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Effect of boron oxide on the microstructure of mullite-based glass-ceramic glazes for floor-tiles in the CaO–MgO–Al_2O_3–SiO_2 system

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Abstract

The effect of increasing replacement of Al_2O_3 by B_2O_3 in a parent glass on the sintering and further crystallization of mullite was investigated. The composition of the parent glass was chosen in the mullite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system. Glass powder pellets were heated under standard (10 °C/min and 2 h of hold time) and fast heatings (25 °C/min and 5 min of hold time) at different temperatures from 700 to 1190 °C. Sintering of B_2O_3-containing glasses took place in the range between 850 and 1050 °C. X-ray diffraction results showed that mullite formed as unique crystalline phase for glasses containing amounts of B_2O_3 larger than 6 wt%. For lower amounts of boron oxide cordierite was formed as secondary crystalline phase. Quantitative determination of mullite by Rietveld analysis indicated that the higher amount of mullite present in the glass-ceramic fast heated at 1160 °C was 19.5 wt% for the glass containing 9 wt% of B_2O_3. The final microstructure of the glass-ceramic glazes showed the presence of well shaped, long acicular mullite crystals dispersed within the residual glassy phase. Results of glass-ceramic glazes when applied as slurry and under industrial heating conditions pointed out promising mechanical properties.

Keywords: Glass-ceramics; Mullite; Microstructure; X-ray methods; Rietveld analysis; Tiles

1. Introduction

Mullite-based glass-ceramic materials have been attracted much attention during last decade. These composed materials present interesting chemical, mechanical and thermal properties. Several applications with this type of materials have been developed, ranging from dental materials to ceramic matrix composites.[1–3]

The floor- and wall-tile ceramics consist of a porcelanized support covered with a glass layer. The final properties of this two-component material depend strongly on the properties of the glassy layer. In general glass-ceramic materials display better properties than their parent glasses. So, a way to improve mechanical and optical properties in floor- and wall-tile ceramics is to develop glass-ceramic layers covering the support.

The development of new glass-ceramic glazes is limited by some constraints, mainly derived from the kind of support and heating conditions (final temperature and rate of heating).[4] Nowadays, in the industry is commonly used a fast firing process, with elapsed times between 40 and 50 min.

A number of new glass-ceramic glazes with nominal compositions in the CaO–MgO–Al_2O_3–SiO_2 (CMAS) quaternary system have been reported in the last years.[5–10] Glass-ceramics materials have been developed containing diopside or cordierite as single crystalline phase, by heating under controlled conditions glassy compositions located in the primary phase field of these crystalline phases. Obviously, to attain the ultimate features of those glass-ceramic glazes several additives were required to favor the crystallization process.

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In order to improve mechanical properties of glazes, it would be interesting to develop mullite glass-ceramic glazes. In this respect, as far as we know there are no reported successful results on mullite glass-ceramic glazes. As it is well known, mullite is the only stable phase in the SiO_2–Al_2O_3 binary system and a refractory crystalline phase. The preparation and crystallization of glasses from compositions in the binary system is quite difficult because very high melting temperatures are required to obtain viscous meltings. Consequently, we have chosen as starting glass to develop mullite glass-ceramic glazes, a glass with composition in the mullite primary phase field of the CMAS quaternary system. However, though the required temperatures to bring about liquid phase are lower than for the SiO_2–Al_2O_3 binary system, the high content of alumina and silica of the parent compositions make difficult the melting of the raw materials mixture. To be able to process compositions in the mullite primary phase field of the CMAS quaternary system, therefore, it is also required to add certain additives in the batch. B_2O_3 has been successfully used as flux to develop diopside- and cordierite glass-ceramic materials.[7–10] It would be, therefore, interesting to study the effect of some amounts of B_2O_3 replacing Al_2O_3 in the sintering and crystallization of mullite-based glass-ceramic glazes.

In the present paper, therefore, we report on the feasibility of developing mullite-based glass-ceramic glazes, by replacement of increasing amounts of Al_2O_3 by B_2O_3 in a parent glass, with composition located in the mullite primary crystallization field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system. Processing conditions employed are similar to the ones nowadays used in the ceramic industry.

