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Effect of B_2O_3/SiO_2 Ratio on Transparency of Anorthite Based Glass-Ceramic Glazes

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The present study was undertaken to determine the influence of B_2O_3/SiO_2 ratio on devitrification behaviour, anorthite crystal size and transparency of glass-ceramic glazes. Measurement by X-ray diffraction combined with scanning electron microscopy and energy dispersive X-ray spectroscopy microanalysis show that needle-like crystals of anorthite are formed. Sinterization and devitrification behaviour of system and viscosity change with temperature were analyzed by combining the datas that belong to differential thermal analysis and heating microscope analysis. Crystal size of anorthite was changed by modifying B_2O_3/SiO_2 ratio. It is confirmed that additional B_2O_3 prevents immediate phase separation during heat treatment in anorthite based glass-ceramic glazes.

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1. Introduction

Dry decoration consists substantially in depositing a decorative motif in semifinished form onto a base constituted by one or more layers of powders (granulars) to be pressed, or on layers of already pressed powders forming a support [1]. For the correct dry application of a layer of frit particles onto a ceramic body, it is advisable for the frit particles to exhibit good flowability for uniform distribution. The greatest flowability is found with a spherical shape granulars [2]. Granulars are frits that are dry milled by different systems, with a carefully selected particle size obtained by sieving. They are normally glassy materials, but given their special chemical composition, they exhibit a high tendency to crystallize on undergoing a heat treatment during tile firing [3].

Arising crystalline phases by devitrification and a residual glassy phase form glass-ceramic composites that increase the hardness and mechanical strength [4]. However, this structure makes mechanical features better, while it affects optical features. The opacity and covering characteristics of glasses and glazes depend on the amounth of diffuse light reflected by the top surface, before reaching the bottom surface. For transparency most of the light must be transmitted and only part diffusely reflected. Therefore, to achieve transparent glass-ceramic coating it is convenient to investigate crystallization processes of crystalline phases whose refractive index is very close to that of glass [5]. Anorthite [6] has a refractive index of ≈ 1.58 which is close to that of glass phase [7] at ≈ 1.5.

The research objectives of the present work are to produce anorthite based transparent glass-ceramic glaze on porcelain tile surfaces by using granulated frit devitrification and to establish correlation between B_2O_3/SiO_2 ratio on transparency of anorthite glass-ceramic glazes.

2. Experimental procedure

First of all, suitable frit compositions were determined on the basis of CaO–Al_2O_3–SiO_2 system. The Seger formula (molar) of T and TB prepared frits is 0.1800 Na_2O, 0.0400 K_2O, 0.6500 CaO, 0.0100 MgO, 0.1200 ZnO, 0.4780 Al_2O_3, 2.0000 SiO_2, with additional 0.0200 B_2O_3 and 0.01 B_2O_3/SiO_2 for TB only. The compositions are rich in silica, alumina, and calcium oxide with other oxides, so that in principle, they could be expected to exhibit a strong tendency to devitrify anorthite.

The weighed batch materials, after thorough mixing were melted in an alumina crucible in an electric furnace at 1450 °C for 1 h. The melt was quenched by pouring into water to obtain a glassy frit. Frit particles were dried in an oven and dry-milled in an alumina ball mill to obtain granulated frit. The milled small frit granules were sieved in an automatic sieving machine that includes 125, 100, 90, and 63 μm sieve and mixed at certain ratios (33% of frit particles is between −125, +100; 14% of frit particles is between −100, +90; and 53% of frit particles is between −90, +63). Firstly, engobe and glaze was applied on the green porcelain body by spraying. Then granulated frit was applied on the glazed body by using screen printing method. 40 mesh screen was used for printing of granules on the glazed tile surface. After that porcelain tile was fired at 1215 °C in the industrial roller furnace for 42 min in Vitra Tiles Incorporation.

The sintering behaviour was investigated by hot stage microscope (Misura 3.32 ODHT-HSM 1600/80). The characteristic glass transition temperatures, T_g, and crystallization temperatures, T_c, were observed using a Netzsch STA 409 PG diferential thermal analysis (DTA). X-ray diffraction analysis (XRD) was performed by a Rigaku Rint 2000 Series difractometer with Cu K_α radiation. X-ray patterns were taken with the scanning velocity of 2°/min working at 40 kV and 30 mA. The samples analysed with XRD were also evaluated with scanning electron microscope (SEM, Zeiss EVO 50 at 20 kV) attached with an energy dispersive X-ray (EDX) spectrometer.

