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Effect of some additives on the development of spinel-based glass-ceramic glazes for floor-tiles

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Abstract

The feasibility of developing spinel-based glass-ceramic glazes from a glass with composition in the system ZnO–MgO–B_2O_3–Al_2O_3–SiO_2 was examined. To do it additional fluxes and/or nucleants were added to a parent glass before melting. Pressed pellets of powdered glasses were submitted to standard thermal treatments up to 1200 °C. The crystallization path and the microstructural development at several temperatures were followed by several experimental techniques. The results showed that additions of TiO_2 as nucleant or additional B_2O_3 as flux to the chosen glass favored the crystallization of cordierite or mullite as main crystalline phase. Glasses which also contained minor amounts of Na_2O and K_2O, as additional fluxes, crystallized rapidly to spinel $(Mg,Zn)Al_2O_4$ using a single relatively fast heating ramp without a previous nucleating heat treatment step. Microstructural examination revealed that a uniform, fine-scale phase separation preceded crystallization. Very small, well-shaped crystals of spinel with octahedral morphology were formed. Slips of these glasses on conventional tile supports thermally treated under single heating ramps developed similar microstructures that the ones raised from pellets. This feature allows to suggesting these spinel-based glass-ceramic glazes as good candidates to improve the mechanical properties of conventional glazes.

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1. Introduction

Glass-ceramics are composed materials of one or more crystalline phases immersed in a residual glassy phase. Their in general outstanding properties have given rise to a wide variety of applications [1]. Glass-ceramic processing has been carried about starting both from bulk glasses and from powder [2].

As it is well known ceramic tiles are materials consisting of two layers, the inner one based on a sintered mixture of powders and the surface layer, i.e. outer one that we see, that in general consists of a mixture of several vitrified oxides and inorganic additives, termed glaze. The final properties of these materials are very dependent on the glaze properties. Nowadays, there is an increasing demand of new ceramic tiles which have improved technical properties compared with those of their parent glasses, encompassing high resistance to wear by abrasion, high surface hardness, low level of closed porosity and good chemical resistance. This means, therefore, to improve the properties of glazes. A possible and interesting way to manufacture wall- and floor-tile materials with better mechanical, chemical and optical can be accomplished by replacing the glaze layer by a glass-ceramic one.

A number of papers have been published during last years dealing with the feasibility of preparing glass-ceramic glazes based on cordierite, pyroxene and β-spodumene solid solution [3–6]. More recently

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mullite-based glass-ceramics have been reported [7,8]. Considering the intrinsic physical properties of the spinel crystalline phase, it would be interesting to develop spinel-based glass-ceramic glazes [9].

Glass-ceramics based on spinel compositions ranging from gahnite ($ZnAl_2O_4$) toward spinel ($MgAl_2O_4$) were obtained by controlled crystallization of glasses in the ZnO–MgO–Al_2O_3–SiO_2 quaternary system, and adding ZrO_2 and/or TiO_2 as nucleating agents [10]. However, even though the crystallization of spinel is possible for the above reported compositions, the glass-ceramic glaze application would require controlling simultaneously the spinel crystallization and the glaze maturing in the temperature range between 1100 and 1200 °C. In order to reach full development of the glass-ceramic glaze layer, it is necessary to add certain fluxes which allow the glass to mature properly, i.e. the glaze should have a suitable surface tension to minimize crawling of the coating away from the edges or any hole that are present on firing. Likewise, to control the amount of crystallization and the size and shape of crystals nucleating and/or fluxes agents should be also added.

The approach followed to check the feasibility of these spinel-based glass-ceramic glazes is to choose a reference composition in the ZnO–MgO–B_2O_3–Al_2O_3–SiO_2 system and to introduce fluxes and nucleating which allowing to develop this type of composed glazes at temperatures up to 1200 °C by single heating ramps without a previous nucleating heat treatment step.

In this paper we report results on the effect that some additives (such as B_2O_3, Na_2O, K_2O and TiO_2) added to a chosen parent glass, have on the crystallization path to the final spinel crystalline phase and also the microstructural features of that final spinel-based glass-ceramic glaze.

2. Experimental procedure

2.1. Preparation of glasses

Based on previous experiments, for this study it was chosen a reference glass of composition, in wt%, $53SiO_2$, $29Al_2O_3$, 9MgO, $6B_2O_3$ and 3ZnO. The reference glass is referred as sample A. Glasses from B to E contain additional nucleant and/or fluxes. The nucleant used is TiO_2 and the fluxes are additional B_2O_3 and/or a mixture of Na_2O and K_2O in a wt ratio of 1–3. The used nomenclature for all glasses is shown in Table 1. Glasses of the five compositions were obtained by melting mixtures of the required amounts of SiO_2, Al_2O_3, $MgCO_3$, ZnO, TiO_2, BO_3H_3, Na_2CO_3 and K_2CO_3, all high quality reagents provided from Merck, at 1600 °C for 2 h. Melted glasses were poured into cold water and, after regrinding they were remelted again. After the second melting a portion of the melt was poured into water and milled up to obtain a powder glass with particle size smaller than 30 μm.