2. Experimental procedure

2.1. Preparation of glass-ceramic glazes

A reference glass with composition in the mullite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system was chosen. The composition of this reference glass is $53SiO_2$, $35Al_2O_3$, 9MgO and 3CaO (wt%). The compositions of the rest of glasses in the series arise by replacement of increased amounts of Al_2O_3 by B_2O_3. The composition (in wt%) and nomenclature for all prepared glasses are shown in Table 1. Glasses were obtained by melting mixtures of the required amounts of SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$ and BO_3H_3, all high quality reagents provided from Merck, at 1650 °C for 2 h. Melted glasses were poured into cold water and after regrinding were remelted again. 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.

Table 1
Composition (in wt%) of prepared glasses

Oxide	M4	M4B6	M4B9	M4B12
SiO_2	53	53	53	53
Al_2O_3	35	29	26	23
MgO	9	9	9	9
CaO	3	3	3	3
B_2O_3	–	6	9	12

Cylindrical pellets of loosely pressed powder, i.e. under a pressure of about 5 MPa, were thermally treated under two different schedules. First, the specimens were heated under standard heating schedules (10 °C/min up to the final temperature and hold 2 h at this temperature). In the second, the specimens were fast thermally treated at 1100, 1160 and 1190 °C. The heating program used was a heating rate of 25 °C/min up to the final temperature and kept 5 min to the final temperature. These conditions were chosen to simulate those in the industrial application of the glaze layer as well as the heating schedule in the fabrication of ceramic tiles. Furthermore, 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 characterisation

X-ray diffraction analysis (Model D-5000, Siemens, Karlsruhe, Germany) was performed using a graphite

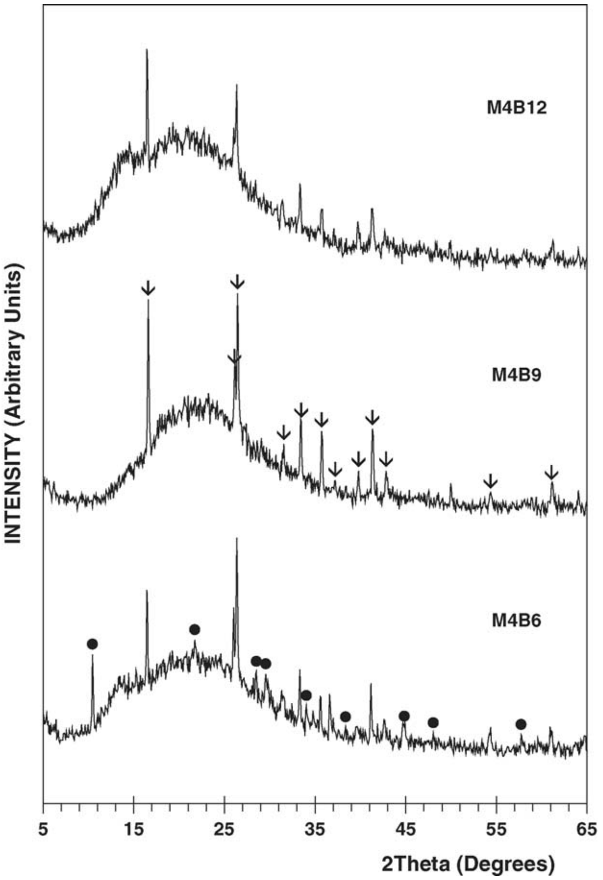

Fig. 1. Powder X-ray diffraction of glasses fast heated at 1160 °C for 5 min (● is cordierite and ↓ is mullite).

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 quantitative determination of mullite in final glass-ceramic glazes was performed from X-ray diffraction data by using Rietveld refinement. It was performed with Fullprof 98,[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 ZnO. 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] cordierite[14] and zincite[15] were taken from the literature.

Hot-stage microscopy (Model Misura 3, Expert System solutions, Modena, Italy) was carried out in the range 40–1300 °C, with a heating rate of 20 °C min^{-1}.

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 (20%) solution for 10 s and subsequently washed with distilled water.

