Pyroxene-based glass-ceramics as glazes for floor tiles

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Abstract

Crystallization of a glass with composition in the diopside primary crystallization field in the $MgO–CaO–Al_2O_3–SiO_2$ quaternary system was investigated. Also the action of some additives, nucleants and fluxes, in the pyroxene development was examined. Glasses were prepared by conventional melting of a mixture of raw materials and cooled by pouring in water. Pellets of glass powder specimens were thermally treated at several temperatures up to 1200 °C. The crystallization path was followed by X-ray diffraction powder (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The results proved that, in addition to the effect of B_2O_3 and TiO_2 in the development of the final pyroxene phase, some amount of alkaline oxides, Na_2O and/or K_2O, are required to obtain well-defined morphologies of pyroxene crystals. Fast fired under industrial conditions glass-ceramic glazes on to porcelain stoneware supports improved hardness of final products
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1. Introduction

Glass-ceramic materials are very important because they have outstanding mechanical, thermal and chemical properties. The development of glass-ceramic glazes in the tile industry has recently received much attention because improved mechanical properties are demanded in the final products. The target is very ambitious since these advanced materials must be processed by the current processing technology, i.e. fast firing in roller kilns.

At the end of the 1980s a glass-ceramic material, known as "Silceram," with composition in the $CaO–MgO–Al_2O_3–SiO_2$ quaternary system was investigated.[1–4] Silcerams were originally designed for application as erosion and abrasion-resistant materials at room temperatures. The main crystalline phase formed during the thermal treatment of these glass-ceramic materials was diopside (or pyroxene), between 900 and 1000 °C, and anorthite appeared as minor phase at higher temperatures.

Since then some papers concerning diopside-based glass-ceramics for tiles have been reported during the last decade.[5–7] A report from the Spanish Ceramic Society stated results on the development of glass-ceramic tiles from compositions in the $CaO–MgO–Al_2O_3–SiO_2$ ternary system, with high abrasion strength and high gloss.[5] Baldi et al.[6] studied the effect of some nucleants on the crystallization of glasses with compositions in the $CaO–MgO–SiO_2$ ternary system. Results indicate that nucleants can change the microstructural morphology of the glass-ceramic glazes obtained. More recently Rincón et al.[7] also reported the possibility of obtaining diopside-based glass-ceramic glazes in the $Li_2O–CaO–MgO–Al_2O_3–SiO_2$ system.

From the above results it seems feasible to develop diopside glass-ceramic glazes for tiles. However, there are some drawbacks mainly concerning the adequated development of the glaze layer. Thus, the glaze surface must be continuous and without faults, and consequently the glaze must reach an optimum viscosity which allows to cover the biscuit. Moreover, this characteristic must be attained at temperatures between 1100 and 1200 °C in thermal treatments lasting 30–40 min. Obviously, all these requirements can only be attained by adding certain additives, such as nucleants and/or fluxes, which permit to obtain final products in the range of conditions used in the industry. This approach has been used successfully for the development of cordierite-based glass-ceramic glazes.[8,9]

The main target of this work is, therefore, to know the action of some additives, fluxes and nucleants, on the

crystallization of diopside (pyroxene) in glasses in the MgO–CaO–Al$_2$O$_3$–SiO$_2$ quaternary system. We will pay close attention to two points, the formation of the maximum amount of well-formed crystals of pyroxene and the suitable maturation (development) of the glass-ceramic glaze. The results obtained will allow testing some chosen glasses as pyroxene glass-ceramic glazes under industrial fast thermal treatments. In addition, Vickers hardness will be evaluated in glazed tiles.

2. Experimental procedure

2.1. Preparation of glass-ceramic glazes

A glass with composition in the diopside primary crystallization field within the CaO–MgO–Al$_2$O$_3$–SiO$_2$ quaternary system was chosen as reference.[10] Some additives, specifically TiO$_2$ and mixtures of Na$_2$O and K$_2$O, were added to the reference glass in amounts of 4 wt.% on 100 g. Also some glasses were prepared substituting 3 wt.% B$_2$O$_3$ by Al$_2$O$_3$ in the reference glass. The compositions prepared and the nomenclature used is displayed in Table 1. The CaO:MgO:Al$_2$O$_3$:SiO$_2$ molar ratios are kept almost constant for all compositions. The raw materials used in the preparation of glasses were SiO$_2$, Al$_2$O$_3$, CaCO$_3$, MgCO$_3$, TiO$_2$, BO$_3$H$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$, all high quality reagents supplied by Merck. Glasses with different compositions were obtained by melting mixtures of the required stoichiometric amounts of reagents at 1600 °C. After crushing, the glasses were remelted. The final glass was poured into water and a frit was obtained. After grinding, pellets of powder were obtained by pressing at low pressure (∼5 MPa) and thermally treated at several temperatures up to 1200 °C and for different heating times. Some industrial tests were made for specimens prepared under actual fabrication conditions, specifically glaze preparation and fast thermal cycle.

