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Effect of MgO/CaO ratio on the microstructure of cordierite-based glass-ceramic glazes for floor tiles

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Abstract

The effect of the MgO/CaO ratio on the microstructure and microhardness of cordierite-based glass-ceramic glazes was studied. For this purpose glasses, with compositions in the cordierite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system and, with different MgO/CaO ratios, were prepared by melting. Glass powder pellets pressed under low pressure were fast heated at several temperatures simulating industrial floor-tile processing, and characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray emission spectroscopy (EDX). The studied glasses crystallized α-cordierite as the only crystalline phase in the range of temperatures between 1160 and 1190 °C. The glass with intermediate MgO/CaO ratio yielded on heating the relative highest amount of α-cordierite as well as the best well-shaped hexagonal prism crystals. These features were coupled with the highest microhardness value obtained for the glass-ceramic glaze on the tile support.

Keywords: B. Microstructure-final; C. Mechanical properties; D. Cordierite; D. Glass-ceramics

1. Introduction

Glass-ceramic materials for different applications have received increasing attention during last years. These materials have improved properties comparing with glasses and ceramics [1–3]. Basically, the glass-ceramic process can be defined as a controlled crystallization of a glass; in such a way that many of the properties are based on the formation of homogeneously dispersed fine crystals in the glass.

Depending on the material type to produce, the starting glass can be processed either as bulk or powder. Also, to give rise to a favourable microstructure some nucleants are added to facilitate a homogeneous crystallization through the material.

A type of materials widely used around the world is the glazed floor-tile ceramic material. As it is well known a ceramic support and a glass layer, usually known as glaze, form these products. Technical features of these binary products are very determined by the glaze characteristics. Among the mechanical properties to improve in these materials are the abrasion resistance and hardness. So, it is interesting to develop new glass-ceramic glazes that enhance the mechanical properties of final two-components floor-tile products.

During last decade some reports on the feasibility of glass-ceramic glazes based on different crystalline phases have been reported in the literature [4–7]. Recently, we have reported results on the possibility of developing cordierite-based glass-ceramic glazes from compositions within the CaO–MgO–Al_2O_3–SiO_2 quaternary system [8,9]. These studies showed the key role played by some additives, as fluxes and/or nucleants, in the development of this kind of materials by processing conditions used actually in the floor-tile ceramic industry. More recently, we have developed a glass-ceramic in the quaternary system, and containing B_2O_3 and TiO_2 as additives [10]. It was found that the addition of B_2O_3 suppressed the formation of μ-cordierite. This fact facilitated densification by viscous flow before crystallization. Moreover, α-cordierite nucleated directly

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from glass on the boundaries of original particles, probably favoured by the addition of TiO_2 as nucleant.

In these $CaO–MgO–Al_2O_3–SiO_2$ quaternary glasses the crystallization of anorthite is favoured by enhancing the amount of CaO and, therefore, preventing the presence of α-cordierite as only crystalline phase [8,11]. On the other hand, the MgO amount is also critical to crystallize high amount of α-cordierite. In this context, it would be valuable to know how the MgO/CaO ratio changes the relative amount of α-cordierite crystalline phase, and consequently the properties of the final glass-ceramic glazes.

The purpose of this paper is, therefore, to study the effect of the MgO/CaO ratio on the development of cordierite-based glass-ceramic glazes, mainly with the aim at obtaining the formation of the highest amount of cordierite, without any secondary crystalline phase, coupled with well-defined morphologies of the final crystals. This combination would allow obtaining glazes with improved mechanical properties.

2. Experimental procedure

2.1. Preparation of glasses and thermal treatments

Three glasses with compositions (in wt.%) 55 SiO_2, 21.5 Al_2O_3, $(16.5 - x)$ MgO, x CaO, 3.8 TiO_2 and 2.9 B_2O_3, with $x = 6.5$, 4.6, and 2.9, were prepared. It is to note that glasses contained increased MgO/CaO ratio and the same amount of the other components. SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, TiO_2 and BO_3H_3, all high quality reagents provided from Merck, were used as starting materials. The composition of the three glasses in oxides is shown in Table 1. The transformation from glass to glass-ceramic glaze for the composition GC11 has been previously studied [10]. Glasses were prepared by the conventional technique of melting at 1600 °C for 2 h and pouring into water to obtain a frit. To improve the glass homogeneity each glass was remelted at the same temperature. After the second melting the melt was poured into water and milled up to obtain a powder glass with particle size smaller than 30 μm.

