Journal of the European Ceramic Society 23 (2003) 817–826
www.elsevier.com/locate/jeurceramsoc

Effect of additives on the crystallization of cordierite-based glass-ceramics as glazes for floor tiles

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Received 8 February 2002; accepted 16 June 2002

Abstract

The effect of several additives such as fluxes and/or nucleants on a parent glass with composition located in the primary field of cordierite within the quaternary system CaO–MgO–Al_2O_3–SiO_2 has been examined. Crystallization path of glasses was determined by differential thermal analysis (DTA) and X-ray powder diffraction (XRD). Pressed pellets of powdered glasses containing different additives were submitted at thermal treatments up to 1200 °C. The microstructural development at several temperatures was followed by field emission scanning electron microscopy and energy-dispersive X-ray analysis. The results shown that additions of TiO_2 as nucleant and/or B_2O_3 as flux to a chosen glass in the cordierite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system favoured the crystallization of cordierite as only crystalline phase. However, the presence of Na_2O and K_2O as fluxes suppress its crystallization. Microstructural examination revealed that with TiO_2 as nucleant and B_2O_3 as flux, crystals of cordierite with hexagonal prismatic morphology were formed after controlled thermal treatment of glass. The approach outlined in this paper to obtain cordierite-based glass-ceramic glazes from a cordieritic glass with additives could represent an useful guide to obtain new glazes with improved mechanical and optical properties.

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Keywords: Cordierite; Crystallization; Glass-ceramics; Glazes

1. Introduction

Glass-ceramics are polycrystalline solids containing residual glassy phase. Since the first practical glass ceramic material was discovered, a wide variety of applications of these versatile materials have been developed as a result of their many outstanding properties. Glass-ceramic technology is based on the controlled nucleation and crystallization of bulk glass. Recently, also the powder processing route has become widely used.

The ceramic floor and wall tile industry has been greatly extended in the last years with the introduction of new technologies and automation into the manufacturing process. As a result of the technological innovations both productivity and efficiency have experienced clear improvement. 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. So far, a great effort has been addressed to improve mainly aesthetic functions of these materials, however, there are an increasing demand of new ceramic tiles with improved technical properties, encompassing high resistance to wear by abrasion, high surface hardness, low level of closed porosity and good chemical resistance.

A new approach to reach high quality in ceramic glaze surfaces has entailed obtaining frits (the major constituent in ceramic tile glaze formulations) which allow to develop glass-ceramic layers and take advantage of the excellent mechanical, chemical and optical properties of these materials. On considering the requirements of compatibility with the body properties and the resultant outstanding properties, formulations that are based on the Li_2O–Al_2O_3–SiO_2, MgO–Al_2O_3–SiO_2 and MgO–CaO–SiO_2 ternary systems have found practical applications as tile glazes. The kind of crystalline phase and also the final properties of the glass-ceramic glaze can be controlled by the starting glass composition

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PII: S0955-2219(02)00206-6

and by its further thermal treatment. Among the specific crystalline phases with interesting properties of glass-ceramic materials based on the above ternary systems are β-spodumene solid solution, α-cordierite and diopside.

To date, only a reduced number of papers have been published on the use of glass-ceramic systems as glaze components. Leonelli et al.[1] studied the devitrification processes of industrial formulations in the Li_2O–Al_2O_3–SiO_2 glass-ceramic system and the effect of some compositional changes in the crystallization of bulk and coating films on clay support. All the systems investigated shown a high tendency toward crystallization, developing a very close network of interlocked crystals based on the solid solution of β-spodumene-silica. Recently, Ferrari et al.[2] studied the ability that mixtures of glass compositions in the MgO–Al_2O_3–SiO_2 ternary system and a sodium borosilicate glass, the latter is commonly used in the tile glaze industry, have to be used as cordierite based glass-ceramic tile glazes. Results indicated that one of the selected compositions was capable of crystallizing cordierite under a fast-firing cycle used for tile production. Also, both the porosity of the glaze layer was sufficiently low and the crystal size small enough to ensure good mechanical and chemical properties.