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

Oxide	Glass				
	A	B	C	D	E
SiO_2	53.0	51.0	49.1	53.0	51.0
Al_2O_3	29.0	27.9	26.9	26.0	25.0
MgO	9.0	8.7	8.3	9.0	8.7
ZnO	3.0	2.9	2.8	3.0	2.9
TiO_2	–	3.8	3.7	–	–
B_2O_3	6.0	5.8	5.6	9.0	8.7
K_2O	–	–	2.8	–	2.9
Na_2O	–	–	0.9	–	1.0

The feasibility for developing spinel-based glass-ceramic glazes with the above glasses was investigated by heating cylindrical pellets of loosely pressed powder, i.e. under a pressure of about 5 MPa. These glass powder pellets were thermal treated by a single heating step at several temperatures up to 1200 °C for 2 h. The heating rate used was 10 °C min^{-1}. These conditions were chosen to simulate those in an industrial application of the glaze layer, as for the fabrication of ceramic tiles. Moreover, in order to check the correct maturing of compositions as glazes they were prepared as slips and used to glaze some conventional tile support.

2.2. Techniques of characterization

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

Differential thermal analysis was carried out in N_2 atmosphere with platinum sample pans, using a heating rate of 10 °C min^{-1}.

Hot-stage microscopy was carried out in the range 40–1300 °C, with a heating rate of 20 °C min^{-1}.

X-ray diffraction analysis was performed using a graphite monochromatic CuK_α 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 quantitative determination of crystalline and amorphous phase in final glass-ceramic glazes was performed from X-ray diffraction data by using Rietveld refinement. It was performed with Fullprof98 [11], available in the software package Winplotr [12]. The X-ray data were collected from 8° to 100° (2θ) with a step size of 0.02 and a step time of 10 s. The internal standard used was CaF_2. The refinement involved the following parameters: a scale factor, zero displacement correction, unit cell parameters, peak profile parameters using a pseudo-Voight function and overall temperature factor. The structural parameters and atomic positions for mullite [13], spinel [14], rutile [15] and fluorite [16] were taken from the literature.

The microstructure of the thermally treated samples was observed on fresh fracture surfaces by field emission scanning electron microscopy at 30 kV. 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 10 kV. This instrument is equipped with an energy-dispersive X-ray spectrometer. 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.

3. Results

3.1. Sintering and crystallization of glasses

The sintering curves of glasses are shown in Fig. 1. It can be seen that the sintering process begins for all glasses at 840 °C. The end of sintering depends on the glass composition. Thus, glasses A and E finish at higher temperatures, around 1060 and 1020 °C, respectively. Glasses B and D complete the sintering at around 950 °C and glass C finish sintering at the lower temperature, around 900 °C. The DTA curves of powdered glass without additives (glass A) and with several ones, as nucleant and/or fluxes, heated up to 1100 °C are shown in Fig. 2. As it can be seen in the above Fig. 2 no sharp exothermic effects may be seen in the DTA curves. This can be understood taking into account that the amount of crystalline phases formed during DTA runs is relatively small. In order to know the crystallization path depending on the type of additives at the parent glass, DTA runs at different temperatures were performed and the final samples were examined by X-ray diffraction. The DTA heating temperatures and the specific phases associated with the corresponding thermal effects through the whole crystallization process are displayed in Table 2. Results of DTA heatings indicate that crystallization starts to occur above 1000 °C.

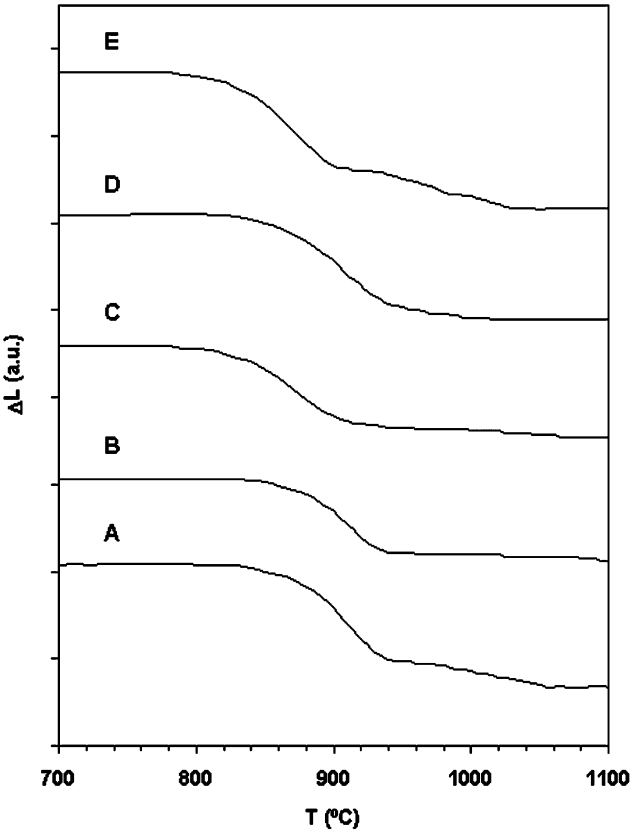

Fig. 1. Sinterization curves of glasses.