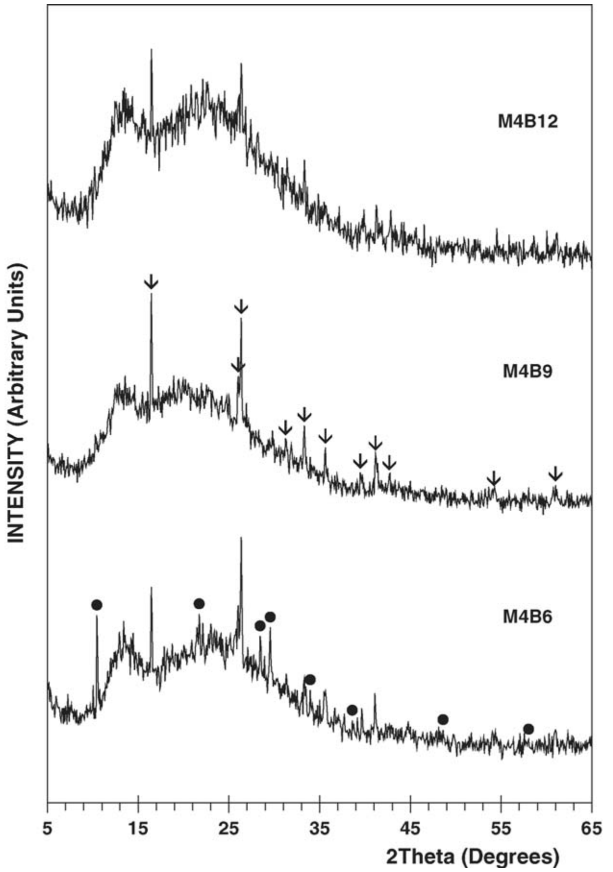

Fig. 2. Powder X-ray diffraction of glasses fast heated at 1190 °C for 5 min (● is cordierite and ↓ is mullite).

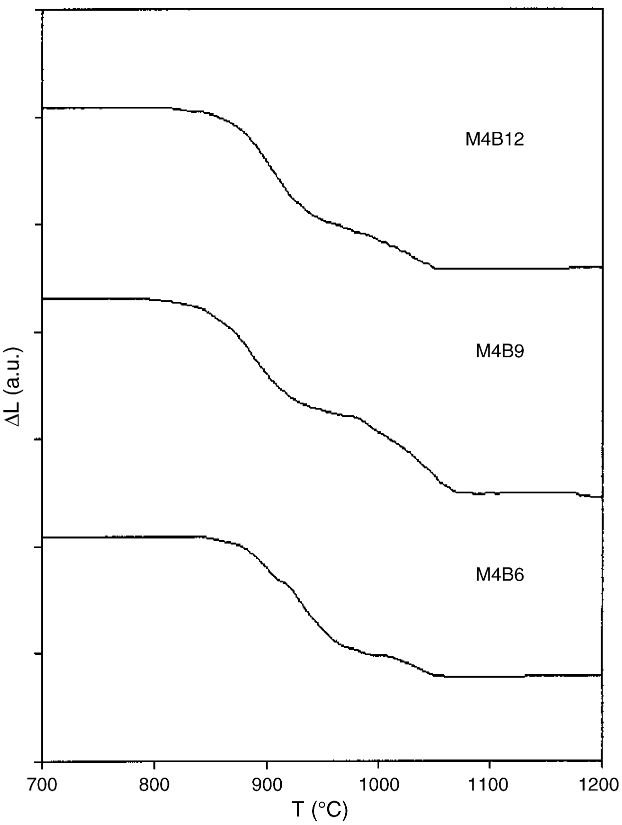

Fig. 3. Hot-stage microscopy curves of glasses with increased contents of boron oxide.

Energy-dispersive X-ray analysis was performed using an environmental scanning electron microscope operated at 10 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. In order to eliminate the residual glassy phase surrounding mullite crystals the polished specimen was etched for 30 s with HF (20%) solution. Before acquiring the X-ray spectra samples were gold/palladium coated. It is to be noted that the acceleration voltage used for elemental analysis was 10 kV. The reason is to reduce the interaction volume and, therefore, the sampling volume and avoid X-ray signal from the glassy phase around the set of crystals analysed.

