# CERAMIC FRITS WITH HIGH ALUMINIUM OXIDE CONTENTS: PROSPECTS FOR USE IN FABRICATING GLASS-CERAMIC GLAZES

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This study has been undertaken with a view testing the applicability of two frit formulations with a high amount of alumina oxide, having the potential to crystallize during fast firing cycles. The mixtures for the frits ZASB and MAS were prepared with three different precursor aluminas, holding the chemical composition detailed in Table 1. The fusion mixtures were duly weighed and then homogenized by dry milling in a ball mill for 5 min. The mixtures were placed in a ZAS (Zirconium-Alumina-Silica) refractory crucible for fusion. A laboratory melting kiln was used, with a heating rate of 5°C/min to a temperature of 1000°C, with a 30-min hold at this temperature for the time required to allow decomposition of the precursor carbonates. The heating rate was then changed to 10°C/min up to fusion peak temperature of 1500°C for the ZASB composition frit and 1550°C for the MAS composition frit, with a 20-min hold at peak temperature. The melt was quenched in water, with subsequent drying of the resulting frits.

| TEST FRIT | CHEMICAL COMPOSITION (MOLES) | | | PRECURSORS |
|---|---|---|---|---|
| **ZASB** | **1,00 ZnO** | **0,53 $Al_2O_3$**<br>**0,39 $B_2O_3$** | **1,80 $SiO_2$** | **Zinc oxide, alumina, boric acid, quartzose sand** |
| **MAS** | **1,00 MgO** | **0,70 $Al_2O_3$** | **2,09 $SiO_2$** | **Magnesium carbonate, alumina, quartzose sand** |

*Table 1. Oxide formulation of the studied frits and raw materials used in preparing the fusion mixtures.*

The glaze compositions for the test were prepared in accordance with the mass proportions: test frit - 59.340%, water - 35.370%, kaolin - 5.180%, carboxymethylcellulose - 0.071% and sodium tripolyphosphate - 0.039%. Milling was performed in the laboratory, controlling the time for the suspensions to reach a reject on a 44 $\mu$m mesh aperture between 2 and 3%. The application was performed with a laboratory apparatus on the unfired engobed base. The ceramic pieces were fired in an industrial kiln with a single-firing cycle of 38 min at a peak temperature of 1150°C. With a view to adjusting the compositions to the firing conditions used in the study, we added a glossy transparent commercial frit (FT) to ZASB and MAS in mass proportions of 10:90, 20:80 and 30:70, respectively.

Characterization was by X-ray diffraction, scanning directly on the consolidated glaze layers, using a scanning rate of 0.1°/min in the range ($2\theta$ ) from 10° to 60°. Bubble quantification was conducted at the surfaces by analysis of images obtained in an optical microscope, where the resulting statistical data were: number of bubbles per $mm^2$ and percentage of total porosity (% surface area occupied by pores) as a function of the range of bubble equivalent sphere diameter.

The results show that the different alumina precursors used for the preparation of the fusion batches caused no differences in the crystallization behaviour and fusibility of the glazes under the set experiment conditions. However, further study is needed on the use of each alumina, with a view to establishing the influence of this precursor on processing conditions that resemble those of fusion on an industrial scale. The glazes formulated with MAS, just like those containing additions of FT, were shown to be inappropriate for the firing conditions set in the study, and gave rise to poorly densified coatings that were inadequately bonded to the substrate. However, the crystallization of indialite (hexagonal cordierite) was detected in these glazes, which occupied a volume proportion exceeding 50%. The results indicate the need to adjust the composition of this glaze, probably by introducing MAS in smaller amounts than those tested, applied in products destined for higher firing temperatures, as in the case of glazes for porcelain tile.