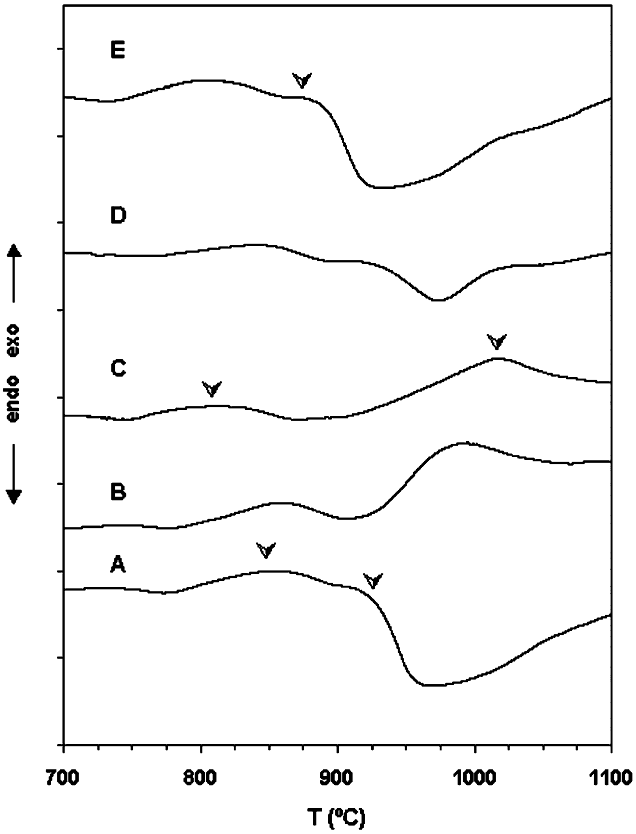

Fig. 2. DTA curves of glasses.

3.2. Microstructural evolution from glasses to glass-ceramics glazes

The main microstructural changes experienced by the glass pellets heat-treated up to 1200 °C were studied by XRD and SEM characterization. The XRD patterns of pellet samples single heated (for 2 h) at 1100 and 1200 °C are shown in Figs. 3 and 4, respectively. From the crystallization results, two crystallization paths can be distinguished for the studied glasses. Glasses containing alkaline oxides, C and E, finally form spinel as

Table 2
DTA runs at different temperatures and crystalline phases associated at each sample

Glass	Temperature (°C)					
	810	850	880	930	1020	1100
A	–	G	–	G	G, (sp + mull)	G, (sp↑ + mull)
B	–	G	–	G	G, (sp + mull)	G, (sp↑ + mull)
C	G	–	G	–	G, (sp + mull)	G, (sp↑ + mull)
D	–	G	–	G	G, (sp + mull↑)	G, (sp↑ + mull)
E	G	–	G	–	G, (sp + mull↑)	G, (sp↑ + mull)

G = glasss, sp = spinel, mull = mullite.
The row indicate the relative amount of crystalline phases.

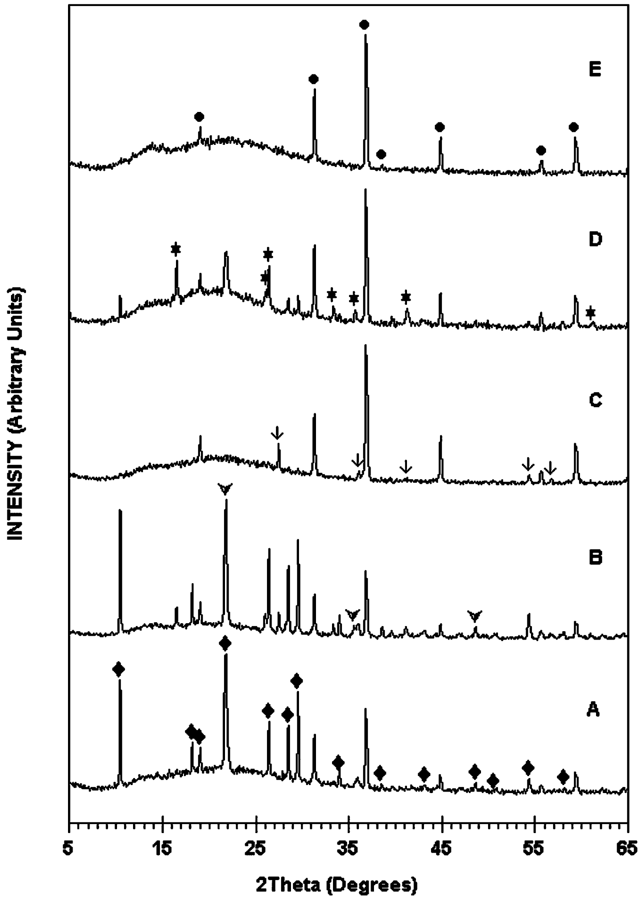

Fig. 3. Powder X-ray diffraction of glasses heated at 1100 °C for 2 h (♦ is cordierite, ⮟ is cristobalite, ↓ is rutile, * is mullite, ● is spinel).