In order to follow the crystallization pathway and microstructural changes, cylindrical pellets of loosely pressed powder, i.e. under a pressure of about 5 MPa, were fast thermal treated at several maximum temperatures in the range between 700 and 1190 °C with soaking time 5 min. The heating rate for the heating schedules was 25 °C/min. These conditions were chosen to simulate industrial processing of glazed ceramic tiles. The correct maturing (development) of glasses as glazes was checked by preparing them as slips and glazing conventional tile support.

Table 1
Composition of prepared glasses (in wt.%)

Glass	SiO_2	Al_2O_3	MgO	CaO	TiO_2	B_2O_3
GC10	55.02	21.58	10.16	6.46	3.86	2.90
GC11	55.00	21.57	12.01	4.66	3.86	2.90
GC13	55.10	21.61	13.61	2.91	3.87	2.90

2.2. Characterization techniques

Crystallization and microstructural evolution of glass powder specimens were examined using several techniques.

X-ray diffraction analysis (Model D-5000, Siemens, Karlsruhe, Germany) was performed using a graphite monochromatic Cu Kα radiation. X-ray patterns were taking by measuring 2θ from 5° to 65° with a step size of 0.02 and a step time of 5 s.

The relative amounts of α-cordierite in final glass-ceramic glazes heated at 1160 and 1190 °C, in which only α-cordierite was formed, was determined by XRD using the internal standard method. In this method a diffraction line from the phase being determined, i.e. α-cordierite, is compared with a line from a standard phase mixed with the sample in known proportions, i.e. NaCl. Mixtures that contained 20 wt.% NaCl and 80 wt.% glass-ceramic glaze were used for the analysis. The relative degree of crystallization was determined by comparing the integrated intensity ratios, $I_{cordierite}/I_{NaCl}$. $I_{cordierite}$ was the intensity of the (1 0 2) peak of α-cordierite and, I_{NaCl} the intensity of the (2 2 0) line of NaCl. Strictly speaking this method is only valid provided that the mass absorption coeficient of the three glass-ceramic glazes is strictly equal. Yet it has been found to be possible to determine relative amounts of α-cordierite because the chemical analysis of the three glasses is relatively quite similar.

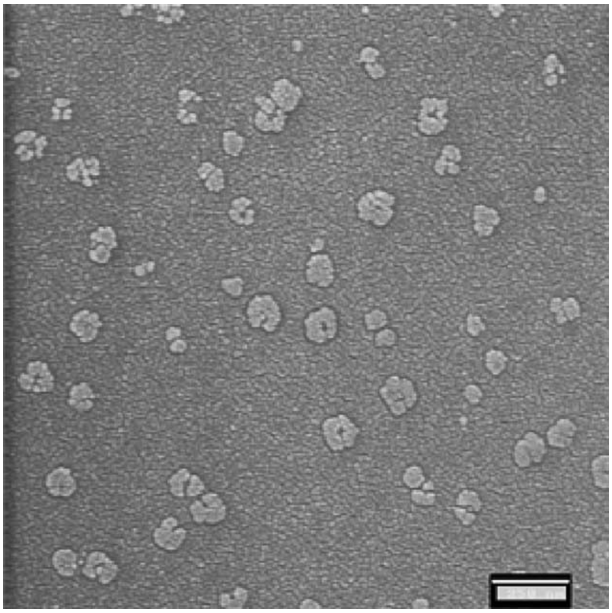

Fig. 1. FESEM micrograph of glass GC13 annealed at 800 °C for 8 h (bar = 250 nm).

