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# Glass–ceramic frits for porcelain stoneware bodies: Effects on sintering, phase composition and technological properties

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**Abstract**

In the present work, the effects of glass–ceramic frits (10 wt.%) added to a porcelain stoneware body in replacement of non-plastic raw materials were evaluated simulating the tile-making process. Each glass–ceramic frit plays its own peculiar effect on the compositional properties and only some precursors behave as real glass–ceramic materials. The positive influence of glass–ceramic precursors in promoting the sintering stands out when temperature onset densification and sintering rate are considered: both of them are improved with respect to the reference body. The presence of glass–ceramic frits allows to preserve good technological properties, complying with the latest requirements of the industrial practice.


*Keywords:* A. Sintering; D. Glass ceramics; Ceramic tiles; Porcelain stoneware

## 1. Introduction

Porcelain stoneware tiles are characterized by a very low water absorption (<0.5% according to standard ISO 13006; <0.2% in current production) and excellent mechanical, tribological and functional properties for a building material [1–5].

Porcelain stoneware is a glass-bonded material manufactured in large size (up to 1 $m^2$) with fast cycles and a wide range of decorative techniques in order to bestow outstanding aesthetical effects [6].

Therefore, pressing exigencies for the tile-making industry are: (a) enhancing the sintering kinetics; (b) actually controlling firing shrinkage to achieve a uniform densification; (c) keeping adequate mechanical strength in large size tiles; (d) obtaining colour of fired stoneware as lightest as possible. In fact, ceramic pigments used to decorate porcelain stoneware present a relevant cost; a light-coloured body, especially if even translucent, allows to lower significantly the amount of pigment necessary to get the desired coloration [7].

In order to fulfil these exigencies, some kinds of glass–ceramic materials have, in the latest years, come in a wide use in porcelain stoneware production. They are vitreous precursors, prepared like ceramic frits, that are expected to devetrify during the fast firing cycle of the tile-making industry (typically 50–60 min cold-to-cold, with heating rates up to 80 °C/min and cooling rate up to 110 °C/min, maximum temperature 1200–1240 °C for 5–10 min soaking). The glass–ceramic systems entered in use are silicate and alumino-silicate of Na, Mg, K, Ca, Zn, Ba and Zr, though some further components may be present in the most complex formulations [7–19].

The effects played by these glass–ceramic frits in the firing process have been essentially studied by the technological viewpoint [20–25]. The role of glass–ceramic precursors on sintering kinetics, phase transformations and microstructure of porcelain stoneware is still to a large extent unknown.

The aim of the present paper is to fill this gap by investigating the firing behavior of seven glass–ceramic systems. The rationale is to introduce each frit in a typical porcelain stoneware body, simulating the industrial manufacturing in controlled laboratory conditions and assessing the changes induced by the glass–ceramic precursors on sintering and technological behaviour as well as microstructure and phase composition.

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Table 1
The glass–ceramic systems

| Glass–ceramic frits | System | Component | Crystalline phases detected after devetrification |
|---|---|---|---|
| F0 | CMAS | $CaO–MgO–Al_2O_3–SiO_2$ | Anorthite, diopside and quartz |
| F1 | ZCS | $CaO–ZrO_2–SiO_2$ | Calcium zircosilicate, wollastonite and baddeleyite |
| F2 | MAS | $MgO–Al_2O_3–SiO_2$ | Indialite, forsterite, quartz, spinel and periclase |
| F3 | BAS | $BaO–Al_2O_3–SiO_2$ | Celsian |
| F4 | NAS | $Na_2O–Al_2O_3–SiO_2$ | Nepheline |
| F5 | MAKZCS | $MgO–Al_2O_3–K_2O–ZrO_2–CaO–SiO_2$ | Diopside, anorthite and baddeleyite |
| F6 | CZnNAS | $CaO–ZnO–SiO_2–Na_2O–Al_2O_3$ | Gahnite and plagioclase |

Table 2
Physical properties of the glass–ceramic frits

| Glass–ceramic frits | Bulk density (g $cm^{-3}$) | Coefficient of thermal expansion ($MK^{-1}$) | Temperature (°C) at log $\eta = 3$ ($\eta$ = viscosity) | Temperature of glassy transition (°C) | Temperature of crystallization (°C) |
|---|---|---|---|---|---|
| F0 | $2.668 \pm 0.002$ | $7.2 \pm 0.1$ | $1273 \pm 5$ | $720 \pm 5$ | $935 \pm 5$ |
| F1 | $2.857 \pm 0.002$ | $5.8 \pm 0.1$ | $1312 \pm 5$ | $800 \pm 5$ | $936 \pm 5$ and $1025 \pm 5$ |
| F2 | $2.484 \pm 0.002$ | $2.8 \pm 0.1$ | $1365 \pm 5$ | $710 \pm 5$ | $890 \pm 5$ and $960 \pm 5$ |
| F3 | – | $6.4 \pm 0.1$ | – | $750 \pm 5$ | $960 \pm 5$ |
| F4 | $2.380 \pm 0.002$ | $12.8 \pm 0.1$ | $1310 \pm 5$ | $650 \pm 5$ | $885 \pm 5$ |
| F5 | $2.630 \pm 0.002$ | $6.8 \pm 0.1$ | $1210 \pm 5$ | $505 \pm 5$ | $750 \pm 5$ and $1025 \pm 5$ |
| F6 | $2.503 \pm 0.002$ | $7.1 \pm 0.1$ | $1330 \pm 5$ | $650 \pm 5$ | $955 \pm 5$ |