Table 2
Results for the quantitative analysis (wt%) and details of the Rietveld refinement for glass-ceramic glazes fast heated at 1160 °C

	M4B6	M4B9	M4B12
Mullite	14.6	19.5	13.9
Cordierite	1.6	–	–
Glassy phase	83.8	80.5	86.1
R_{p} (%)	6.59	5.68	5.67
R_{wp} (%)	9.24	7.40	7.40
R_{wp} (expected) (%)	5.27	5.22	5.25
χ^2	3.08	2.01	1.99

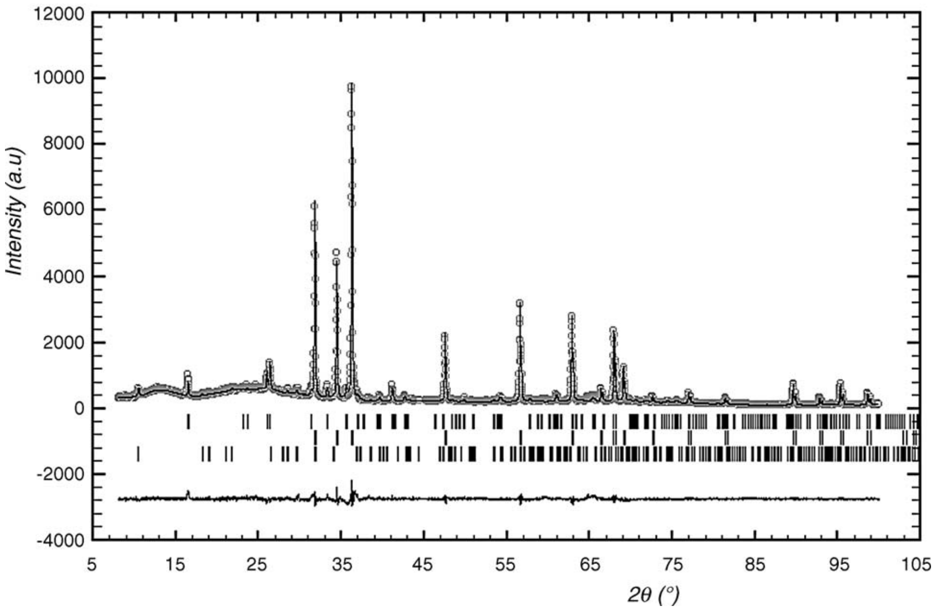

Fig. 4. Rietveld plot of glass-ceramic glaze M4B6 fast heated at 1160 °C for 5 min. The calculated pattern is compared with observed data. The small vertical bars indicate the position of allowed *h k l* reflections. The difference between the observed and calculated profiles is the lower trace plotted below the diffraction pattern.

3. Results and discussion

3.1. Crystallization of glasses

The general study of glasses heated at different temperatures between 800 and 1200 °C under standard heating schedules indicated the formation of cordierite and mullite as main crystalline phases. The relative amount of both phases was dependent on both the final temperature and the glass composition. The higher amount of boron oxide and the higher temperature the smaller amount of secondary phase cordierite. The composition without boron oxide will be not further included in the discussion because the formation of mullite is very slow. Moreover, it is too refractory and it is required a long heating to obtain a homogeneous melt. Since, the range of temperatures in which the glass-ceramic glaze will be developed spreads over 1100 and 1200 °C and, if possible, under fast heatings, we will only consider the results obtained under these conditions. The main crystalline phases formed on fast heating glasses-containing boron oxide at 1160 and 1190 °C are shown in Figs. 1 and 2. At 1160 °C the heated, boron oxide-containing glasses form mullite and in the glass M4B6 also cordierite is detected. At 1190 °C the crystalline phases detected are similar but it seems that the total amount of crystalline phase has decreased. From Fig. 1 it can be seen a clear splitting of peaks (1 2 0) and (2 1 0), between 25.8° and 27.1° (2θ), in the XRD patterns of M4B6 and M4B9. This fact can be related with the composition of