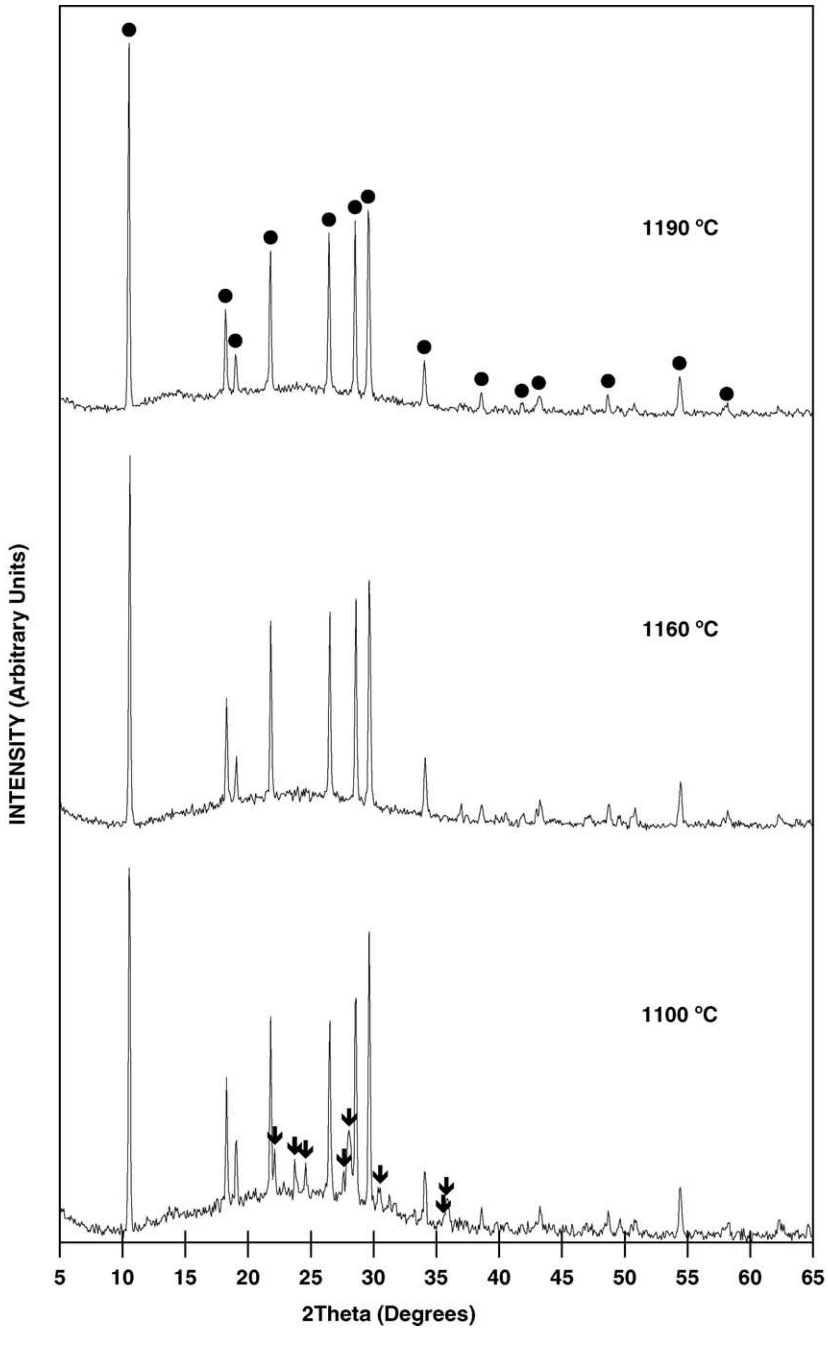

Fig. 2. X-ray diffraction patterns of glass GC10 fast fired (25 °C/min) at different temperatures for 5 min (↓ is anorthite and ● is α-cordierite).

The microstructure of the thermally treated samples was observed on fresh fracture surfaces by field emission scanning electron microscopy (FESEM) at 30 kV (Model S-4100, Hitachi Ltd., Tokyo, Japan). To check the quality of the observation, some of the samples were etched with a diluted HF solution for 10 s and subsequently washed with distilled water.

Energy dispersive X-ray analysis was performed using an environmental scanning electron microscope operated at 20 kV (Model XL30, Philips, Eindhoven, The Netherlands). This instrument is equipped with an energy dispersive X-ray spectrometer (Model DX-4, Edax, New York, USA). Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Before acquiring the X-ray spectra samples were gold/palladium coated. Quantitative analyses of specimens were made using the program with ZAF correction procedures and the default standards.