Glass crystallization of compositions in the CaO–MgO–Al_2O_3–SiO_2 quaternary system allows to develop cordierite based glass-ceramics.[3–6] However, even though the required temperatures to bring about liquid phase are lower than for the MgO–Al_2O_3–SiO_2 ternary system, to reach full development of the glaze layer it is necessary the addition of certain fluxes which allowing to mature, i.e. the glaze should have a suitable surface tension to minimise crawling of the coating away from the edges or any hole that are present on firing. Moreover, in order to control the amount of crystallization and the size and shape of crystals certain components known as nucleating agents are also added. Results recently reported[6] on crystallization and microstructural development of several compositions in the cordierite primary crystallization field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system,[7] have shown the ability that some of them have to crystallize well developed cordierite on thermal treatment. However, these compositions must be adjusted to ensure the above required physico-chemical properties to proper maturing as well as good adhesion to the surface of the ceramic body and thermal expansion coefficient adequate to match the body requirements.

The purpose of the present paper is, therefore, to study the effects that several additives (fluxes and/or nucleants), added on the chosen glass to improve maturing, have on (1) the crystallization behaviour of the starting frits, and (2) the morphological features of cordierite crystals formed after several heat treatments. Moreover, we will test the feasibility that this potential glass-ceramic for tiles has to be developed by fast single firing.

2. Experimental procedure

2.1. Preparation of glasses

Based on previously reported results,[6] for this study it was chosen a reference glass of quaternary composition of 55/25/15/5 in wt.% of SiO_2, Al_2O_3, MgO and CaO, respectively. The reference glass without any type of additive, is referred to as sample A. For the rest of the glasses containing additional fluxes and/or nucleants, they have been added on the reference composition in amounts of 4 wt.% of oxides and the molar ratio between the four basic oxides CaO:MgO:$A1_2O_3$:SiO_2 is kept constant. The nucleant used is TiO_2 and the fluxes are B_2O_3 and/or a mixture of Na_2O and K_2O in a wt ratio of 1 to 3. The used nomenclature for all glasses is shown in Table 1. Glasses of the seven compositions were obtained by melting mixtures of the required amounts of SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, 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 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 20 μm.

To study the crystallization and microstructural evolution as a function of the thermal treatment for the several compositions cylindrical pellets of loosely pressed powder, i.e. under a pressure of about 5 MPa, were thermal treated at several temperatures up to 1200 °C and soaking periods. These conditions were chosen to simulate those in a 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 (Model TGA/SDTA 851^e, Mettler-Toledo, Schwerzenboch, Switzerland) was

Table 1
Nomenclature for the prepared glasses

Specimen	Composition
A	Glass reference without additives
B	A + TiO_2
C	A + TiO_2 + (Na_2O + K_2O)
D	A + B_2O_3
E	A + B_2O_3 + (Na_2O + K_2O)
F	A + TiO_2 + B_2O_3 + (Na_2O + K_2O)
G	A + TiO_2 + B_2O_3

carried out in N_2 atmosphere with α-Al_2O_3 liners, using a heating rate of 10 °C min^{-1}.

X-ray diffraction analysis (Model D-5000, Siemens, Karlsruhe, Germany) 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 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 the above field emission scanning electron microscope operated at 20 kV. 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 gold/palladium coated.

3. Results and discussion

3.1. Crystallization of glasses

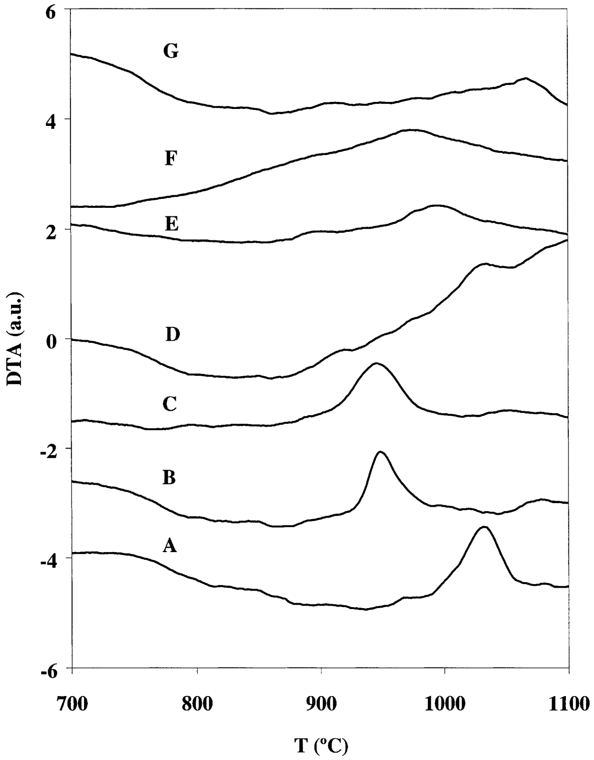

Fig. 1. DTA curves for glasses A–G.