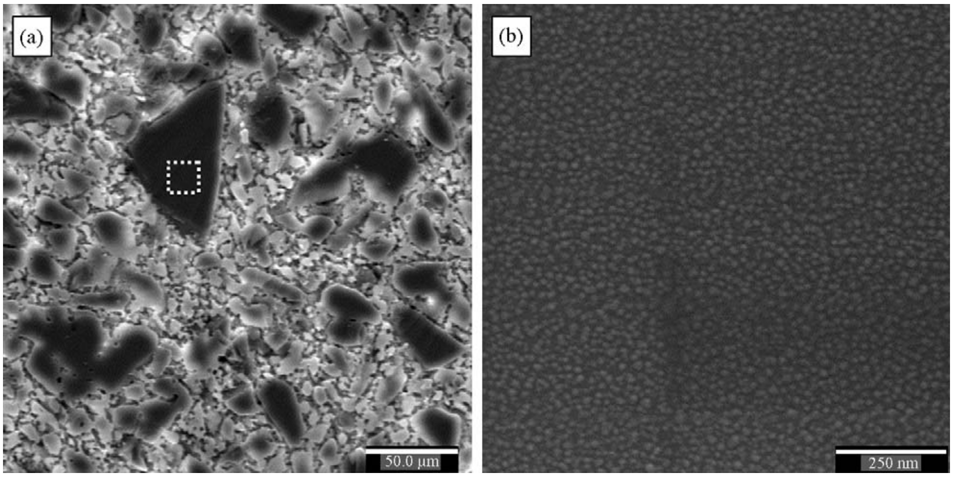

Fig. 5. Micrographs of glass M4B12 after fast heating at 800 °C, shown: (a) sintering of glass particles (bar = 50 μm) and (b) phase separation in the glass (bar = 250 nm).

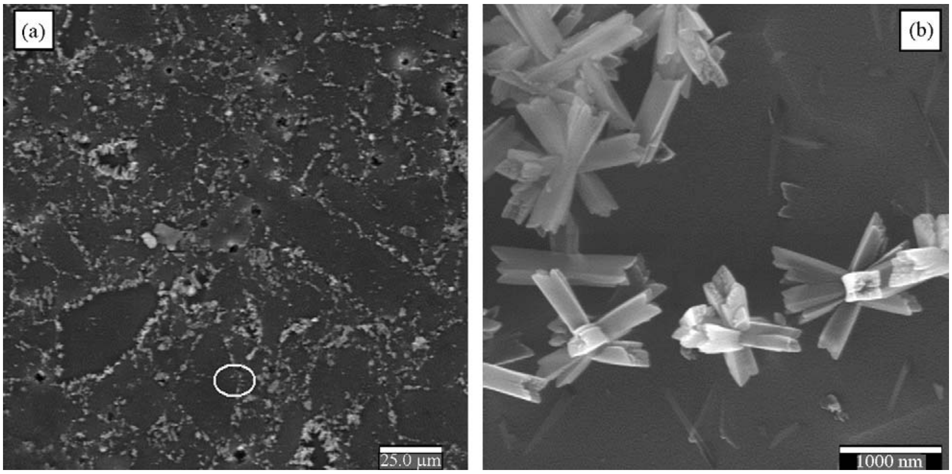

Fig. 6. Micrographs of glass M4B6 fast heated at 900 °C, shown: (a) the microstructure at the beginning of crystallization (bar = 25 µm) and (b) the morphology of mullite crystals at this stage (bar = 1000 nm).

mullite. Mullite is actually a solid solution with stable composition in the range $3Al_2O_3{\cdot}2SiO_2$ to $2Al_2O_3{\cdot}SiO_2$ (hereafter denoted as 3:2 and 2:1).[16] The orthorhombicity of the mullite crystalline phase, i.e. the splitting of (1 2 0) and (2 1 0) reflections is larger for SiO_2-richer mullites.[17] The observed splitting in the mullite peaks of glass-ceramics at 1160 °C indicates, therefore, that these mullites are rich in silica. From the relative intensity of the crystalline phases in Figs. 1 and 2, it can be assumed that the largest crystallization is obtained for glasses thermal treated at 1160 °C.