Vickers microhardness measurements of glass-ceramic glazed tiles developed under industrial fast firing treatments were made with an indenter (Model MHT-1, Matsuzawa Seiki Co., Tokio, Japan). A load of 200 g for 25 s was used to

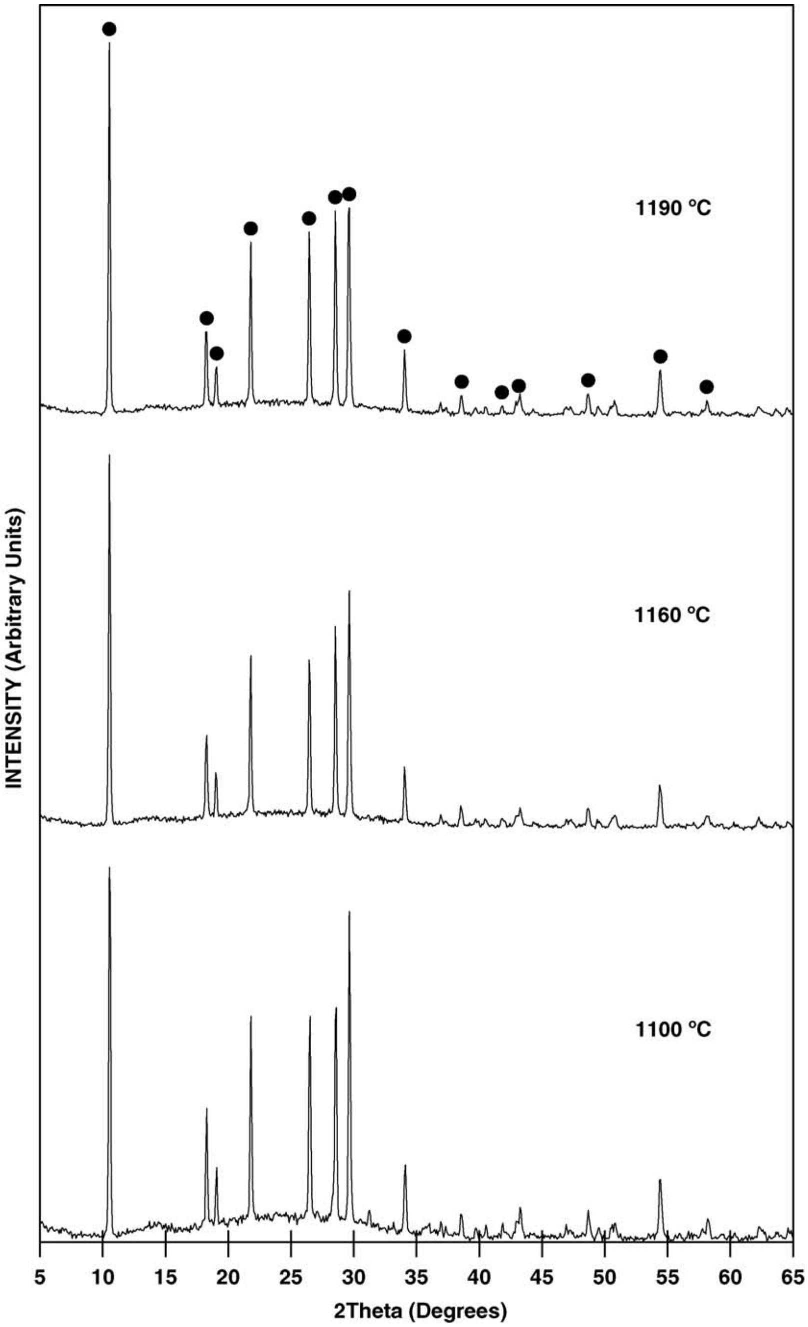

Fig. 3. X-ray diffraction patterns of glass GC11 fast fired (25 °C/min) at different temperatures for 5 min (● is α-cordierite).

indent their surfaces. In order to obtain reliable statistical data, at least 15 indentations were made on each sample.

3. Results and discussion

3.1. Dependence of the phase separation in glasses on thermal treatment

Phase separation has been investigated for the three glasses submitted to fast heating at temperatures preceeding the formation of α-cordierite. It is to note that after heating at 700 and 800 °C for 5 min no areas of different contrast are detected by FESEM. In contrast after annealing for 8 h at 800 °C, some round areas are inside the glass matrix existing a sharp boundary between the two phases. This fact is shown in Fig. 1 for glass GC13, shown as representative. It is well known that phase separation is dependent on the glass starting composition. The higher amount of modifier cations, i.e. magnesium and calcium the larger separated areas [11]. However, for all glasses studied the amount of modifier cation is the same. Also the nucleant, i.e. Ti^{4+} as TiO_2, must be favourable to produce liquid inmiscibility in glasses with high SiO_2 contents [12]. The dependence of the