2.2. Techniques of characterization

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-monochromated Cu-K$_\alpha$ radiation. X-ray patterns were acquired by measuring 2θ from 5 to 65° with a step size of 0.02° and a step time of 5 s. The degree of the crystallization of the glass ceramic was estimated from the scattering intensity of X-ray radiation by the amorphous glass phase, using pure glass as the reference sample.[11] The percentage of crystalline phase can be expressed by the equation:

$$X(\%) = \frac{I_g - I_x}{I_g - I_p} \times 100$$

where I_g is the measuring scattering intensity of the amorphous phase for the initial glass, I_x is that for the partly crystallized glass and I_p is the background for a 100% crystallized sample. The diffraction angle to measure scattering intensities must be selected so that noncrystalline scattering intensity is sufficently large and so that overlapping with the diffraction lines of the crystalline phase does not occur.

The microstructure of the thermally treated samples was observed on fresh fracture surfaces by field emission scanning electron microscopy 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 a scanning electron microscope operated at 20 kV (Model XL-30, Philips, Eindhoven, The Netherlands). This instrument is equipped with an energy dispersive X-ray spectrometer (Model EDR288, Rontec, Berlin, Germany). Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Before acquiring the X-ray spectra, samples were etched with HF 20% for 10 s and coated with gold/palladium coating. After identifying regions of chemical homogeneity, i.e. pyroxene crystals and glassy phase, spot analyses of these areas were carried out. The results from the analysis were obtained using ZAF routine corrections.

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 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. Phase separation in glasses

The phenomenon of phase separation in the pattern glass A, annealed at 800 °C for 30 min, is shown in Fig. 1a. As it can be seen, the structure of the liquid–liquid phase separation consists of spherical particles dispersed in the glassy matrix. The appearance of phase separation for glass compositions in the CaO–MgO–Al$_2$O$_3$–SiO$_2$ quaternary system

Table 1
Composition and nomenclature of prepared glasses (wt.%)

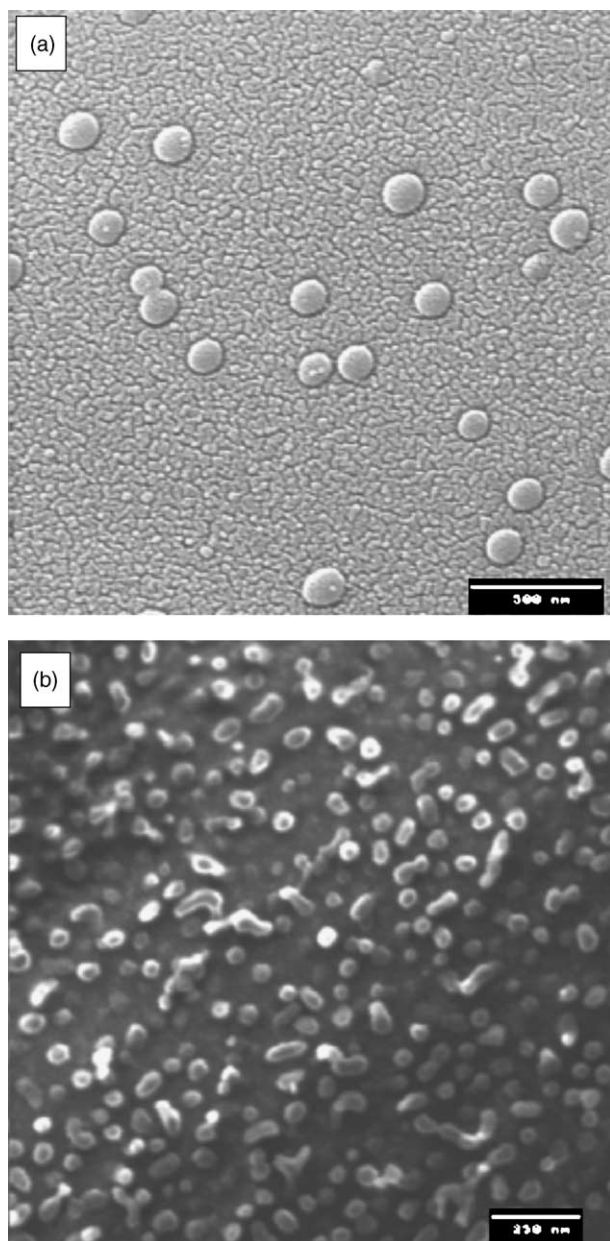| Oxide	Glass				
	A	B	C	D	E
SiO$_2$	60	57.69	55.56	60.0	57.69
Al$_2$O$_3$	14	13.46	12.96	11.00	10.58
MgO	10	9.61	9.26	10.00	9.62
CaO	16	15.38	14.82	16.00	15.39
TiO$_2$	–	3.85	3.70	–	–
B$_2$O$_3$	–	–	–	3.00	2.88
K$_2$O	–	–	2.78	–	2.88
Na$_2$O	–	–	0.93	–	0.96