In order to get low porosity in glass-ceramic materials the sintering must be largely complete before crystallization. The hot-stage microscopy results of glasses with increased amounts of boron oxide are displayed in Fig. 3. It can be seen that the contraction of glasses starts around 850 °C and ends between 1020 and 1050 °C. Thus the major crystallization takes place when the sintering is almost finished.

3.2. Glass-ceramic characterisation

The properties of glass-ceramics are dependent on the microstructure. Thus, in order to relate the properties with the microstructure of glass-ceramic glazes it is necessary to characterize the final glass-ceramic. Thus, in the next sections we report results on the amount of crystalline phases,

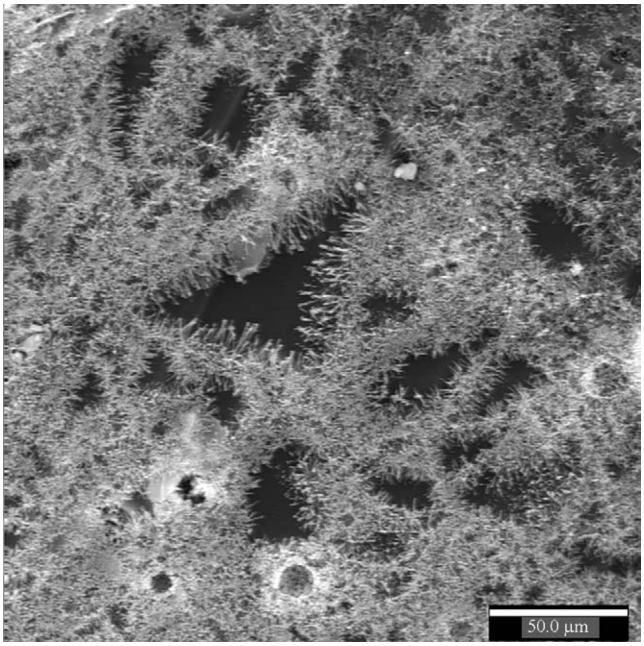

Fig. 7. Micrograph of glass M4B12 fast heated at 1160 °C for 5 min (bar = 50 µm).

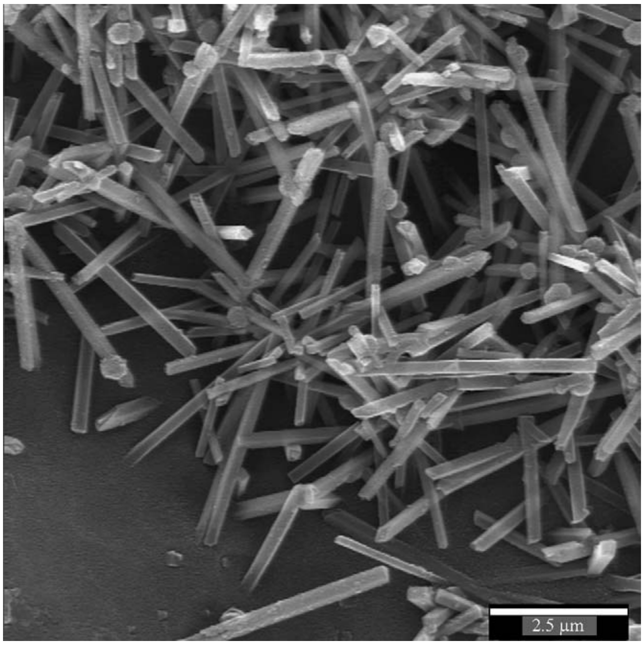

Fig. 8. Mullite acicular crystals formed in the glass-ceramic glaze M4B12 on heating glass at 1160 °C for 5 min (bar = 2.5 µm).

mullite and cordierite, and the size, distribution, morphology and qualitative microanalysis of the final mullite crystals for the three studied glasses.

3.2.1. Variation of the mullite amount in the glass-ceramic glazes fast heated at 1160 °C

The results for the quantitative analysis of glass-ceramic glazes fast heated at 1160 °C are summarized in Table 2. Also some details of the Rietveld refinement are included. The final Rietveld plot for the glass-ceramic glaze M4B6, shown as representative, is given in Fig. 4. As an indication of Rietveld refinement quality, the difference between the observed and calculated pattern for this sample is displayed in the lower trace of Fig. 4. As it can be seen there is 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 5.67 and 9.24 for all the glass-ceramic specimens.