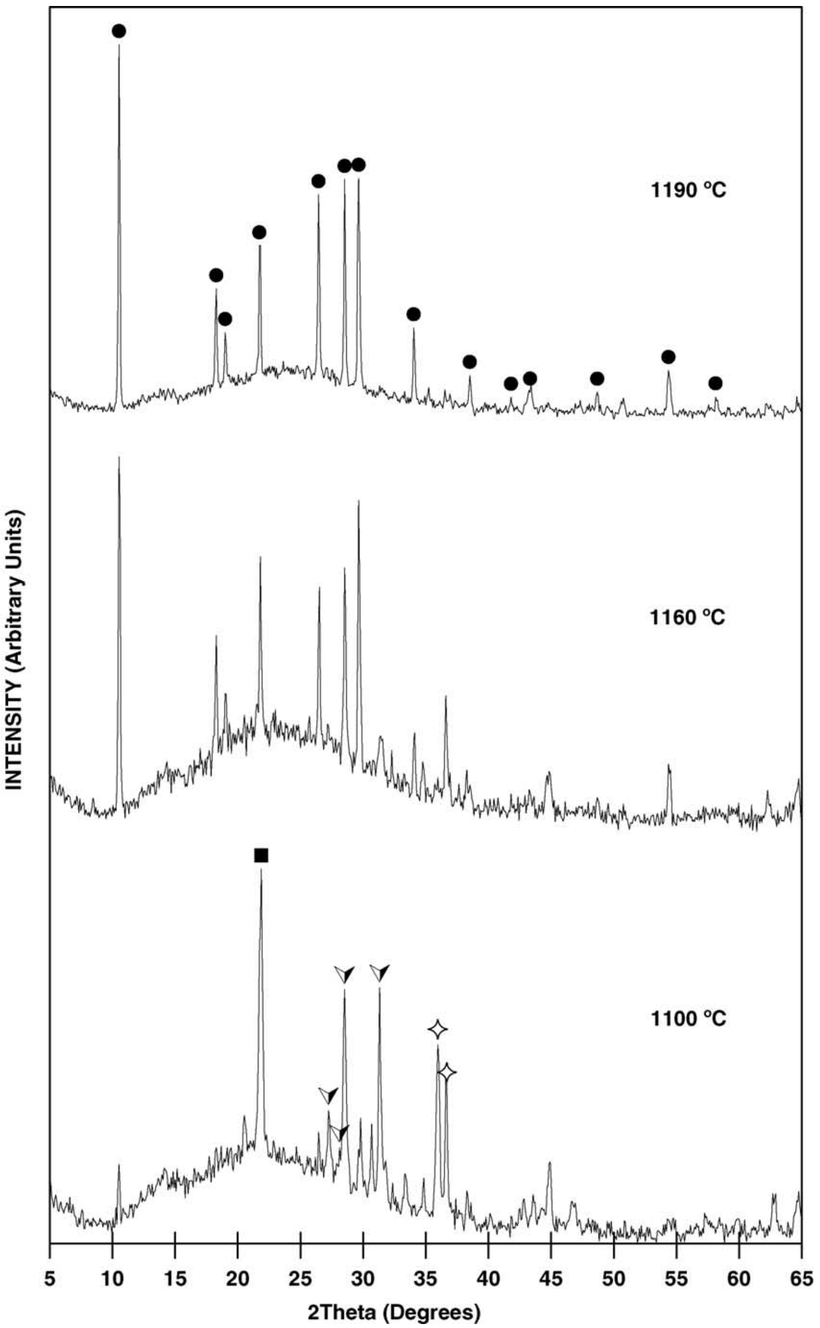

Fig. 4. X-ray diffraction patterns of glass GC13 fast fired (25 °C/min) at different temperatures for 5 min (■ is cristobalite, ⋎ is enstatite, ✧ is forsterite and • is α-cordierite).

phase separation on the annealing time is consistent with a mechanism of nucleation and growth. The above facts suggest that phase separation occurs after annealing glasses for several hours and it seems not to affect the crystallization process under fast heating processing.

3.2. Crystallization of glasses fast fired in the 1100 and 1200 °C temperature range

The crystallization path of glasses GC10 and GC11 on heating following standard thermal processing, i.e. heat up to the different final temperatures with a heating rate of 10 °C/min and hold to every final temperature for 2 h, has been reported elsewhere [9]. The glass GC13 follows a different sequence of reaction at low temperature. Anyway, it has been previously proven either that the high amount of cordierite and the well-defined shape of crystals have been obtained with fast thermal treatments [9]. So, we are considering in these study fast thermal processing of glasses. X-ray powder diffraction patterns of materials prepared by heating up to 1100, 1160 and 1190 °C with heating rate of 25 °C/min and holding for 5 min at the final temperature, are

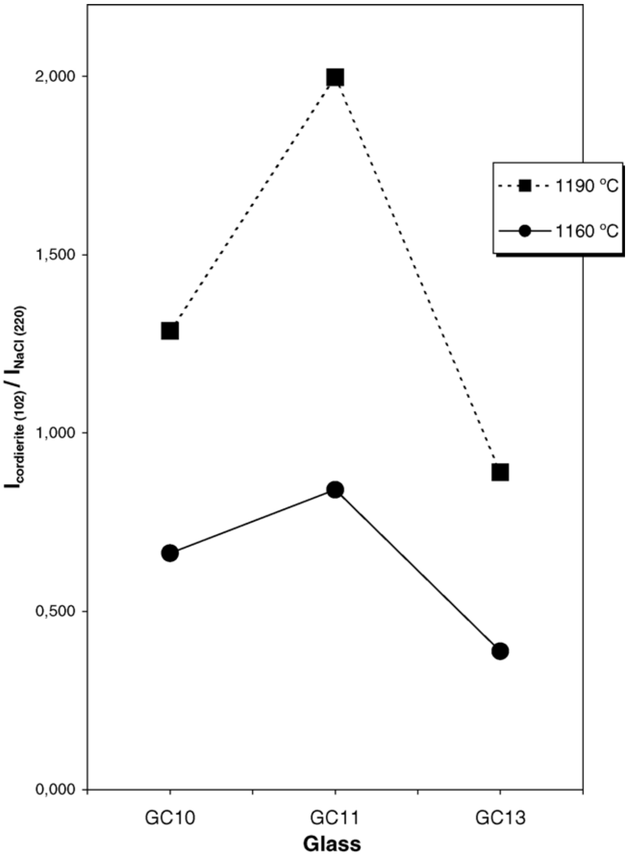

Fig. 5. Variation of $I_{cordierite}/I_{NaCl}$ ratios, for the (1 0 2) peak of α-cordierite and the (2 2 0) line of NaCl, for glasses GC10, GC11 and GC13 fast heated at 1160 and 1190 °C.

shown in Figs. 2–4. As it can be seen for specimens fired at 1100 °C only for the composition GC11 is obtained a unique crystalline phase. For GC10 some amount of anorthite is also formed and for GC13 cristobalite, enstatite and forsterite are the main crystalline phases as well as a small amount of α-cordierite. At 1160 and 1190 °C the only crystalline phase formed for the three glasses is α-cordierite.

The estimation of α-cordierite contents for fast heated glasses was performed by comparing the $I_{cordierite}/I_{NaCl}$ ratios for the (1 0 2) peak of α-cordierite and the (2 2 0) line of NaCl. The intensity ratios for the three glasses fast heated at 1160 and 1190 °C are shown in Fig. 5. It can be noted that the highest amount of cordierite is developed for the glass GC11 after heating at the highest temperature, i.e. 1190 °C.

3.3. Microstructural characterization of glass-ceramic glazes

Figs. 6–8 show the microstructure of GC10, GC11 and GC13 final materials after fast heating glasses at 1160 °C for 5 min. Figs. 6 and 7 correspond to fresh fractures of specimens GC10 and GC11, respectively. The image shown in Fig. 8 corresponds to the smooth surface of the specimen GC13 polished for performing energy dispersive X-ray analysis. As it can be seen in Figs. 6–8, hexagonal prism crystals are formed from the three glasses, but fully, well-shaped prisms are only obtained for glass GC11. The size of crystals ranges below 3 μm. It is to note that a high dispersion of crystals inside a glass matrix is also obtained for the three compositions. In this stage of growth, crystals exhibit flat prism faces, with well faceted basal (0 0 1) faces. However, such a perfectly developed hexagonal prisms only has been encountered for composition GC11. For compositions containing either more or less calcium oxide than GC11, i.e. GC10 and GC13, controlled pits in the central portion of prisms are observed. The formation of smooth faces has been interpreted as resulting from the faster spreading rate of surface layers than the nucleation rate [13]. From the above facts it can be inferred that the amount of