almost single crystalline phase, whereas in the rest of glasses, cordierite (A and B) and mullite (D) appears as the main crystalline phases. In order to evaluate the microstructural differences between both set of glasses at different crystallization stages, the microstructure of two representative glasses (A and E) heated at different temperatures (both before and after crystallization) was studied. In this respect, the microstructure of glasses A and E heated at temperatures both before beginning and at the final crystallization will be studied. In

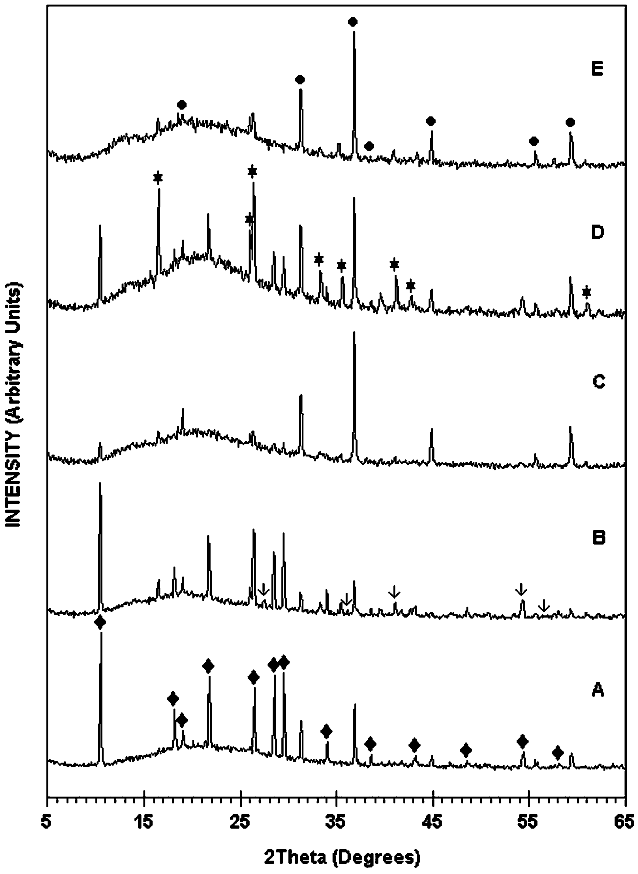

Fig. 4. Powder X-ray diffraction of glasses heated at 1200 °C for 2 h (♦ is cordierite, ↓ is rutile, * is mullite, ● is spinel).

Fig. 6 corresponding to a representative detail of glass A heated at 800 °C for 2 h, areas of different contrast were not observed, thus discarding the occurrence of phase separation. The starting of crystallization of glass A on heating at 900 °C for 2 h occurs at the original surface of glass particles (Fig. 7(a)). Furthermore, a few small circular areas with different contrast may be appreciated in the glassy phase (Fig. 7(b)). The final microstructure of glass A heated at 1100 °C for 2 h, is displayed in Fig. 8. The phase separation in glass E heated at 800 °C is displayed in Fig. 9. Small circular areas of different contrast may be seen in the glass matrix. The crystallization also begins on heating at 900 °C for 2 h and it is also started on the original surface of glass particles. The final microstructure at 1100 °C developed in this glass, containing as crystalline phases spinel as well as a very small amount of mullite is shown in Fig. 10. The distinct distribution and features of both crystalline phases and glassy phase may also be appreciated in Fig. 10. The SEM micrograph shows a homogeneous arrangement of spinel crystals and, at the centre of the original glass particles, almost circular areas containing well shaped, acicular mullite crystals. Finally, the distinct morphologies of spinel and mullite

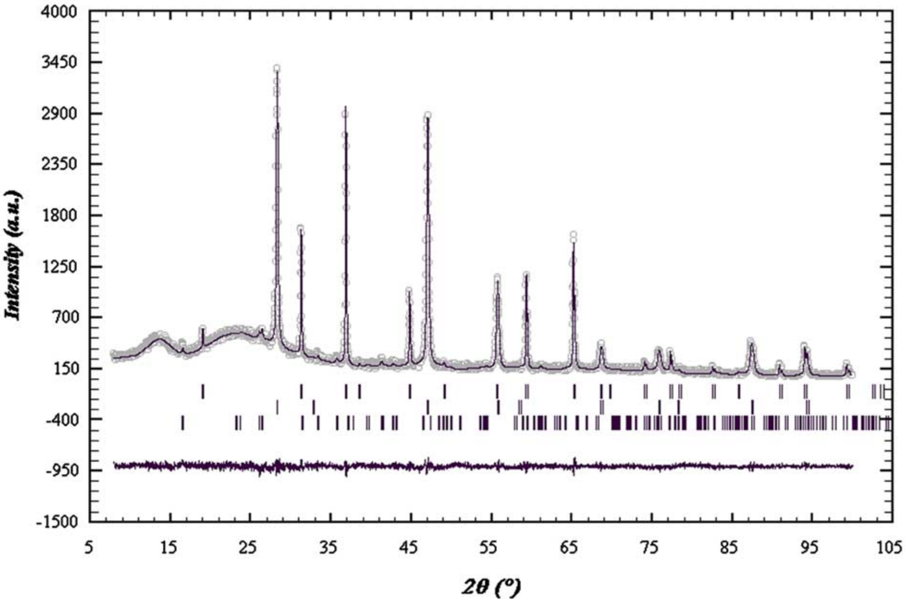

Fig. 5. Rietveld plot of glass E heated at 1100 °C for 2 h. The calculated pattern is compared with observed data. The small vertical bars indicate the position of allowed *hkl* reflections. The difference between the observed and calculated profiles is the lower trace plotted below the diffraction pattern.