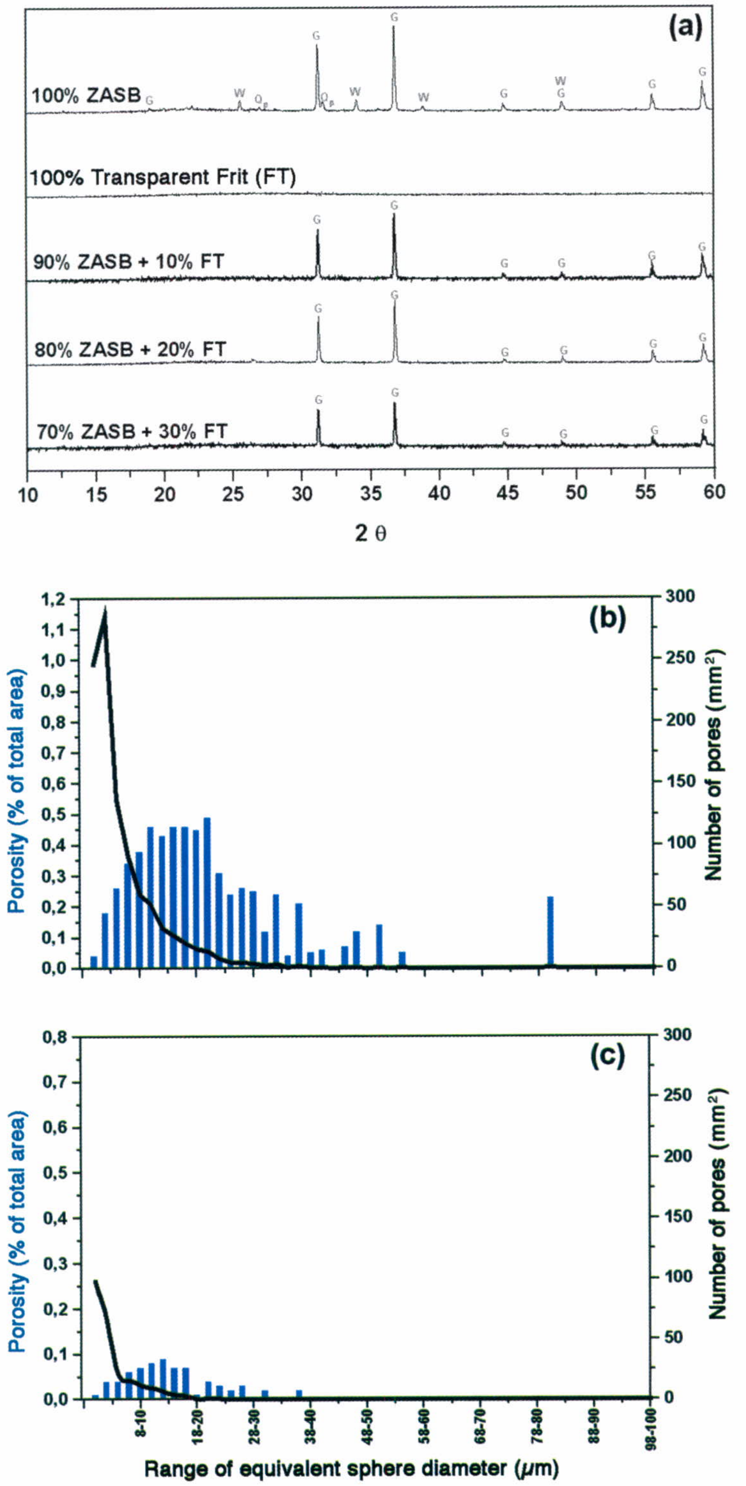

*Figure 1. (a) X-ray diffraction analysis of the glaze compositions containing FT and ZASB treated at 1150°C: G-gahnite, W-willemite, Qβ – solid solution with β-quartz structure; (b) and (c) pore distribution and quantity of bubbles retained in the glazes containing 100%ZASB and 80%ZASB-20%FT.*

The glaze that contained only ZASB displayed crystallization of gahnite and willemite phases and a solid solution with a β–quartz structure (Figure 1-a). When only frit FT was used as a precursor, no crystallizations were detected in the glaze. In the ZASB compositions with the FT addition, the major crystalline band of gahnite was detected (Figure 1-a), and these yielded opaque white glazes with a glossy surface. In addition to these interesting aesthetic characteristics, the glazes prepared with ZASB and FT gave rise to a very small amount of residual bubbles, also of highly reduced dimensions, always below 40 μm, as can be observed in Figure 1-c compared with the Figure 1-b. With regard to the hardness obtained on the Mohs scale, the glazes that devitrified gahnite phase exhibited hardness 5, which was significantly higher than that of the glazed commercial products with a glossy topology that normally displayed hardness between 3 and 4 on the Mohs scale.

The results indicated the feasibility of the development and use of the compositions that contained devitrifiable frits with a high alumina oxide content together with transparent frits, for glazes that generate glossy surfaces with superior technical performance features to those of commercial glazes with this topology.

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