Fig. 1. FESEM micrograph of glass A (a) and glass E (b) both thermally treated at 800 °C for 30 min (bar = 500 and 250 nm, respectively).

Table 2
Relative amounts of crystalline phases for glasses thermally treated at different temperatures for 2 h

Glass	900 °C	1000 °C	1100 °C
A	Anorthite (s) Pyroxene (w)	Anorthite (s) Pyroxene (w)	Anorthite (s) Pyroxene (w) Cristobalite (m)
B	Anorthite (s) Pyroxene (w)	Anorthite (s) Pyroxene (w)	Anorthite (s) Pyroxene (w) Cristobalite (m)
C	Pyroxene (s) Anorthite (w)	Pyroxene (s) Anorthite (w)	Pyroxene (s)
D	Anorthite (s) Pyroxene (w)	Anorthite (s) Pyroxene (m) Cristobalite (m)	Anorthite (s) Pyroxene (w) Cristobalite (m)
E	Pyroxene (s) Anorthite (w)	Pyroxene (s) Anorthite (w)	Pyroxene (s)

s, m and w denotes strong, medium and weak diffraction peaks, respectively.

3.2. Crystallization of glasses

The relative amounts of crystalline phases for glasses thermally treated at different temperatures for 2 h is shown in Table 2. As it can be seen, anorthite and a phase with the structure of pyroxene are detected after heating 2 h at 900 °C for all compositions, independently on the presence of additives. On increasing the maximum temperature of the thermal treatment to 1000 °C, no great changes are observed with respect to 900 °C. X-ray diffractograms of thermally treated glasses at 1100 °C for 2 h are displayed in Fig. 2. Pyroxene is present as the unique crystalline phase for glasses containing alkaline oxides as additives. On the contrary, anorthite and cristobalite are detected as secondary phases either in the glass A, without additives, or in glasses B and D, which do not contain alkaline oxides.