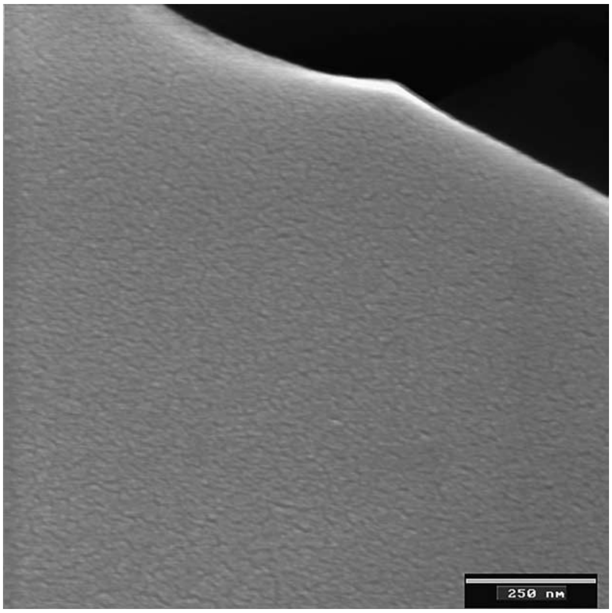

Fig. 6. Micrograph of glass A heated at 800 °C for 2 h (bar = 250 nm).

crystals formed in this heated glass are shown, at high magnification, in Fig. 11(a) and (b), respectively.

3.3. Quantitative determination of the crystalline phases amount

In those glasses with a higher crystallization of spinel (C and E), the relative amounts of crystalline and glassy phases were obtained by Rietveld refinement, after heat treatment at 1100 °C for 2 h. The results for the quantitative analysis are shown in Table 3. Likewise, the difference between the observed and calculated pattern for the glass E, which can be related with the Rietveld refinement quality, is displayed in the lower trace of Fig. 5. It can be seen a very good agreement in the range of diffraction angles between 8° and 100° (2θ). The R_p and R_{wp} values from the Rietveld refinement converged between 5.25 and 7.99 for all the glass-ceramic specimens.

4. Discussion

4.1. Crystallization of glasses

From DTA and sintering experiments, it is evident that in the heated glasses an almost complete sinterization occurs before starting crystallization. The glass without additives is the only one in which crystallization starts before the sintering completes. In Fig. 1 two similar set of DTA traces can be distinguished depending on whether the glasses contains or not titanium oxide or additional boron oxide. In both cases, the effect of the additional presence of Na_2O and K_2O is to shift the thermal effects to lower temperatures. The crystallization path in these glasses, as shown in Table 2, starts at temperatures around 1000 °C. The crystalline phases detected during the whole process of crystallization were spinel and mullite. In general, in DTA heated glasses the amount of glassy phase is quite large. In Table 2, the relative amount of crystalline phases is indicated by arrows (thus ↑ indicates a higher amount of one crystalline phase with respect to the other). In order to evaluate the extent of the spinel phase crystallization (to see if

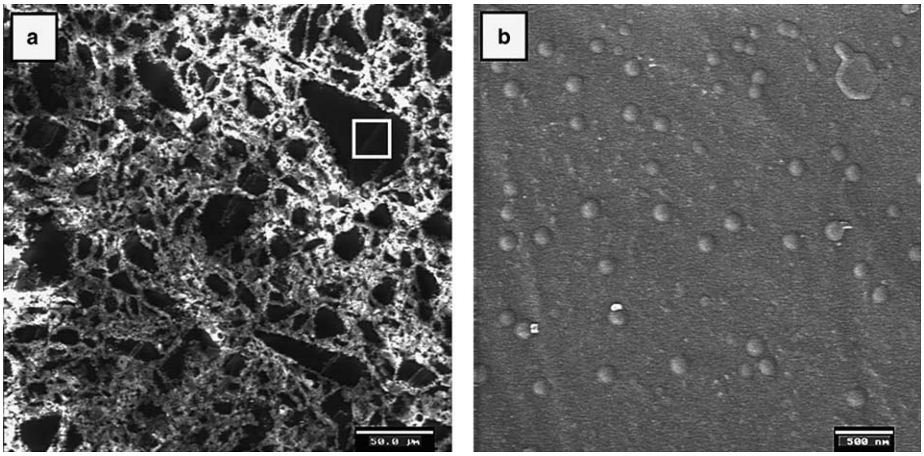

Fig. 7. (a) Micrograph of glass A heated at 900 °C for 2 h (bar = 50 μm); (b) a higher view of phase separation developed in the remaining glassy phase.

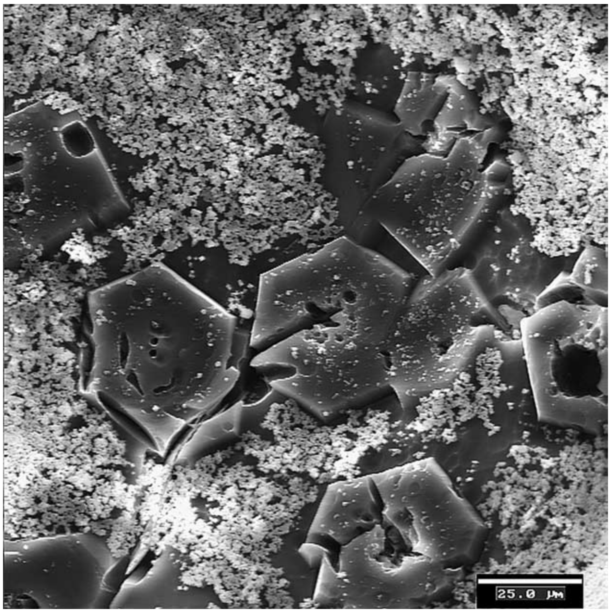

Fig. 8. Micrograph of glass A heated at 1100 °C for 2 h (bar = 25 μm).

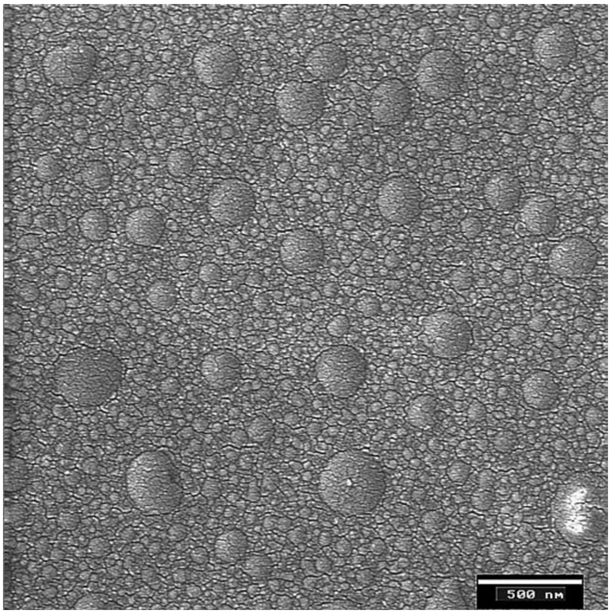

Fig. 9. Micrograph of glass E heated at 800 °C for 2 h (bar = 500 nm).

it was the main crystalline phase or not) at the final firing temperatures and with short holding times, the different glass pellet samples were heated at 1100 and 1200 °C and 2 h holding time. The corresponding XRD patterns are displayed in Figs. 3 and 4. From the XRD results can be inferred that for glasses without additives and containing TiO_2 as nucleant or B_2O_3 as additional flux, the major crystalline phase formed is cordierite but some minor amounts of mullite, cristobalite and spinel are also present. Rutile is also detected in the TiO_2-containing heated glasses. In contrast, in glasses containing alkaline oxides as fluxes (in our case a combination of Na_2O and K_2O) the main and almost single crystalline phase is spinel. Moreover, it is to be noted that at 1200 °C the amount of glassy phase increases with respect to the glasses heated at 1100 °C. This fact can be inferred from the stronger humps appearing between 15° and 30° (2θ) at 1200 °C.

From the above DTA and XRD results on powdered and/or pellet specimens thermal treated at several temperatures can be draw that glasses C and E (the reference quaternary glass A containing as key additives Na_2O and K_2O) are good candidates to develop spinel-based glass-ceramic glaze by using single heating ramps.

4.2. Crystalline phase amounts

From Fig. 5 it can be inferred that a very good agreement in the range of diffraction angles between

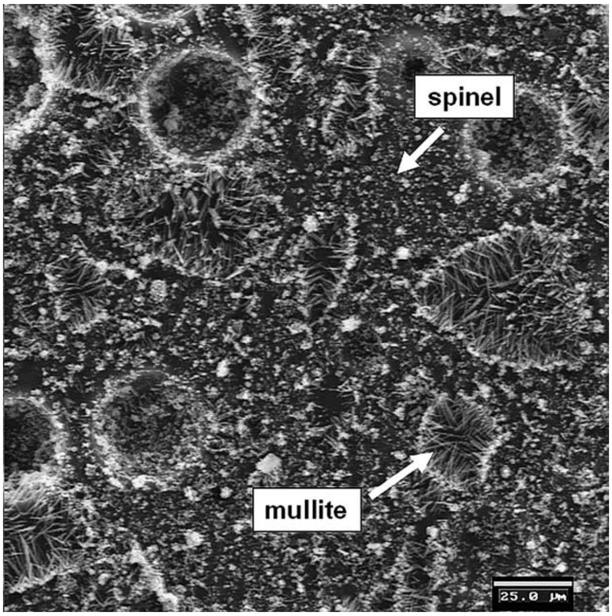

Fig. 10. Micrograph of glass E heated at 1100 °C for 2 h (bar = 25 µm).