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. 1. The samples in the DTA cell were cooled down by switching off the DTA furnace when reaching the final temperature and were examined by X-ray diffraction (Fig. 2). Since the only crystalline form of cordierite detected from our experiments is the hexagonal form of cordierite, α, hereafter it is referred to as cordierite.

As can be seen in Fig. 1 for the reference glass A an exothermic peak at 1020–1030 °C is displayed. XRD of the cooled sample after the DTA experiment displays the formation of cordierite as main crystalline phase as well as anorthite. For glasses containing different additives a main exothermic peak is also shown. The temperatures at which those exothermic effects appear are dependent on the nature and amount of the added additive. Thus, for samples B and C the exothermic effects appear at around 950 °C. However, it is of note that XRD of cooled specimen B displays the presence of both cordierite and anorthite whereas for the specimen C the detected phase is almost only anorthite. Specimens D and E display an exothermic peak at 1030 and 1000 °C, respectively, which can also be associated with the crystallization of cordierite and anorthite, respectively. In the case of specimen D, anorthite appears as a minor crystalline phase. Finally, specimens F and G do not show sharp exothermic peaks in DTA curves but after switching off and cooling down the samples displayed anorthite and cordierite phases, respectively, as main crystalline phases. Also, an small amount of anorthite is displayed by specimen G.

From the above results it is of note that for glasses containing TiO_2 as nucleant and/or B_2O_3 as flux, the major crystalline phase formed is cordierite but some minor amount of anorthite is also present. In contrast, glasses containing alkaline oxides as fluxes (in our case a combination of Na_2O and K_2O) the main and almost only crystalline phase is anorthite.

In order to confirm the above crystallization sequence depending on the type of additive added to the quaternary composition and to compare the relative availability of compositions to mature, pressed pellets of specimens were thermal treated at 900 and 1100 °C for 3 h. The set of crystalline phases detected by XRD are shown in Figs. 3 and 4. As can be seen at 900 °C only compositions B and G contain some amount of cordierite as well as anorthite, further heating of compositions containing TiO_2 and/or B_2O_3 as additives at 1100 °C develop cordierite as main crystalline phase. It is of note that for specimen A (without additives) at 1100 °C the crystallization of cordierite is outstanding. However, for compositions containing alkaline oxides (Na_2O and K_2O) no presence of cordierite is evidenced even after annealing for 3 h. For specimens containing these additives the one crystalline phase detected is anorthite.

The role of TiO_2 in the controlled crystallization of glasses in the cordierite primary phase field of the CaO–MgO–Al_2O_3–SiO_2 quaternary system has been the subject of several investigations.[8–9] De Vekey and Majumdar claimed the important role played by TiO_2 from the point of view of producing cordierite glass-ceramics with the desirable properties. They found that depending on the concentrations of nucleant in the glass the crystallization mechanism changes. Thus, for concentrations of TiO_2 in the glass of less than 7 wt.%, crystallization starts from the surface but once this limit is exceeded volume or bulk crystallization becomes the predominant mode. The concentration of TiO_2 in the glass used in our study was lower than 7 wt.%, however, X-ray diffraction results seem to indicate its favourable effect on the cordierite formation. The addition of B_2O_3 to cordierite glasses has also been extensively studied by several authors.[10,11] It has been found that this additive plays an important role in governing the crystallization behaviour and also improving the sinterability of the powders. As can be seen from our results the simultaneous action of both TiO_2 and B_2O_3 is quite effective in aiding the crystallization of cordierite