In order to know the possibility to obtain glass-ceramic products by fast firing, pellets of powdered glasses of compositions A, C and E were thermally treated to 1160 and 1190 °C and hold at these temperatures for 5 min; the heating rate for both schedules was 25 °C/min. So, the thermal processing of glasses took between 45 and 50 min cold-to-cold. Fig. 3 shows X-ray diffraction patterns of glasses submitted to either 1160 or 1190 °C of maximum temperature. As it can be seen, some weak peaks attributable to anorthite are detected in glass A heated at 1160 °C. For glass C, the pyroxene phase is the only detected at 1160 °C, while for the glass E it is detected at both maximum temperatures, 1160 and 1190 °C. Anyway, as it can be inferred from the hump in the 2θ range between 20 and 40° in the X-ray diffractograms (Fig. 3), which can be associated to the amount of glassy phase present in the specimen, the greater amount of crystalline phase, for both glasses C and E, is obtained at 1160 °C. The semiquantitative estimation of the amount of glassy phase from the scattering intensity of X-ray radiation confirms previous evidence. Thus, the
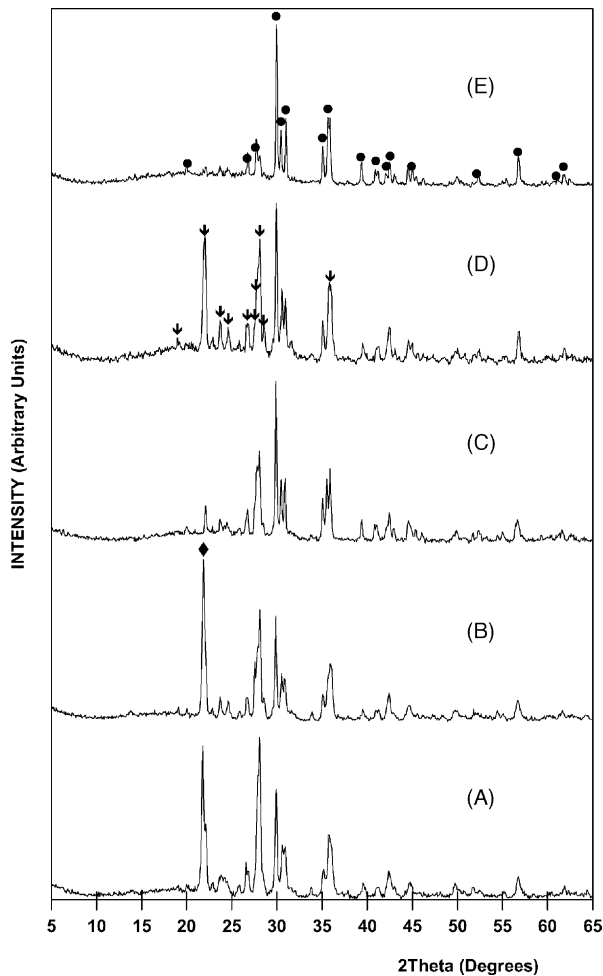
was considered by several authors. Thus, De Veckey and Majumdar[12] stated that the phase separation, which takes place at high temperature, is due to segregation of calcium and magnesium ions. Microscopical examination of glasses with different additives also shown phase separation. FE-SEM micrograph of glass E, also annealed at 800 °C for 30 min, is shown in Fig. 1b. It is to notice, that the immiscibility texture of this glass, containing as additives B_2O_3, Na_2O and K_2O, is different with respect to the one of pattern glass A. It seems to consist of an interconnected liquid network. This latter texture is according with similar volume fractions of two liquids.

Fig. 2. X-ray diffractograms of thermally treated glasses at 1100 °C for 2 h (●: pyroxene, ↓: anorthite, ◆: cristobalite).

Fig. 3. X-ray diffractograms of fast fired glasses A, C and E heated at 1160 and 1190 °C for 5 min (●: pyroxene, ↓: anorthite).

percentage of crystalline phase in glasses C and E, fast fired at 1160 °C, are 50 and 46 wt.%, respectively. The amount of crystalline phase, i.e. pyroxene, in glass E decreases on increasing the fast firing maximum temperature. Thus, at 1190 °C an increase of the scattered intensity in the range 20–40° (2θ), with respect to the one shown for glass heated at 1160 °C, can be clearly seen in the X-ray diffractograms (Fig. 3). This fact can be due to dissolution of pyroxene in the residual glass.

From the above mentioned results, it can be inferred that the crystallization of pyroxene, as the almost only crystalline phase, is accomplished for glasses containing alkaline oxides as additives. The role played by these additives in the further crystallization of glasses might be related with their abilitiy as fluxes.[13] Moreover, the crystallochemistry of the pyroxene structure is very wide and both Na$^+$ and even K$^+$ cations could entry into it.[14]

