

# Effect of boron oxide on the microstructure of mullite-based glass-ceramic glazes for floor-tiles in the CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system

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## Abstract

The effect of increasing replacement of Al<sub>2</sub>O<sub>3</sub> by B<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>-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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>. 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.

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## 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.<sup>1–3</sup>

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).<sup>4</sup> 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<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (CMAS) quaternary system have been reported in the last years.<sup>5–10</sup> 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  $\text{SiO}_2\text{--Al}_2\text{O}_3$  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  $\text{SiO}_2\text{--Al}_2\text{O}_3$  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.  $\text{B}_2\text{O}_3$  has been successfully used as flux to develop diopside- and cordierite glass-ceramic materials.<sup>7–10</sup> It would be, therefore, interesting to study the effect of some amounts of  $\text{B}_2\text{O}_3$  replacing  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  by  $\text{B}_2\text{O}_3$  in a parent glass, with composition located in the mullite primary crystallization field of the  $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$  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  $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$  quaternary system was chosen. The composition of this reference glass is 53 $\text{SiO}_2$ , 35 $\text{Al}_2\text{O}_3$ , 9 $\text{MgO}$  and 3 $\text{CaO}$  (wt%). The compositions of the rest of glasses in the series arise by replacement of increased amounts of  $\text{Al}_2\text{O}_3$  by  $\text{B}_2\text{O}_3$ . 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  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  and  $\text{BO}_3\text{H}_3$ , all high quality reagents provided from Merck,

Table 1  
Composition (in wt%) of prepared glasses

Oxide	M4	M4B6	M4B9	M4B12
$\text{SiO}_2$	53	53	53	53
$\text{Al}_2\text{O}_3$	35	29	26	23
$\text{MgO}$	9	9	9	9
$\text{CaO}$	3	3	3	3
$\text{B}_2\text{O}_3$	–	6	9	12

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  $\mu\text{m}$ .

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

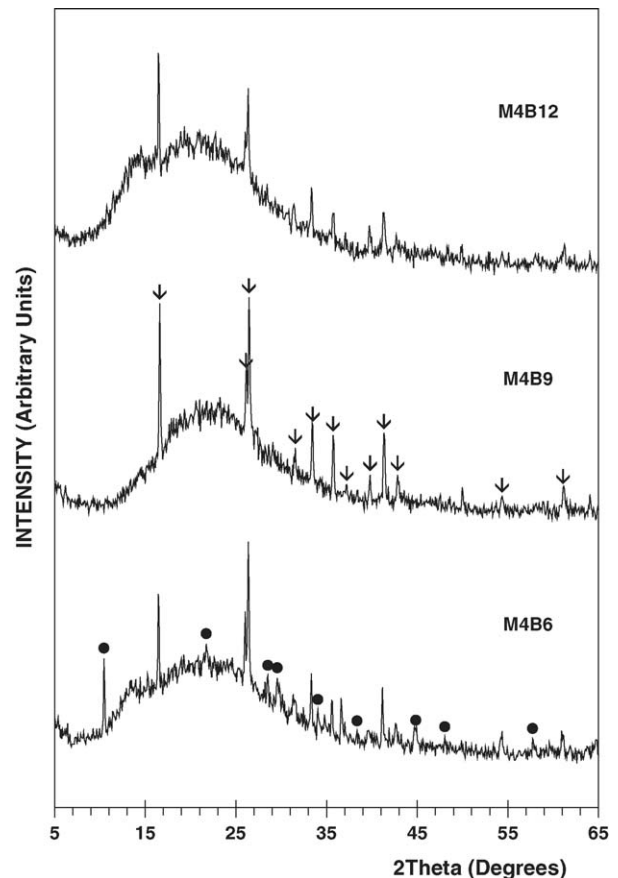


Fig. 1. Powder X-ray diffraction of glasses fast heated at 1160 °C for 5 min (● is cordierite and ↓ is mullite).

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