3. Results and discussion

In Figs. 1 and 2, sintering and crystallization behaviour of frit T and frit TB are given. B_2O_3 addition reduced both crystallization and softening temperature.

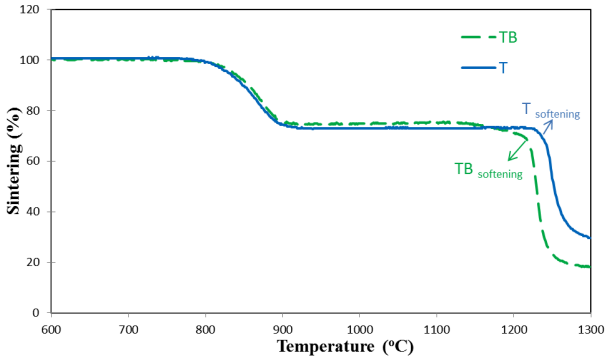

Fig. 1. Sintering behaviour of frit T and TB.

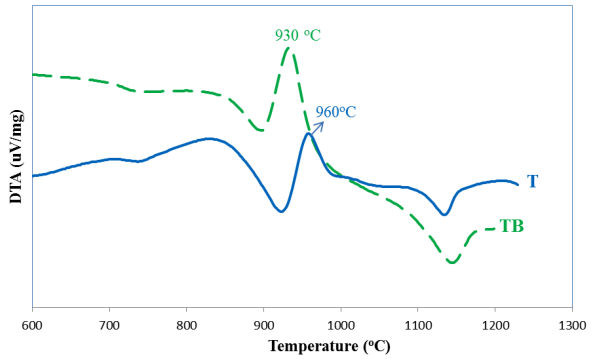

Fig. 2. DTA analyses of frit T and TB.

X-ray diffraction results of the granulated frit TB after firing at 1215 °C (Fig. 3) show that exothermic crystallization peak at 930 °C in DTA graph belongs to anorthite.

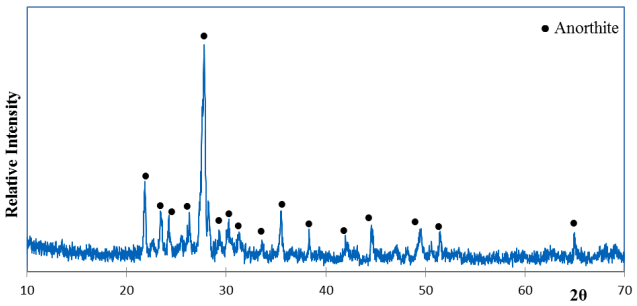

Fig. 3. XRD pattern of frit TB fired at 1215 °C for 42 min.

In composition TB (Fig. 4), wider and bigger (< 20 μm) rod-like crystals are shown. It can be concluded that in composition T intense phase separation and nucleation happened and stopped each other during growing. The best transparency was obtained for the porcelain tile coated with TB frit granules. These results suggest that B_2O_3 addition decreases phase separation and nuclei can grow easily [8, 9]. Wider and bigger anorthite crystals with low refractive index decreases light refraction and transparency of glaze increases [9].

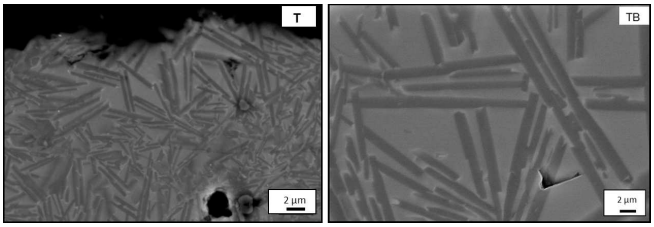

Fig. 4. SEM images taken from cross-section of T and TB.

4. Conclusions

The present study suggests that anorthite crystals had a chance to grow better with B_2O_3 addition in anorthite based glass-ceramic system. Additional B_2O_3 increases anorthite crystal size in $CaO–Al_2O_3–SiO_2$ system by preventing immediate phase separation from happening during heat treatment.

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