3.3. Microstructural changes

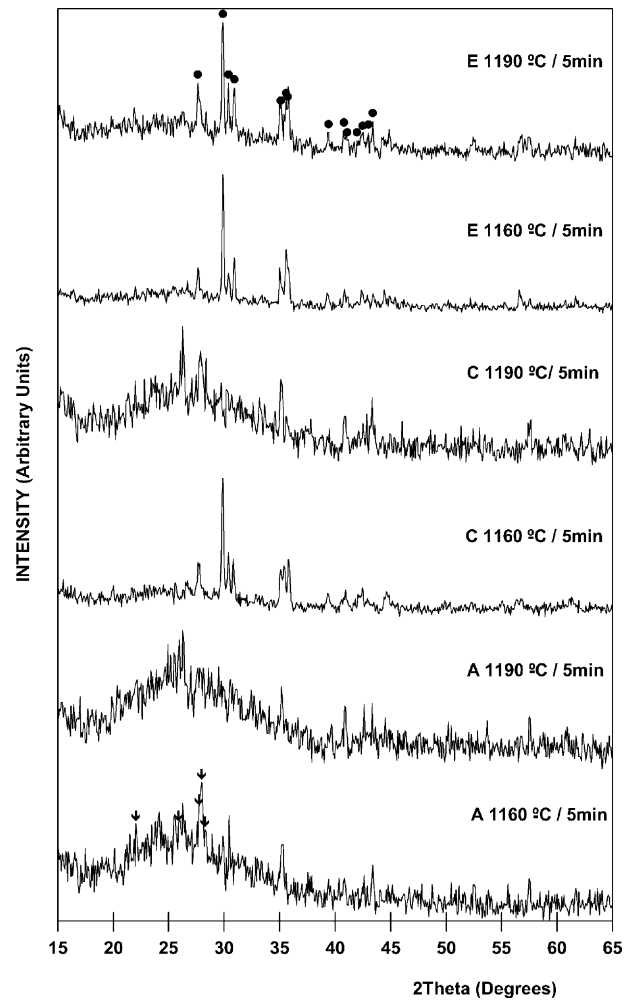FESEM micrographs of glasses A, C and E, heated at 1100 °C for 2 h, are shown in Figs. 4–6, respectively. As it
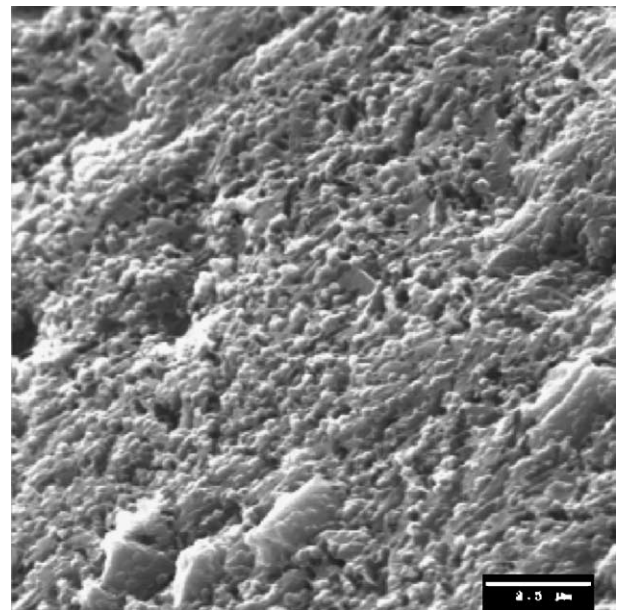

Fig. 4. FESEM micrograph of glass A heated at 1100 °C for 2 h (bar = 2.5 μm).
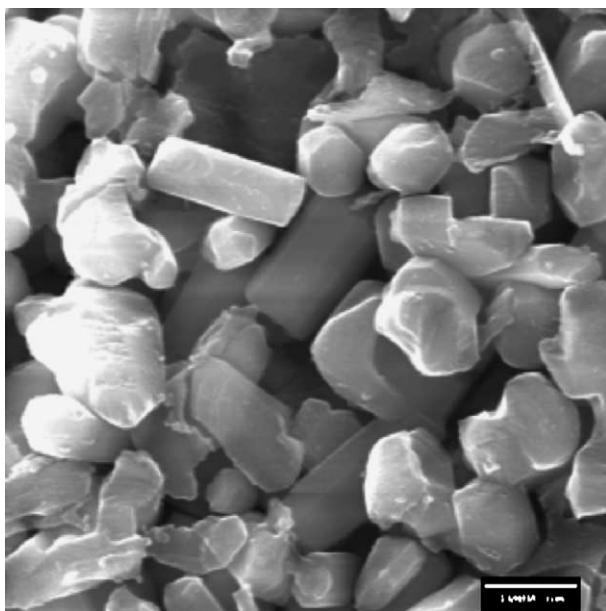
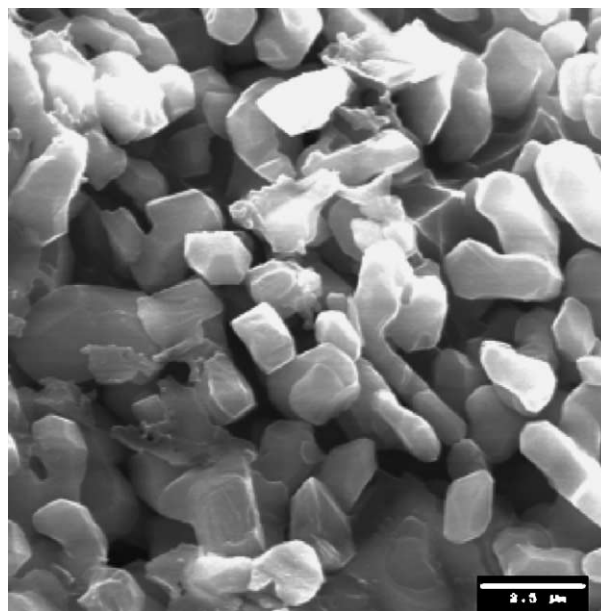Fig. 5. FESEM micrograph of glass C heated at 1100 °C for 2 h (bar = 1 μm).