## 2. Experimental

Seven glass–ceramic systems (F0–F6) were selected among the most widely utilized by the ceramic industry (Table 1). They are prepared like ceramic frits, admixing the raw materials (oxides and carbonates) in almost stoichiometric proportions and adding small amounts of melting promoters [24,25]. These frits were characterized determining: bulk density (water pycnometry, ASTM C329), viscosity at high temperature (VEZAS), coefficient of thermal expansion (ASTM C 372), temperatures of glassy transition and crystallization (Table 2). Moreover the glass–ceramic systems underwent a thermal treatment, such as that of porcelain stoneware tiles, and the crystalline phases formed were determined (XRPD, Philips X'Pert Pro x, Cu Kα radiation, 10–80° $2\theta$ range, 0.05° stepscan) (Table 1).

An industrial spray-dried powder (BR), made up of ball clays (37 wt.%) plus feldspars and quartz (63 wt.%), commonly employed for porcelain tile manufacture, was modified by adding the different frits; these latter were added in replacement (10 wt.%) of the non-plastic materials. The mineralogical composition of the industrial mixture BR is: 32.5 wt.% of kaolinitic and illitic clays, 31.2 wt.% of quartz, 30.8 wt.% of plagioclase and 5.5 wt.% of potassium feldspar.

The overall chemical composition of the frit-bearing bodies, from BF0 to BF6, is listed in Table 3 and compared with the reference one.

The simulation of the industrial tile-making process was carried out at laboratory scale by:

- mixing and wet grinding in porcelain jar with dense alumina grinding media for 20 min in a planetary mill (C.I. Magellano);
- slip drying at $105 \pm 5$ °C overnight, powder deagglomeration (by hammer mill, 0.75 mm grid) and humidification with 7–8% water;
- uniaxial pressing (40 MPa) of 110 mm × 55 mm × 6 mm tiles;
- drying in an electric oven at $105 \pm 5$ °C overnight;
- firing in an electric roller kiln (Nannetti, ER 15) at maximum temperature from 1200 °C up to 1240 °C with a thermal cycle of 51 min cold-to-cold.

Fired tiles were characterized by determining: firing shrinkage (ASTM C326), water absorption, bulk density ($\rho_f$) and open porosity (OP, ISO 10545-3), real density by helium pycnometry ($\rho_r$), total porosity ($TP = [1 - (\rho_f/\rho_r)] \times 100$), closed porosity ($CP = TP - OP$), CIE-Lab colourimetry (ISO 10545-16, Hunterlab MSXP-4000).

Table 3
Chemical composition (wt.%) of porcelain stoneware bodies

| | BR | BF0 | BF1 | BF2 | BF3 | BF4 | BF5 | BF6 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 71.34 | 68.98 | 69.43 | 68.98 | 68.22 | 68.55 | 69.48 | 69.13 |
| $TiO_2$ | 0.52 | 0.47 | 0.47 | 0.47 | 0.47 | 0.47 | 0.47 | 0.47 |
| $Al_2O_3$ | 16.89 | 17.14 | 15.20 | 18.53 | 16.97 | 18.13 | 16.33 | 17.97 |
| $Fe_2O_3$ | 0.56 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| MgO | 0.47 | 1.35 | 0.42 | 2.12 | 0.42 | 0.42 | 1.13 | 0.42 |
| CaO | 0.56 | 2.85 | 3.64 | 0.50 | 0.50 | 0.62 | 2.20 | 0.69 |
| $Na_2O$ | 4.02 | 3.61 | 3.61 | 3.61 | 3.61 | 5.52 | 3.61 | 4.28 |
| $K_2O$ | 2.19 | 1.97 | 1.97 | 1.97 | 1.97 | 1.97 | 2.22 | 2.18 |
| $ZrO_2$ | – | – | 1.64 | – | – | 0.17 | 0.93 | 0.26 |
| ZnO | – | – | – | – | – | – | – | 0.44 |
| BaO | – | – | – | – | 4.21 | – | – | – |
| $B_2O_3$ | – | – | – | – | – | 0.50 | – | 0.43 |
| $Li_2O$ | – | – | – | 0.20 | – | – | – | 0.09 |
| $P_2O_5$ | 0.11 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| L.O.I. | 3.34 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |