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Mechanism of crystallization of fast fired mullite-based glass–ceramic glazes for floor-tiles

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Abstract

The mechanism of crystallization from a B_2O_3-containing glass, with composition based in the CaO–MgO–Al_2O_3–SiO_2 system, to a glass–ceramic glaze was studied by different techniques. Glass powder pellets were fast heated, simulating current industrial tile processing methods, at several temperatures from 700 to 1200 °C with a 5 min hold. Microstructural study by field emission scanning electron microscopy revealed that a phase separation phenomenon occurred in the glass, which promoted the onset of mullite crystallization at 900 °C. The amount of mullite in the glass heated between 1100 and 1200 °C was around 20 wt%, as determined by Rietveld refinement. The microstructure of the glass–ceramic glaze heated at 1160 °C consisted of interlocked, well-shaped, acicular mullite crystals longer than 4 μm, immersed in a residual glassy phase.

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1. Introduction

Glass–ceramic glazes are interesting materials that improve mechanical and optical properties of floor- and wall-tile ceramics [1–4]. The simultaneous development of both the glass–ceramic layer component and the support is a challenge, because the processing temperature and time range are quite restricted [5].

In order to reach a dense, continuous and defect-free glaze, the precursor glass, produced as a layer of powdered glass on the unfired support, must sinter before the start of crystallization [6]. The glass–ceramic process from glass powder particles has some advantages over the one from bulk glass [7]. In this sense, the application of the glassy layer on the unfired support and the transformation of the glassy layer from glass to glass–ceramic are favorable process conditions.

The microstructural changes experienced through the glass to glass–ceramic transformation determine the final physical properties. The mechanism of crystallization must be fully controlled to reach the glass–ceramic final properties. So, it is necessary to design appropriate thermal processing conditions to reach the desired microstructure.

The intrinsic mechanical, thermal and optical properties of mullite suggest that mullite-based glass–ceramic materials used as glazes can improve the physical properties of conventional glazes [8]. As far as we know, there is little information on mullite-based glass–ceramic materials [9–13]. Beall et al. have reported the preparation and properties of transparent, mullite-based glass–ceramics with interesting optical properties. These materials have been produced from glasses in the Al_2O_3–SiO_2 binary system. To improve the melting characteristics of these refractory glasses as well as suppress their spontaneous phase separation some additives, such as B_2O_3, MgO, ZnO and M_2O

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(M = Na or K) are used [9,10]. Of these materials, chromium-doped mullite glass–ceramic has been extensively studied for its outstanding optical properties, that include broad visible absorption, wide emission in the infrared, and high quantum efficiencies [11]. More recently, composite mullite-apatite glass–ceramics have been developed for dental applications [12,13].

In the case of regarding mullite-based glass–ceramic glazes, however, there is a lack of information in the literature regarding their feasibility. Recently we have studied some compositions in the quaternary system containing increasing amounts of B_2O_3 [14]. Results shown that it was possible to crystallize mullite as a single crystalline phase in a glass powder with a composition located in the mullite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system by replacing a certain amount of Al_2O_3 by B_2O_3. It was also determined that the boron oxide amount should be larger than 6 wt%. In order to increase our basic knowledge regarding this material, it would be interesting to obtain further information on the specific mechanism of crystallization of these mullite glass–ceramic materials.

The purpose of this paper, therefore, is to study the mechanism of crystallization of mullite from a parent glass in the quaternary system containing some amount of B_2O_3. The pellets of glass powder will be fast heated up to 1200 °C and the microstructural changes will be examined by X-ray diffraction and scanning electron microscopy.

2. Experimental procedure

2.1. Preparation of glasses and thermal processing

The composition of the parent glass, hereafter named MU9B, is derived from the quaternary glass 3 wt% CaO, 9 wt% MgO, 35 wt% Al_2O_3, and 53 wt% SiO_2. This composition lies within the mullite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system. The glass MU9B was prepared by replacing 9 wt% Al_2O_3 by the same amount of B_2O_3. The specific batches in oxide weight percentages are 3CaO, 9MgO, $26Al_2O_3$, $53SiO_2$ and $9B_2O_3$.

The glass was prepared using commercial chemicals (SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, and BO_3H_3, all provided from Merck). The calculated batches were mixed and melted in an alumina crucible at 1650 °C for 2 h. After pouring the melt into water, the formed small flakes of glass (frit) were crushed and milled. The obtained glass powder was remelted at the same temperature and duration. The final glass powder was milled to a particle size <30 μm. Powder glass pellets were obtained by pressing under 5 MPa. Pellets were submitted to fast thermal treatments at different temperatures up to 1190 °C for 5 min. The heating rate in the firing schedules used was 25 °C/min. After each heating the sample was cooled in air in the furnace.

2.2. Characterization techniques

The chemical and microstructural changes experienced by specimens on fast heating from glasses to the final glass–ceramic glazes were followed by several techniques. Phase identification was performed by X-ray diffraction analysis 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 phase in the final product was performed from X-ray diffraction patterns by using the Rietveld method. The refinement was performed with Fullprof98 [15], available in the software package Winplotr [16]. For the quantification of the glass–ceramic sample it was used ZnO as internal standard. The X-ray diffraction pattern of the mixtures of glass–ceramic and ZnO as internal standard (containing 16.6 wt% ZnO) were collected from 8° to 100° (2θ) with a step size of 0.02° (2θ) and a step time of 10 s. 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 [17], cordierite [18] and zincite [19] 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 (EDS) 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 etched with HF solution (20%) for 1 min and finally gold/palladium coated. Quantitative analyses of specimens were made using the program with ZAF correction procedures and the default standards. The quantification was implemented for oxide stoichiometries and normalized data.

3. Results

3.1. Transformation sequence during fast heating of glass

The crystallization path of the parent glass after fast heating at temperatures between 700 and 1190 °C and holding for 5 min at the final temperature is displayed in Fig. 1. As it can be seen the crystallization begins to be detectable by XRD after heating in the range between 900 and 1000 °C. Between 1100 °C and 1190 °C the degree of crystallization of mullite is very similar. Results on the quantitative determination of the amount of mullite in this range of temperature will be given in the next point. However, from the XRD patterns of crystallized glasses can be

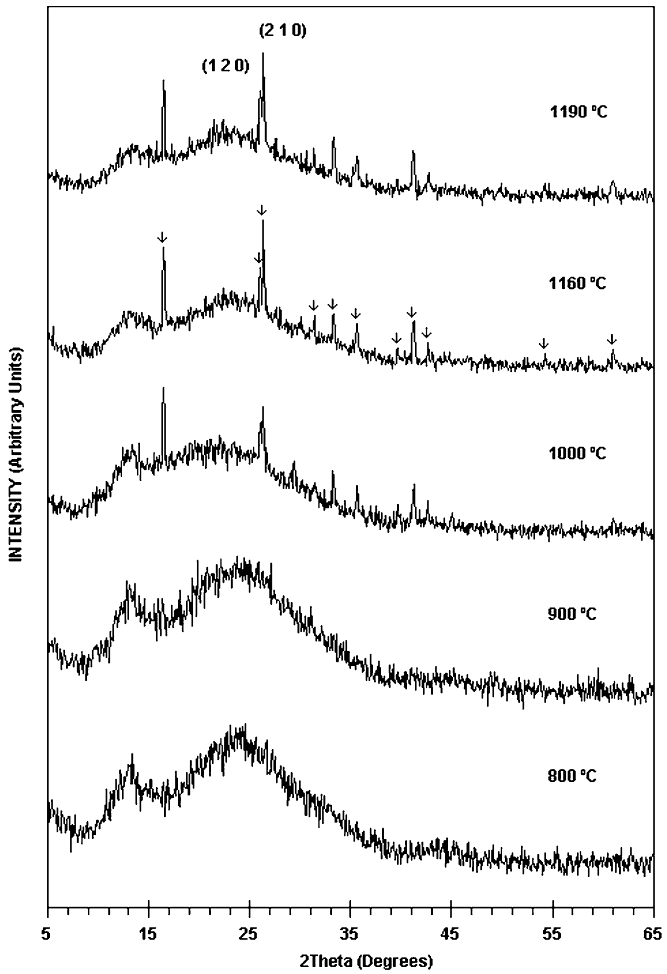

Fig. 1. Powder X-ray diffraction of glasses fast heated at different temperatures for 5 min (↓ is mullite).

inferred that the amount of residual glassy phase is important.

3.2. Variation of the mullite content between 1100 and 1190 °C

The amount of mullite and glassy phase of glass–ceramic specimens prepared after fast heating of glasses at 1100, 1160 and 1190 °C were determined by Rietveld refinement. The results and some reliability factors of the refinements are displayed in Table 1. Fig. 2 displays the experimental and calculated patterns for glass heated at 1160 °C. The difference between both patterns, which is related with the refinement quality, is also shown at the bottom of Fig. 2.

Table 1
Results for the quantitative analysis (wt%) and details of the Rietveld refinement for the glass–ceramic glaze fast heated at 1100, 1160 and 1190 °C for 5 min

	1100 °C	1160 °C	1190 °C
Mullite	20.1 ± 0.5	19.5 ± 0.4	20.2 ± 0.5
Glassy phase	79.9 ± 0.9	80.5 ± 0.9	79.8 ± 0.9
R_p (%)	5.33	5.68	5.67
R_{wp} (%)	7.14	7.40	7.40
R_{wp} (expected) (%)	5.28	5.22	5.25
χ^2	1.82	2.01	1.99

3.3. Microstructural changes during the glass–ceramic development

It has been examined the microstructure of the fast heated glass at different temperatures between 700 and 1190 °C. Figs. 3–7 display microstructural transformations from the powdered glass to the final glass–ceramic glaze. The beginning of the sintering process in the glass heated at 800 °C is shown in Fig. 3(a). The phase separation occurred at this heating stage in the glass is displayed in Fig. 3(b). The starting of the crystallization process at 900 °C and some features of the acicular mullite crystals formed at this stage are shown in Fig. 4(a) and (b). The progress of mullite crystallization on increasing the final temperature to 1000 °C and some characteristics of the mullite crystals developed are evidenced in Fig. 5(a) and (b). Fig. 6 displays the general view of the final glass–ceramic glaze fast heated at 1160 °C and Fig. 7(a) and (b) shows the two types of mullite developed.

Quantitative microanalysis of mullite crystals and residual glassy phase for the final glass–ceramic glaze developed at 1160 °C for 5 min is shown in Table 2. The boron oxide was not analyzed. Although the analysis of mullite crystals is difficult because they have small cross-section, it has been possible to analyze areas larger than 1 μm where several crystals are interlocked. A crucial factor to avoid X-ray signal from the glassy phase was to use an accelerating voltage of 10 kV.

4. Discussion

4.1. Crystallization of glass on fast heating

It can be inferred from the XRD patterns (Fig. 1) that all diffraction peaks can be associated with the mullite structure. Furthermore, in the mullite formed after 5 min at 1000 °C, a splitting of peaks (120) and (210) can be seen. That splitting increases on raising the final temperature. Some comment about the crystallization behavior from chemically homogeneous precursors is worthwhile because orthorhombic mullite is present at the first stage in the crystallization path. Mullite is actually a solid solution in the SiO_2–Al_2O_3, and their stable range of compositions has been established between $3Al_2O_3 \cdot 2SiO_2$ and $2Al_2O_3 \cdot SiO_2$, also called 3:2 and 2:1, respectively [20]. The equilibrium crystal structure of mullite with a composition 3:2 is orthorhombic [20]. On increasing the Al_2O_3 content the lattice constants change. In fact, Al_2O_3-rich mullites have sometimes termed pseudo-tetragonal mullites. Anyway, there is only a very subtle difference between both pseudo-tetragonal and orthorhombic mullites, which is based on the extent of splitting between the (120) and

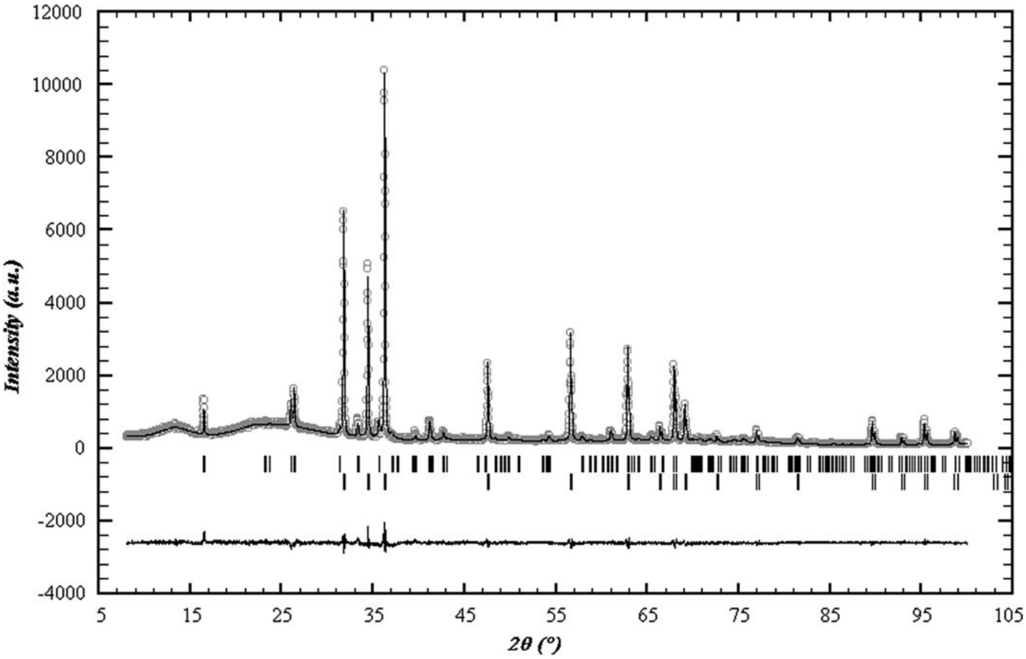

Fig. 2. Rietveld plot of glass fast heated at 1160 °C for 5 min. The calculated pattern is compared with observed data. The small vertical bars indicate the position of allowed *hkl* reflections. The difference between the observed and calculated profiles is the lower trace plotted below the diffraction pattern.

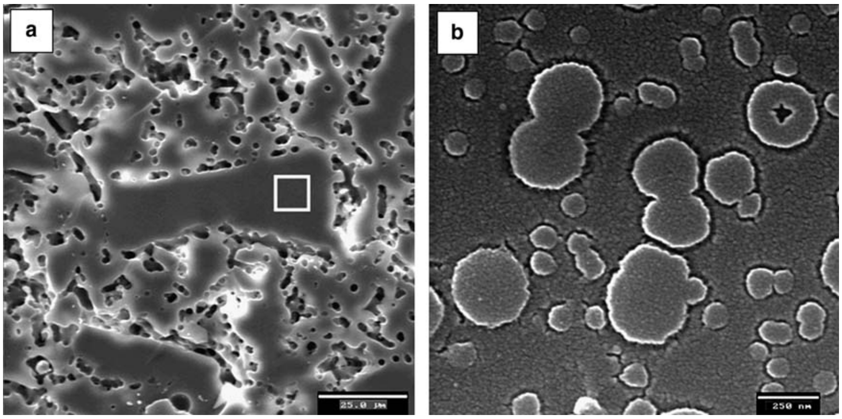

Fig. 3. Micrograph of glass fast heated at 800 °C for 5 min: (a) general view of the glass prior to crystallization (bar = 25 µm); (b) phase separation in glass (bar = 250 nm).

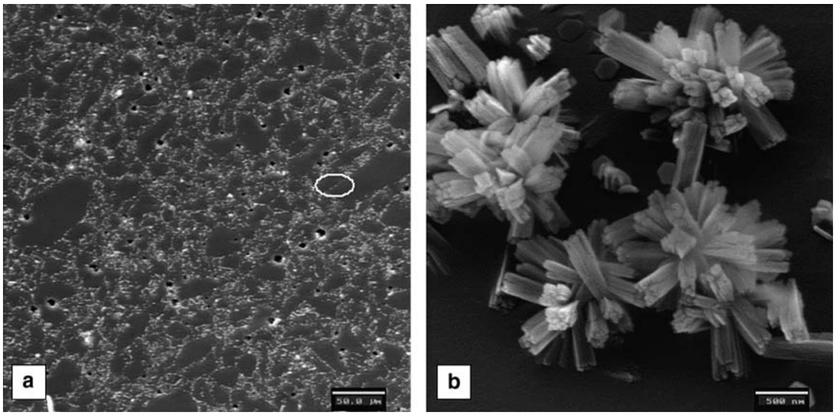

Fig. 4. Micrograph of glass fast heated at 900 °C for 5 min: (a) general view of the specimen at the beginning of the crystallization (bar = 50 µm); (b) detail of the spherulitic growth of mullite crystals (bar = 500 nm).

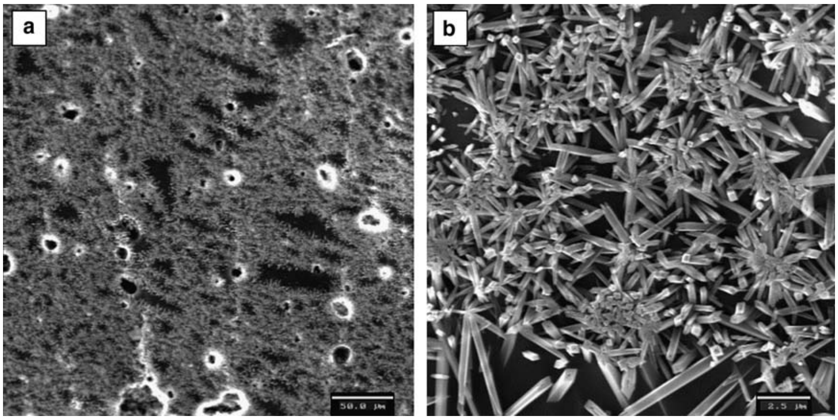

Fig. 5. Micrograph of glass fast heated at 1000 °C for 5 min: (a) general view of the specimen (bar = 50 μm); (b) detail of mullite crystals (bar = 2.5 μm).

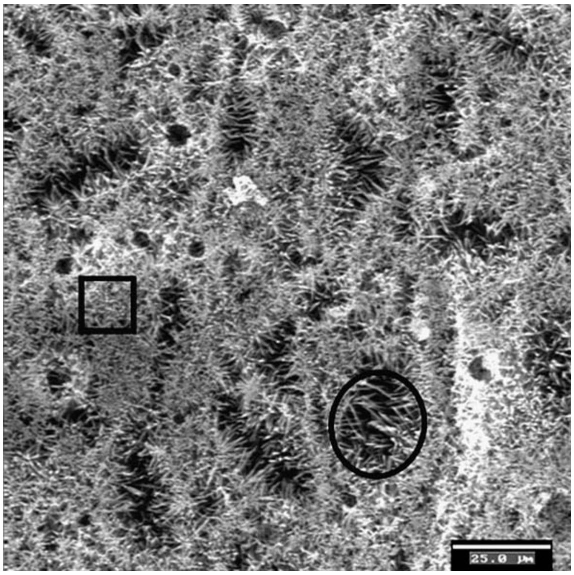

Fig. 6. Micrograph of glass fast heated at 1160 °C for 5 min (bar = 25 μm).

Table 2
Quantitative microanalysis[a] (in wt%) of mullite crystals and residual glass for glass fast heated at 1160 °C for 5 min

	SiO_2	Al_2O_3	MgO	CaO	Al_2O_3/SiO_2[b]
Mullite crystals	27.5 ± 2.6	67.3 ± 2.9	5.3 ± 0.5	–	2.9/2
Glassy phase	56.4 ± 1.4	29.4 ± 1.3	10.5 ± 0.5	3.7 ± 0.4	0.6/2

[a] Boron oxide was not analyzed.

[b] Molar ratio.

(2 1 0) peaks at approximately 26° (2θ). Cameron [21] and Ban and Okada [22] reported correlations between the variation in the lattice parameters and the composition of mullite. It has been reported that when forming mullite from molecularly mixed precursors, with stoichiometry in the range between 3:2 and 2:1, at temperatures less than 1200 °C, the first mullite crystals formed tend to be Al_2O_3-rich [23,24]. However, Huling and Messing have reported the crystallization of orthorhombic mullite from a true molecular mullite gel when suppressing de-homogenization [25]. More recently, we have reported that both 3:2 and 2:1 mullite gels formed orthorhombic mullite under fast heating at 900 °C [26]. As it can be seen in Fig. 1, the crystallized mullite is clearly orthorhombic, i.e. the mullite formed in the glass is SiO_2-rich enough to show a