Fig. 6. FESEM micrograph of glass E heated at 1100 °C for 2 h (bar = 2.5 μm).

can be seen, no defined morphologies are observed in the crystallized parent glass, i.e. without additives. However, for glasses containing alkaline oxides as additives, well-formed prismatic crystals are detected after the thermal treatment at 1100 °C for 2 h. As it was stated above, the presence of Na_2O and/or K_2O facilitates the crystallization of pyroxene as the only crystalline phase. The role of these additives is primarily to act as flux and to decrease the viscosity of glass. However, there is no doubt that, in addition, they can play a structural role in the formation of pyroxene. The pyroxene structure has stoichiometry XYZ_2O_6 where X represents Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, etc. in the distorted 6- to 8-coordinated site, Y represents Mg^{2+}, Al^{3+}, Cr^{3+}, Ti^{4+}, etc. in the octahedral site and Z represents Si^{4+} and Al^{3+} in the tetrahedral site.[11] The composition of pyroxenes, including cations in the bulk composition of the melt, therefore, can be expressed as (Ca, Na, K, Mg) (Mg, Al, Ti) $(Si, Al)_2$ O_6. EDX analyses of crystals and residual glass around them are shown in Table 3. For glass A, the

composition of pyroxene seems to have the stoichiometry (Ca, Mg) (Mg, Al) $(Si, Al)_2$ O_6. In this crystalline phase, the whole mechanism of solid solution formation may be written out as $(Si^{4+} + Mg^{2+}) \rightarrow (2Al^{3+})$ and $Ca^{2+} \rightarrow Mg^{2+}$. This means that taking into account the diopside stoichiometry, $\{Ca\}^{VIII} [Mg^{2+}]^{VI} (Si^{4+})_2^{IV} O_6$, the substitution of $(Si^{4+})^{IV}$ and $[Mg^{2+}]^{VI}$ by $(Al^{3+})^{IV}$ and $[Al^{3+}]^{VI}$ takes place simultaneously and also some Mg^{2+} replaces to Ca^{2+} in higher coordinated sites. IV, VI and VIII denote four-, six- and eight-coordinated sites, respectively. As it can be inferred from Table 3, the pyroxene crystals developed from glasses containing Na_2O, K_2O and TiO_2 or B_2O_3, also contain some amount of these components. It is significant the high amount of TiO_2 in the pyroxene crystals developed from glass C. Also it is to be noticed the amount of K_2O and Na_2O in pyroxenes from glasses C and E. From the above results, it can be inferred that the role of this additives in the formation of pyroxene glass-ceramic glazes is not only to lower the viscosity and

Table 3
Composition (wt.%) of pyroxene crystals and residual glass in glasses heated at 1100 °C for 2 h

Oxide[a]	Crystals			Glass phase		
	A	C	E	A	C	E
SiO_2	59.7 ± 0.1	54.8 ± 1.2	58.4 ± 1.0	60.4 ± 0.4	57.6 ± 1.1	60.5 ± 1.7
Al_2O_3	10.1 ± 0.7	11.3 ± 1.4	6.6 ± 0.9	10.1 ± 0.2	12.9 ± 1.5	15.4 ± 3.2
MgO	13.5 ± 1.5	12.8 ± 1.2	15.0 ± 0.8	12.5 ± 0.1	7.6 ± 0.8	6.0 ± 1.5
CaO	16.7 ± 0.9	15.0 ± 1.4	18.2 ± 1.2	17.0 ± 0.2	12.3 ± 1.4	14.8 ± 3.7
TiO_2	–	3.7 ± 0.4	–	–	5.2 ± 0.8	–
K_2O	–	1.9 ± 0.8	1.1 ± 0.2	–	3.8 ± 0.8	3.2 ± 0.6
Na_2O	–	0.8 ± 0.1	0.7 ± 0.1	–	0.8 ± 0.2	1.1 ± 0.5

[a] The amount of B_2O_3 was not determined.

facilitate the sintering but it is also a structural role, taking part in the formation of solid solutions with the pyroxene structure.

