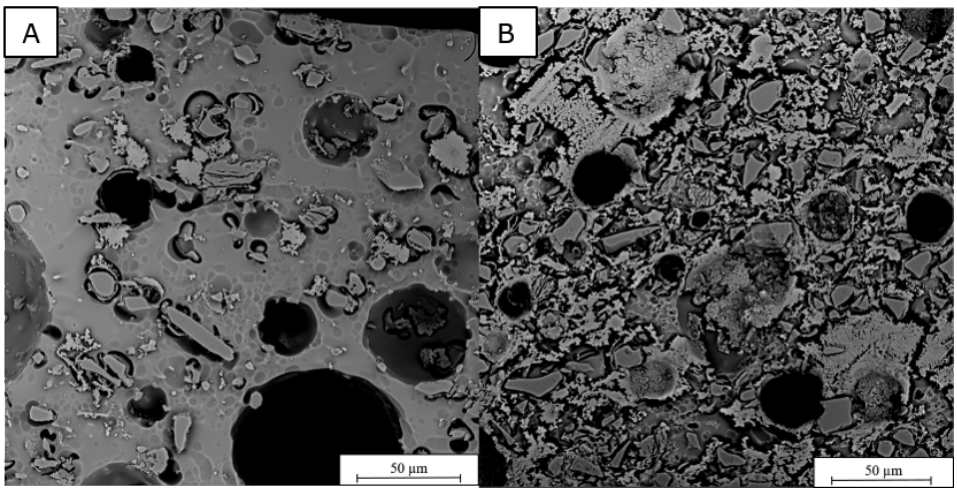

Figure 3. *SEM micrographs of composition A (A) and composition B (B).*

In Figure 4A, the opacity, given by the L* value of compositions A and B, is lower than that of composition C and D as expected due to increasing amount of zircon. Comparing the opacities of composition A and B or C and D, a significant increase in opacity is not observed despite the increase in anorthite. This is because the refractive

index of anorthite ($n_{anorthite}$=1.58 [2]) is close to that of the glassy phase. In Figure 4B, an increase of anorthite crystals (composition B and D) increases the matte appearance. It was composition D which had the highest mattness due to the additional presence of opacifying zircon crystals.

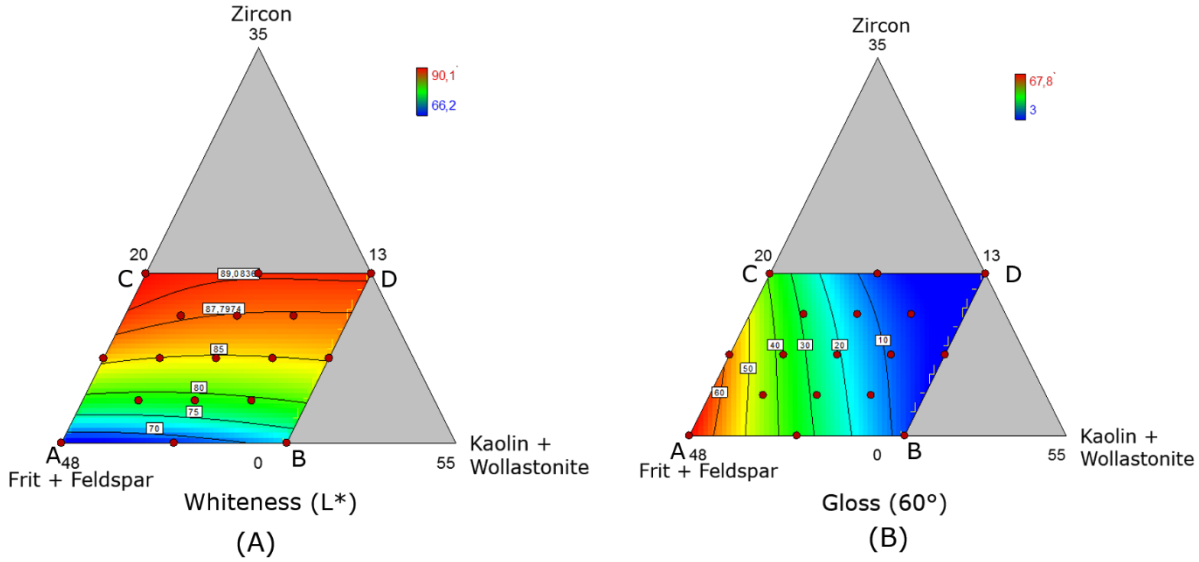

Figure 4. *Whiteness (A) and Gloss (B) values of glaze compositions.*

In order to obtain a higher opacity, composition E (Figure 1) was formulated where zircon content was increased to 20 wt% and, at this zircon content, further modifications were made to the frit/feldspar ratios and the added quartz amount, as shown in Table 1.

	E1	E11	E12	E2	E21	E22	E3	E31	E32
Frit/feldspar weight ratio	1/3	1/3	1/3	1/5	1/5	1/5	1/11	1/11	1/11
Added quartz (wt%)	-	10	20	-	10	20	-	10	20

Table 1*. Compositional modification of E series glazes.*

The gloss and opacity of these compositions are found on Table 2. Opacity varies from 91.90 to 89.72 and glossiness varies from 19.4 to 3.3. Increasing the feldspar amount shows a decrease in gloss and opacity. The gloss values in composition E1 markedly decrease with the addition of quartz to the compositions, while this change is lower in compositions E2 and E3. The increase on the amount of added quartz in the compositions and the decreased opacity is due to the decreasing percentage of zircon in the compositions.

	E1	E11	E12	E2	E21	E22	E3	E31	E32
Whiteness (L^*)	91.90	91.30	90.55	91.41	90.82	89.80	91.08	90.60	89.72
Gloss (60°)	19.4	16.9	16.2	5.8	5.7	5.3	3.6	3.3	3.4

Table 2. *Opacity and gloss values of E series glazes.*

In Table 3, the thermal expansion coefficient (25-400 °C) varies from 61.94×10^{-7} 1/°C to 73.60×10^{-7} 1/°C and increases as the frit/feldspar ratio decreases in the compositions. This is believed to be due to the reduction of quartz solubility with a reduction in frit content. In addition, as the amount of quartz increases, TEC increases as expected.

	α_{300} ($1/°C*10^{-7}$)	α_{400} ($1/°C*10^{-7}$)	α_{500} ($1/°C*10^{-7}$)	α_{600} ($1/°C*10^{-7}$)
E1	60.07	61.94	63.96	67.79
E12	63.89	65.78	68.04	72.26
E3	67.6	70.24	73.45	80.76
E32	71.86	73.6	76.32	84.1

Table 3. *Thermal expansion coefficient of E1, E12, E3 and E32.*

4. CONCLUSION

Glaze compositions consisting of anorthite, quartz, zircon and glassy phases are developed by controlling the amount of these phases. This systematic approach made it possible to obtain glazes with high opacity, varying degree of mattness and adjustable thermal expansion coefficients. The high opacity of the glazes allows them to be used without an engobe layer. This may reduce the cost in terms of labour, process and materials.

5. REFERENCES

[1] Eppler, R. A. and Eppler D. R., (2000). *Glazes and glass coatings.* America Ceramic Society

[2] Cheng, X., Ke, S., Wang, Q., Wang, H., Shui, A., Liu, P. (2012). Fabrication and characterization of anorthite-based ceramic using mineral raw materials. *Ceramics International,* 38 (4), 3227–3235.