8° and 100° (2θ) was reached. The R_p and R_{wp} values from the Rietveld refinement converged between 5.25 and 7.99 for the two glass-ceramic specimens. These reliability parameters for the two refinements are good enough. It is to remark in this sense, that in the quantification of crystalline phases in multicomponent materials, as the glass-ceramics, by the Rietveld method used here, a high precision with smaller errors than 3.0 (wt%) has been already attained [17]. Also remarkably, it is to be noted that the extent of spinel crystallization in the final glass-ceramic glazes, around 20 wt%, is significant enough to have a key role in the final mechanical properties of the glass-ceramic glaze and consequently in the ceramic tile products.

Table 3
Results for the quantitative analysis (wt%) and details of the Rietveld refinement for glass-ceramic glazes C and E heated at 1100 °C for 2 h

	C	E
Spinel	26.9	17.0
Mullite	5.3	4.3
Rutile	1.3	–
Glassy phase	66.5	78.7
R_p (%)	5.91	5.25
R_{wp} (%)	7.99	6.99
R_{wp} (expected) (%)	6.19	6.07
χ^2	1.67	1.33

4.3. Microstructural changes up to the glass-ceramic formation

In order to understand the difference in the crystallization path of glasses A, without sodium and potassium oxides, and E (with a slight increase of boron oxide as well as alkaline oxides) we have compared the microstructure displayed in both glasses at three stages of the heating process, i.e. before crystallization occurs (800 °C), at the beginning (900 °C) and at the end (1100 °C) of the glass-ceramic formation. The comparison of Figs. 6 and 9, corresponding to glasses before crystallization, indicates that a extended phase separation occurs in glass E at 800 °C, while in glass A is not detected yet. However, as mentioned above a very few droplets immersed in the glassy matrix, i.e. areas with different contrast, are seen at 900 °C after the crystallization starts (Fig. 7(b)). Glass-ceramics based on spinel from glasses with compositions lying in the ZnO–MgO–Al_2O_3–SiO_2 system, with ZrO_2 and/or TiO_2 as nucleating agents, have been already reported in the literature [18]. The results indicated that the role played by ZrO_2 and TiO_2 is quite different. Thus in ZrO_2-containing glasses, precipitated crystals of tetragonal ZrO_2 acted as nucleating sites for heterogeneous crystallization of spinel crystals whereas in TiO_2-containing glasses

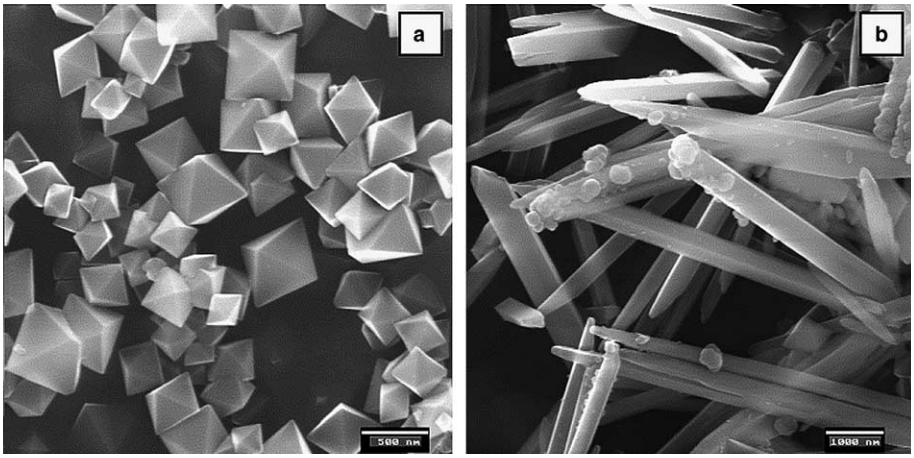

Fig. 11. Morphology of crystals formed in glass E heated at 1100 °C for 2 h: (a) spinel (bar = 500 nm), (b) mullite (bar = 1000 nm).

the nucleation of spinel was preceded by a highly uniform, ultra-fine-scale phase separation into SiO_2-rich and TiO_2/Al_2O_3-rich areas. Considering the results with heated glasses A and E, it can be inferred that the addition of an additional small amount of boron oxide and alkaline oxides favor the extent of phase separation. In this respect, a very large phase separation can be seen in glass E. In Fig. 9 the small globular areas should be ZnO- and Al_2O_3-rich. Therefore, the nucleation and growth of spinel should occur in these globular shaped areas.