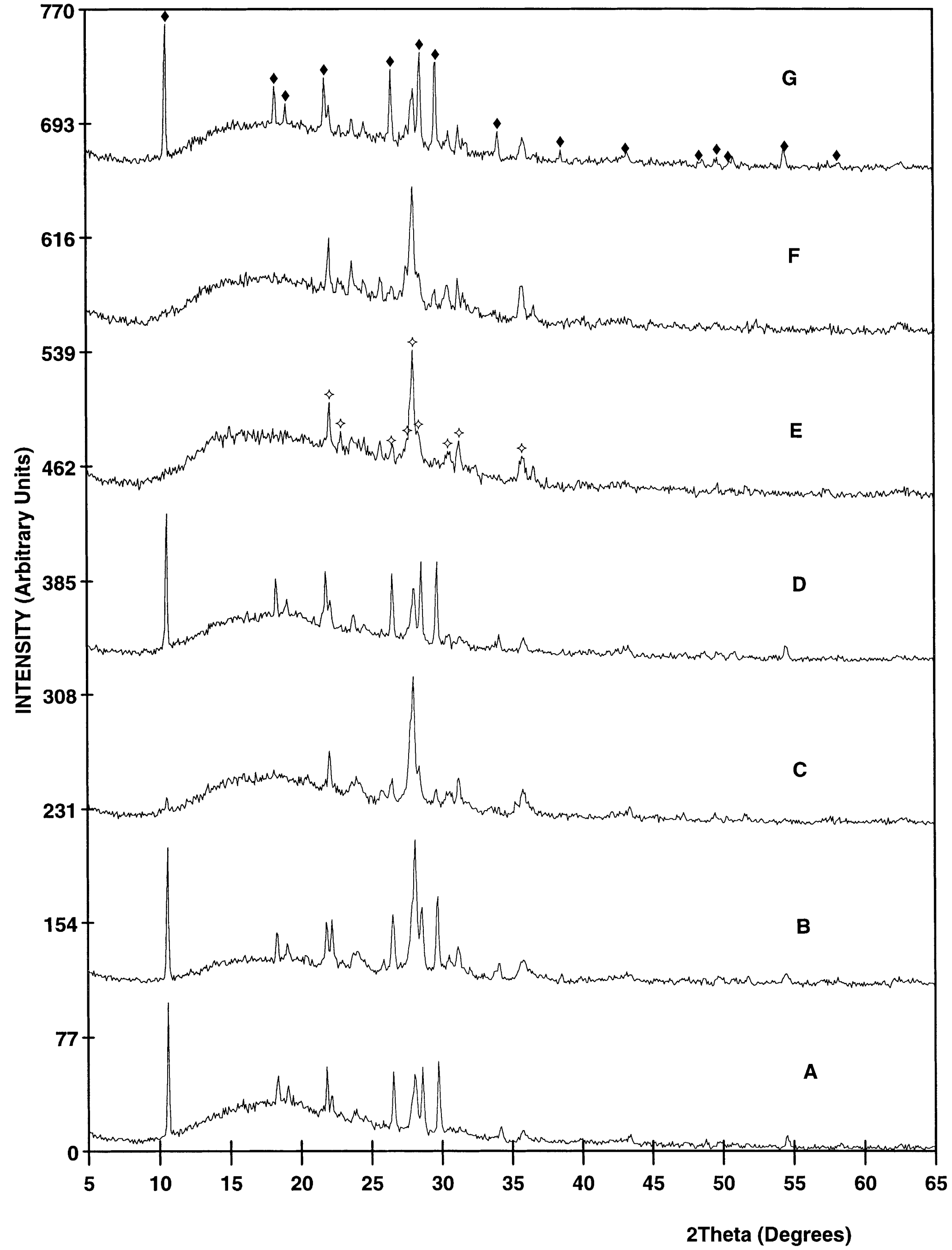

Fig. 2. XRD pattern of glasses A–G submitted to DTA runs (◇ is anorthite and ◆ is α-cordierite).

as major crystalline phase. It is to note the negative effect of Na_2O and K_2O as additives on the cordierite crystallization from our composition. Some authors, however, have reported results on cordierite crystallization from glasses containing alkaline oxides.[12]

From the above DTA and XRD results on powdered specimens thermal treated at several temperatures it can be concluded that glass G (the reference quaternary glass with TiO_2 and B_2O_3 as additives) is a good candidate to develop a cordierite-based glass-ceramic glaze.