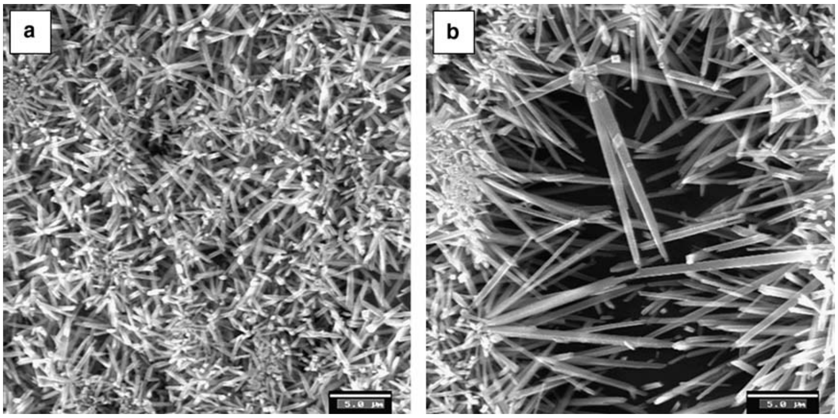

Fig. 7. A higher view of the two types of mullite remarked in Fig. 6: (a) interlocked mullite crystals with aspect ratio around 10 (bar = 5 μm); (b) acicular mullite with aspect ratio higher than 20 (bar = 5 μm).

clear splitting of peaks (1 2 0) and (2 1 0), between 25.8° and 27.1° (2θ). It has been proved that the SiO_2-richer mullite the larger splitting between the (1 2 0) and (2 1 0) reflections [27]. The starting glass used in this study contains a relatively high content of silica, so that it seems reasonable that the crystallized mullite from this SiO_2-rich glass under very fast heating is quite orthorhombic.

4.2. Variation of the mullite content between 1100 and 1190 °C

The R_p and R_{wp} reliability parameters for the three Rietveld refinements are good enough. Previously reported results have proved that this quantification technique allows reaching small errors than 3.0 (wt%) for synthetic multicomponent materials that contained crystalline and amorphous substances [28]. That means that the amounts of crystallinity, i.e. mullite as single crystalline phase, are quite reliable. As it can be seen the amount of crystalline phase does not change noticeably in the range of temperatures in which glazes are developed. In this respect is to note, that the whole process of mullite formation is finished below 1100 °C.

4.3. Microstructural evolution from glass to glass–ceramic

As it can be seen in Fig. 3 sintering of glass particles is starting on heating at 800 °C for 5 min. Results previously reported from heating microscopy showed that this glass sinters between 850 and 1050 °C [14]. The sintering process takes place in two stages. The first step ends at around 950 °C, at which the most of crystallization occurs. A closer look to the glass particles shown in the previous Fig. 3(a) evidences the formation of phase separation in the glass fast heated at 800 °C. As can be seen in Fig. 3(b), the separated phase appears as uniformly dispersed spherical droplets, of different contrast, in the glass matrix. It is also observed that some coalescence of the separated droplets is present. MacDowell and Beall reported spontaneous phase separation to two amorphous phases on cooling binary Al_2O_3–SiO_2 glasses containing from 10 to 50 mol% Al_2O_3 [9]. Beall and Pinckney reported that additions of components, such as B_2O_3, MgO and CaO, improve the melting characteristics of these extremely refractory glasses [10]. Furthermore, it has been claimed that those oxides suppress spontaneous phase separation in Al_2O_3–SiO_2 glasses, yielding stable glasses that separate controllably on further thermal treatment [10]. The composition of these dispersed droplets should determine the chemical composition of the crystalline phase produced on further reheating. The beginning of the crystallization is detected on fast heating at 900 °C. The XRD pattern of this sample indicates the presence of a small amount of mullite crystalline phase. The location in the glass heated and some microstructural features of that mullite are shown in Fig. 4(a) and (b), respectively. As it can be seen in Fig. 4(a) the crystallization occurs at the surface of the early glass particles, probably favored by defects present at the position of the original particle surfaces. The examination of crystals formed at this initial stage confirms the formation of mullite spherulites (Fig. 4(b)). The homogeneous distribution of mullite particles at the glass particle surfaces can be due to that spherulites crystallize in a controlled manner within the phase separated droplets. Consequently, the separated glass phase where mullite crystallizes must be Al_2O_3-rich.

Fig. 5(a) and (b) shows the increase in crystallization and some changes experienced by the mullite crystals on heating at 1000 °C, respectively. In Fig. 5(a) it is evident that the dark contrast areas corresponding to glassy phase are smaller. The interlocked mullite crystals formed at this stage (Fig. 5(b)) display long axes size between 2 and 3 μm.