The residual glass of specimen A, heated at 1100 °C for 2 h, has a composition very similar to the pyroxene crystals (Table 3). In the case of compositions of the glassy phase for specimen E, the amount of B_2O_3 was not determined. It is assumed that all boron is in the residual glass. The specific crystallochemical features of the pyroxene structure are not favourable for the entry of a cation, as small as B^{3+}, in solid solution. For these glasses, it seems that the composition of the residual glass is somehow different in respect of the bulk composition. Consequently the developed microstructures, as it can be seen in Figs. 5 and 6, consist of subeuhedral grains, tending in part towards euhedral morphology, with relatively large, flat crystal–glass interfaces.

3.4. Hardness measurements on fast fired ceramic tiles

A porcelain stoneware support, glazed with the glass E, was fast fired under industrial conditions at 1190 °C for 5 min. The X-ray diffractogram on the surface of the glazed tile, i.e. on the developed glass-ceramic coating, displays traces similar to the ones shown in Fig. 3 for the glass E heated at 1190 °C for 5 min. SEM observations on etched cross sections of glazed supports (with glasses C and E) revealed no microstructural changes with respect to the ones obtained from loosely pressed powder pellets (Fig. 7). Vickers microhardness measurements performed also on the E glass-ceramic glazed tile yielded the value of $620 \pm 20 \, \mathrm{kg \, mm^2}$. That value is higher than the one
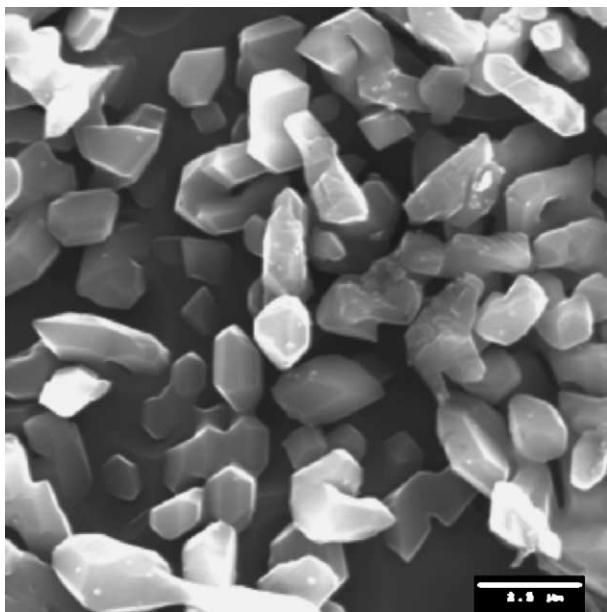
obtained for conventional glazes, which are usually lower than $560 \, \mathrm{kg \, mm^2}$. However, it is to be noted that for the glass E fast fired at 1190 °C, to get a well-developed support, the amount of pyroxene crystallization is lower than at 1160 °C. So, it is possible that, with increasing the crystallization amount, i.e. at lower maximum temperature, the Vickers microhardness also increases. The lowering of the maximum temperature will depend on the type of support used.

4. Conclusions

XRD results showed that crystallization of pyroxene, as the only crystalline phase, for a glass with composition in the diopside primary crystallization field in the $MgO–CaO–Al_2O_3–SiO_2$ quaternary system, only occurred by adding some additives to the base glass. Specifically, the addition of some amount of alkaline oxides (a mixture of K_2O and Na_2O) was required. It was also proved that these additives allowed obtaining well-defined morphologies of pyroxene crystals.

Fast fired glass-ceramic glazes were developed with the glasses containing alkaline oxides and the results confirmed the suitability of these frits to be used under industrial processing. Vickers microhardness of these glass-ceramic glazes measured on porcelain stoneware tiles exhibits higher values than conventional glazes used now in the industry. This finding is related to the microstructural features of the developed glass-ceramic glaze.

Fig. 7. FESEM micrograph of glass E fast heated at 1190 °C for 5 min (bar = 2.5 μm).

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