These results confirm the higher crystallinity for the glass-ceramic glaze M4B9. For glasses containing higher amounts of boron oxide the content of mullite developed is lower. It is to remark that the accuracy of analysing the crystallinity of multicomponent materials by the Rietveld method has been checked.[18] Results previously reported have demonstrated high precision with small errors than 3.0 (wt%) for synthetic multicomponent materials that contained crystalline

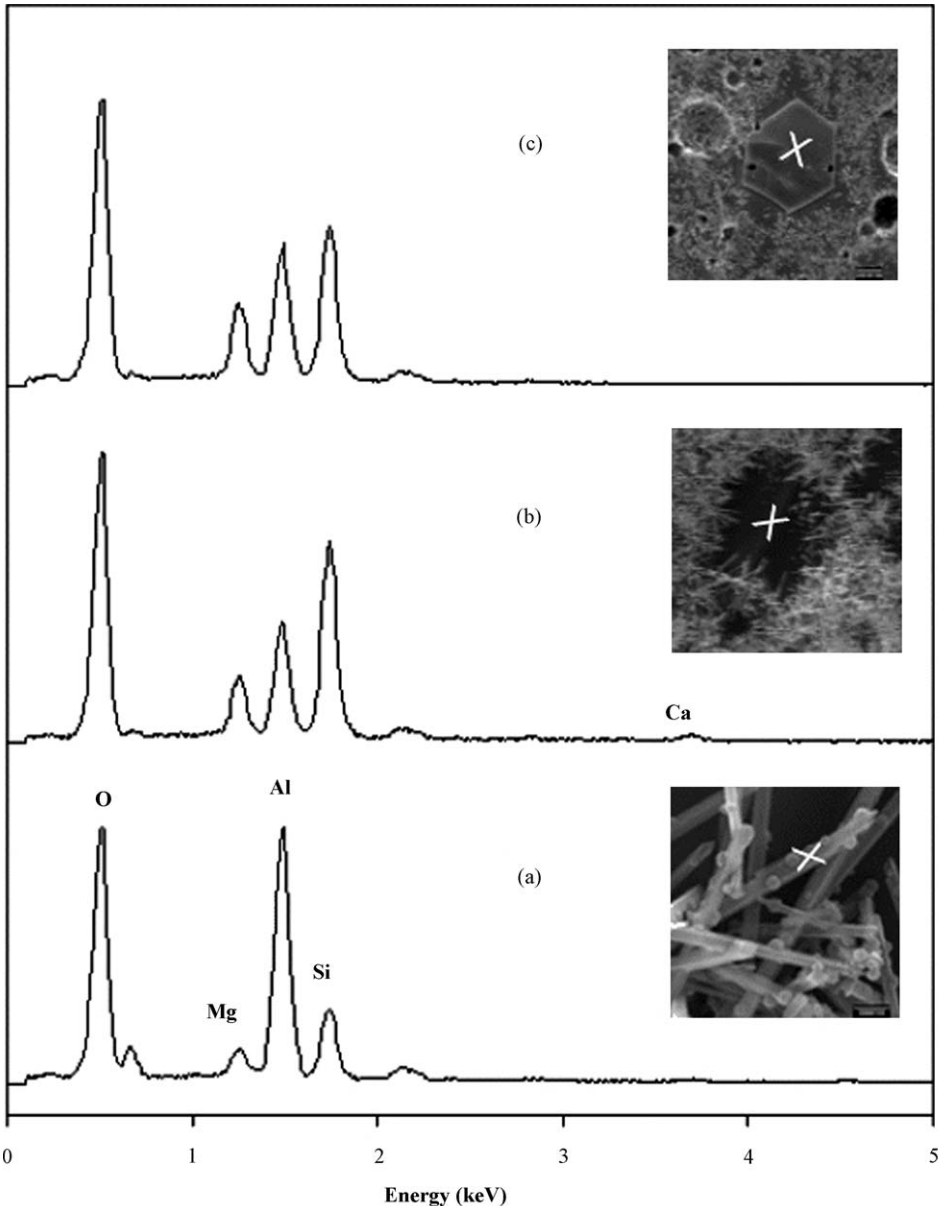

Fig. 9. Qualitative composition of (a) mullite crystals; (b) residual glassy phase in M4B12 and (c) cordierite crystals in M4B6, for all glasses fast heated at 1160 °C for 5 min.

and amorphous components, such as the glass-ceramic materials.