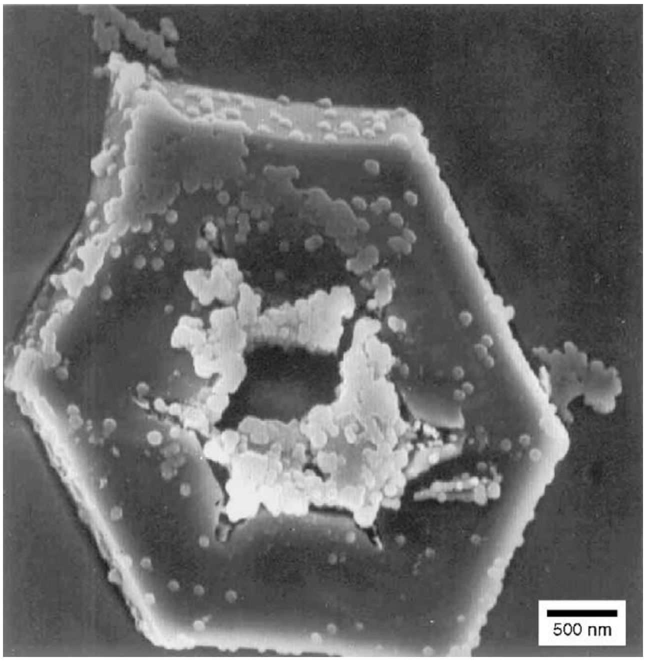

Fig. 6. FESEM micrograph of glass GC10 fast fired at 1160 °C for 5 min (bar = 500 nm).

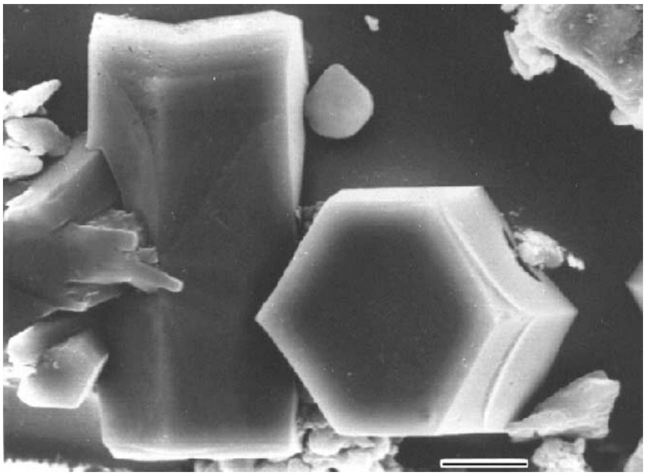

Fig. 7. FESEM micrograph of glass GC11 fast fired at 1160 °C for 5 min (bar = 1 μm).

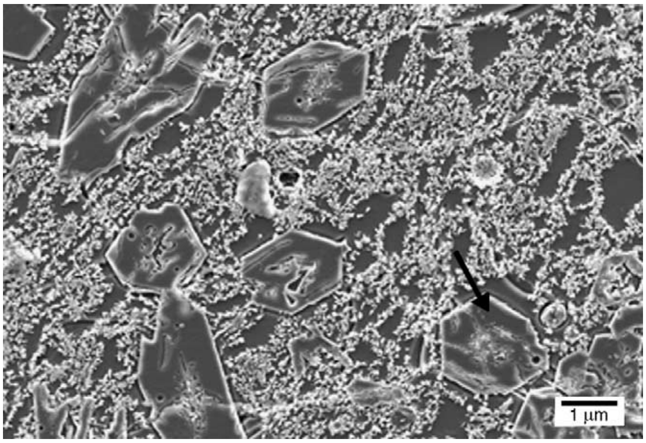

Fig. 8. SEM image of a polished surface of glass GC13 fast fired at 1160 °C for 5 min (bar = 1 µm).

CaO is quite significant for obtaining well-shaped cordierite crystals. It has been stated that if a small amount of CaO is incorporated in the MgO–Al_2O_3–SiO_2 ternary glass, both the glass melting temperature and the crystallization temperature of the glass-ceramic can be substantially reduced [14].