The crystallization starts in both glasses on heating at around 900 °C. As it was evidenced in many glass-ceramic glazes processed from glass powder, the nucleation begins at the surface of the glass particles during sintering [4,5]. The final microstructure of both glass-ceramic glazes is displayed in Figs. 8, 10 and 11. It should be noted the formation in glass A of large hexagonal prisms of cordierite as well as small spinel crystals. This lower crystallization of spinel can be understood because the nucleation of spinel in the glass is not so effective because the phase separation is not so largely extended in this glass. However, for glass E the presence of the additional amount of B_2O_3 and alkaline oxides allows to reach a more extended phase separation and the spinel nucleates and growth throughout the whole heated glass. It should be noted that a small amount of mullite appears in areas located at the centre of the glass particles where, some small glass pockets remain without crystallizing.

The qualitative composition of spinel and mullite crystals as well as the residual glassy phase for glass E heated at 1100 °C for 2 h is shown in Fig. 12. From the EDX microanalysis is confirmed that the small and well-shaped octahedral spinel crystals contain Al, Mg and Zn as main components. Probably these crystals are solid solutions in the $ZnAl_2O_4$–$MgAl_2O_4$ binary system. The mullite crystals as expected contain basically Al and Si. It has been reported that for SiO_2-rich glasses the stoichiometry of mullite crystals is close to $3Al_2O_3 \cdot 2SiO_2$ [19]. This stoichiometry is also consistent with the acicular morphology of mullite crystals [20].

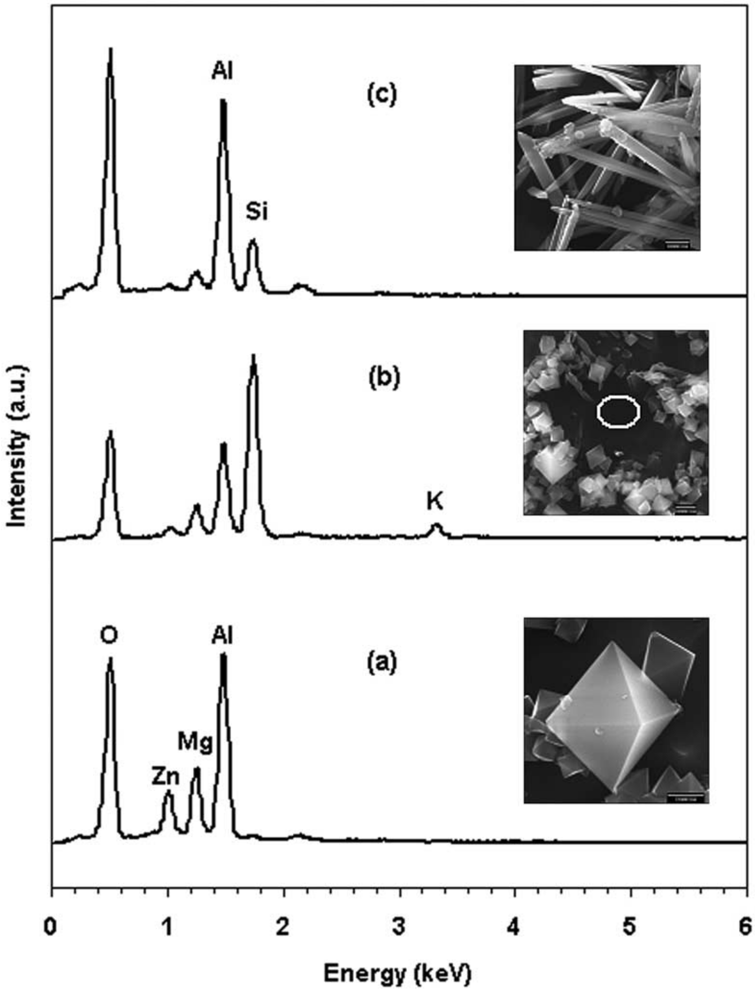

Fig. 12. Qualitative chemical composition of different phases in the glass E heated at 1100 °C for 2 h: spinel (a); glassy phase (b); and mullite (c).

Finally the composition of the residual glass reflects the one of the parent glass.

5. Conclusion

Crystallization behaviors of a parent glass with composition in the system $ZnO–MgO–B_2O_3–Al_2O_3–SiO_2$ and containing small amounts of different additives, as additional fluxes and/or nucleants, were examined. Pressed pellets of powdered glasses were submitted to thermal treatments up to 1200 °C with a holding time of 2 h. The crystallization sequence and the microstructural changes at several temperatures were followed by several experimental techniques.

Glasses with additions to the parent glass of TiO_2 as nucleant or additional B_2O_3 as flux crystallized cordierite or mullite as main crystalline phase. Glasses with an additional small content of Na_2O and K_2O as fluxes crystallized spinel as almost the only crystalline phase using a single relatively fast heating ramp. The amount of spinel phase (with $(Mg,Zn)Al_2O_4$ stoichiometry) in these glasses determined by Rietveld refinement reached 25 wt%. Microstructural examination revealed that prior to crystallization a uniform, fine-scale phase separation occurred. Very small crystals of spinel with well-shaped octahedral morphology formed. Finally, it should be remarked that these glass-ceramic glazes developed by the application of slips on conventional tile supports thermally treated under single heating ramp developed similar microstructures that glass pellets. This feature would suggest that these spinel-based glass-ceramic glazes are good candidates to improve the mechanical properties of conventional glazes.

Acknowledgement

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