On heating the glass at 1160 °C for 5 min the dark contrast areas are smaller than for glasses heated at lower final temperatures, as displayed in Fig. 6. The examination of the mullite crystals indicates that two types of interlocked crystals can be distinguished. The first type of interlocked mullite crystals shown in Fig. 7(a) has between 4 and 5 μm in size and is almost uniformly distributed over the sample. The second type are very long, between 15 and 20 μm, occurring only on the boundaries of small residual glass areas left after heating, as shown in Fig. 7(b). In this respect, it is to be remarked that the main type of mullite crystals in the final glass–ceramic glaze is the first.

The estimated composition of mullite crystals formed in fast heated glass at 1160 °C for 5 min and the remaining glass are displayed in Table 2. It is to be noted that boron oxide was not analyzed. From these data it can be inferred that the composition of mullite crystals is close to the 3:2. This means that it is in the SiO_2-rich end of the stable compositional range of mullite solid solution in the SiO_2–Al_2O_3 system [29]. The acicular morphology of mullite crystals is also in agreement with their growth in a SiO_2-rich glass [30]. From the analytical results it seems that some amount of Mg^{2+} can entry in the mullite crystals forming a solid solution. Although it has been postulated that metastable solid solutions with mullite structure containing MgO may be formed, there are no definitive experimental evidence. The crystallochemistry of the mullite structure is quite rich, a large number of transition metal cations have been incorporated into the mullite structure [31]. The transition metal ions are preferably incorporated into the oxygen octahedral in the mullite structure. However, in the case of Mg^{2+} ions it can be thought that the mullite solid solution formation involves a partial replacement of the tetrahedral aluminum by magnesium ions with two possible simultaneous mechanisms of charge compensation: substitution of aluminum by silicon also in the tetrahedral site or formation of oxygen vacancies. In definitive, the possible entry of Mg^{2+} into the mullite crystals requires further study. The effect of boron oxide in the formation of the glass–ceramic deserves some consideration. Hong and Messing reported results on densification and anisotropic grain growth in boria-doped diphasic mullite gels

[32]. They showed that boria reduced the viscosity of silica glass and enhanced densification. In addition, boria reduced the grain size and resulted in a fine, equiaxed grain microstructure of 0.5 μm at high temperature. Richards et al. in a study on microstructural and compositional changes during heat treatments of sol-gel derived mullite fibers with additions of B_2O_3, suggested that the formation of aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$) might precede the formation of an aluminum borosilicate phase, presumably a solid solution of aluminum borate and mullite [33]. Therefore, whether or not the formation of mullite at lower temperatures in fibers having Al_2O_3:SiO_2 ratios of 3:2 are initiated by the prior formation of aluminum borate remains uncertain. It is to note, that B^{3+} commonly enters in tetrahedral coordination, and it is much smaller than Al^{3+} and Si^{4+}. The entry of B^{3+} into the mullite structure in tetrahedral coordination is therefore not easy. Moreover, in general the mullite crystals obtained in the final developed glass–ceramic are quite large, with aspect ratio – a measure of the degree of anisotropy – higher than 10. In this sense it is to note that mullite crystals growth on the few small pockets of residual glass remaining in the glass–ceramic have aspect ratios even larger, up to 25. This finding is consistent with the fact that the role played by the oxide of boron is mainly as flux in the formation of the final glass–ceramic glazes. It is to be remarked that in previous studies on the microstructure of mullites prepared from B_2O_3-doped mullite gels results indicated that equiaxed, fine-grained mullite were obtained, less than 500 nm, in a wide range of temperatures [32,33].

5. Conclusion

Crystallization in a glass with composition 3CaO, 9MgO, $26Al_2O_3$, $53SiO_2$ and $9B_2O_3$ (in wt%) was studied by different techniques. Glass powder pellets were fast heated between 700 and 1200 °C for 5 min. X-ray diffraction of heated glasses showed that mullite started to form at around 900 °C. The largest amount of mullite, determined by Rietveld refinement, was developed in the temperature range where industrial glazes are processed. The microstructural study by field emission scanning electron microscopy (FESEM) showed that a phase separation phenomenon occurred in the glass fast heated at 800 °C. At 1000 °C the crystallization was almost completed. The boron oxide-containing glass produced a glass–ceramic glaze with fine grained interlocking microstructure after fast heating at 1160 °C. The interlocked, well-shaped, acicular mullite crystals developed were long, between 4 and 5 μm, and were immersed in the residual glassy phase.

Acknowledgements

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