In order to evaluate the composition of the α-cordierite crystals from the three different glasses, EDX microanalysis of crystals in fast thermal treated glasses at 1160 °C were obtained. Results, as wt.% in oxides, are shown in Table 2. Is to note that the amount of B_2O_3 contained in crystals was not evaluated because it is assumed that no boron oxide enter into sites within the cordierite structure. The main reason is the difference in size of B^{3+} and those of Al^{3+} and Si^{4+} in tetrahedral coordination. It is well known that the α-cordierite structure consists of six-membered rings of tetrahedral coordinated cations (T_2) linked through tetrahedral (T_1) and octahedral polyhedra (M). Silicon occupies mostly T_2 tetrahedra and aluminum T_1, whereas magnesium is placed in octahedral coordination [15].

From Table 2 it can be inferred that there is no variation important in the amounts of SiO_2, Al_2O_3 and MgO in cordierite crystals for the three different glass-ceramics. The CaO content in the crystalline phase seems to increase slightly in specimens from CaO-richer glasses. The TiO_2 content in crystals seems to hold constant. From these results it can be assumed that some Ca^{2+} and Ti^{4+} enter into solid solution in the α-cordierite structure. It has been reported that Ti^{4+} may replace in small amounts to Al^{3+} or Si^{4+} in tetrahedral coordination [16] or even to Mg^{2+} in octahedral coordination [17]. However, as far as we know, there is no reported data on the solubility limit of Ti^{4+} in α-cordierite. Concerning to the Ca^{2+} incorporation into the α-cordierite, our results are in agreement with previously reported stating the formation of single-phase cordierite in the $Mg_{2-x}Ca_x Al_4Si_5O_{18}$ for x up to 0.5 [18]. Anyway, we are currently doing work to clarify structural distribution of both cations.

Table 2
Composition of α-cordierite crystals for fast-heated specimens at 1160 °C for 5 min (in wt.%)

Specimen	SiO_2	Al_2O_3	MgO	CaO	TiO_2
GC10	56.2 ± 0.4	30.1 ± 0.4	12.4 ± 0.3	0.6 ± 0.1	0.7 ± 0.1
GC11	56.5 ± 0.4	29.6 ± 0.4	12.7 ± 0.3	0.4 ± 0.1	0.8 ± 0.1
GC13	55.3 ± 0.4	30.5 ± 0.4	13.5 ± 0.1	0.1 ± 0.05	0.7 ± 0.1

3.4. Microhardness measurements

To assess the evolution of Vickers hardness when the glass-ceramic was formed on the tile support, glazed tiles were prepared by depositing slurry of glass powder on the tile support. The values of microhardness measurements (H_v) for glass-ceramics GC10, GC11 and GC13, fast fired at 1160 °C for 5 min, are 576 ± 15 kg/mm^2, 680 ± 12 kg/mm^2 and 562 ± 16 kg/mm^2, respectively. It can be noted that the higher of H_v correspond to glass-ceramic GC11, in which the higher amount of crystalline phase was developed (Fig. 5). By increasing the final firing temperature to 1190 °C, in which the three glass-ceramics glazes displayed large crystallization comparing with the ones fired at 1160 °C, the microhardness values show the same increasing trend. Thus, the obtained values 610 ± 15 kg/mm^2, 710 ± 12 kg/mm^2 and 579 ± 16 kg/mm^2 for GC10, GC11 and GC13, respectively, can be related to the higher crystallization developed by enhancing the final firing temperature.

4. Conclusions

Three glasses with compositions (wt.%) 55 SiO_2, 21.5 Al_2O_3, $(16.5 - x)$ MgO, x CaO, 3.8 TiO_2 and 2.9 B_2O_3, with $x = 6.5$, 4.6, and 2.9, were studied in order to examine the effect of the MgO/CaO ratio on the microstructure and microhardness of final glass-ceramics glazes developed by fast heating. Glass powder pellets were fast heated at several temperatures up to 1200 °C and the resultant glass-ceramic glazes were characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray emission spectroscopy (EDX). Results indicated that in the range of temperatures between 1160 and 1190 °C the only crystalline phase detected was α-cordierite for all glasses. The higher amount of this phase, the best well-shaped crystals, and the highest microhardness in the final glass-ceramic glaze were obtained for glass with intermediate MgO/CaO ratio, i.e. with $x = 4.6$.

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