3.2.2. Microstructural features of the glass-ceramic glazes

The main microstructural changes from the boron oxide-containing glasses to the final mullite glass-ceramic glazes on fast heating are the following. Crystallization starts between 900 and 950 °C. In this respect, studies performed on heating microscopy showed that in general glasses containing different amounts of boron oxide start to sinter at 850 °C and around 950 °C was detected a change in the slope of the sinter curve, which can be associated to the beginning of crystallization. The microstructure of glass M4B12 after fast heating at 800 °C, shown as representative, is displayed in Fig. 5(a). It can be seen that at this stage the glass is formed by particles of different sizes no sintered yet. The surface of particles displays a bright contrast, as a consequence of the fluorhidric etching. As it was commented above no crystallization occurred at this temperature. In general, it can be observed in the dark contrast a homogeneous distribution of small droplets of different contrast (Fig. 5b) which can be attributed to phase separation, i.e. liquid–liquid phase separation, in the glass. The larger amount of boron oxide the greater number of phase separated small droplets. De Vekey and Majumdar[19] stated that the phase separation, which takes place at high temperatures in CMAS glasses, is due to the segregation of calcium and magnesium ions. The immiscibility texture observed in B_2O_3-containing glasses is similar to the one shown in glass CMAS. It is to note, however, that B_2O_3 has a limited solubility into some aluminosilicate glasses and high tendency to create ordered zones with high alumina content.[20] This feature can enhance the tendency to produce a phase separation process.

After fast heating at 900 °C for 5 min starts the crystallization of glasses. The first step in the crystallization process for glass M4B6, shown as representative, is displayed in Fig. 6(a). It can be seen that small aggregates of needle-like crystals are formed in the early surface of particles. A closer look to these sets of crystals is also shown in Fig. 6(b). On increasing the final temperature the number of aggregates of mullite crystals increases. Thus in glasses fast heated at 1160 °C an almost continuous distribution of mullite crystal sets occurred all around the surface of particles. Fig. 7 corresponds to a general view of glass M4B12 fast heated at 1160 °C for 5 min. A closer look to this specimen is displayed in Fig. 8. The general microstructure of these three fast heated B_2O_3-containing glasses is similar. The only difference is that in the specimen with the smaller B_2O_3 content, i.e. M4B6, very well shaped hexagonal prisms of α-cordierite are formed. The qualitative composition of the cordierite phase in M4B6, and the mullite crystals and residual glassy phase in M4B12 heated at 1160 °C for 5 min is shown in Fig. 9. The presence of B_2O_3 has not been determined. Anyway, we can assume that the boron oxide will be mainly located at the residual glassy phase.

4. Conclusions

The effect of increased amounts of Al_2O_3 replaced by boron oxide in a parent glass with composition within the mullite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system was studied. Glasses with larger amounts of B_2O_3 improved the melting characteristics. Sintering of B_2O_3-containing glasses took place in the range between 850 and 1050 °C. Crystallization started at around 1000 °C independently of the heating schedule. Fast heating of B_2O_3 containing-glasses at 1160 °C crystallized only mullite when the boron oxide amount was larger than 6 wt%. The amount of mullite phase developed in the glass containing 9 wt% B_2O_3 (sample M4B9) fast heated at 1160 °C, determined by Rietveld analysis, was 19.5 wt%. The final microstructure of the glass-ceramic glaze showed the formation of well-shaped, long acicular mullite crystals dispersed within the residual glassy phase. Glass-ceramic glazes yielded under industrial conditions were correctly developed and the mechanical properties were very promising.

Acknowledgements

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