3.2. Optimization of thermal treatment for glass G

In order to check whether or not it is possible to crystallize cordierite as the alone crystalline phase and the ability of the corresponding glaze to develop in a one-step thermal treatment, the glass with composition G has been submitted to several one- and two-step thermal treatments. It is of note that the processing temperature to which the glass can be heated must be lower than 1200 °C because tile supports produce faults

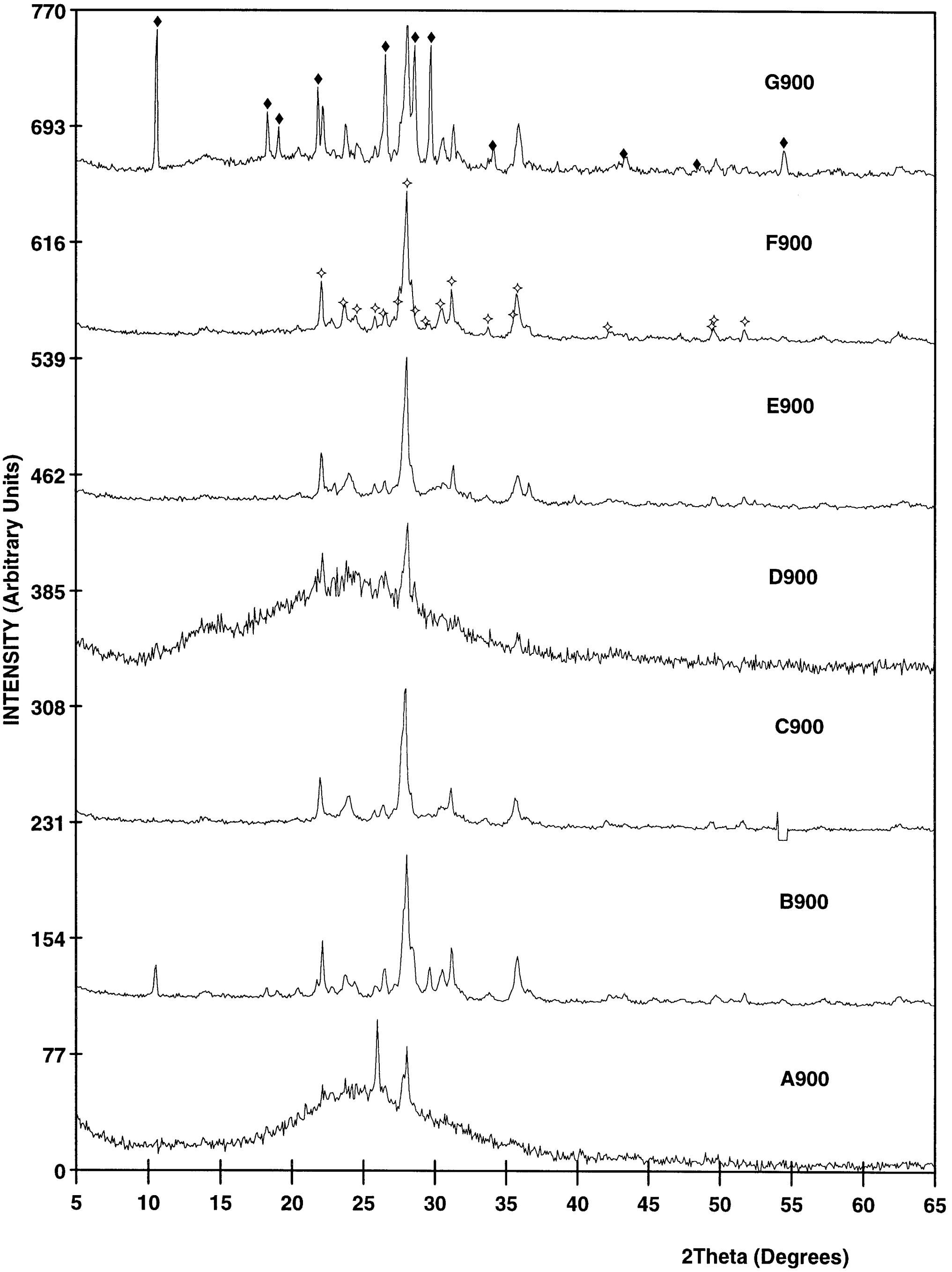

Fig. 3. XRD pattern of glasses A–G thermally treated at 900 °C for 3 h (◇ is anorthite and ◆ is α-cordierite).

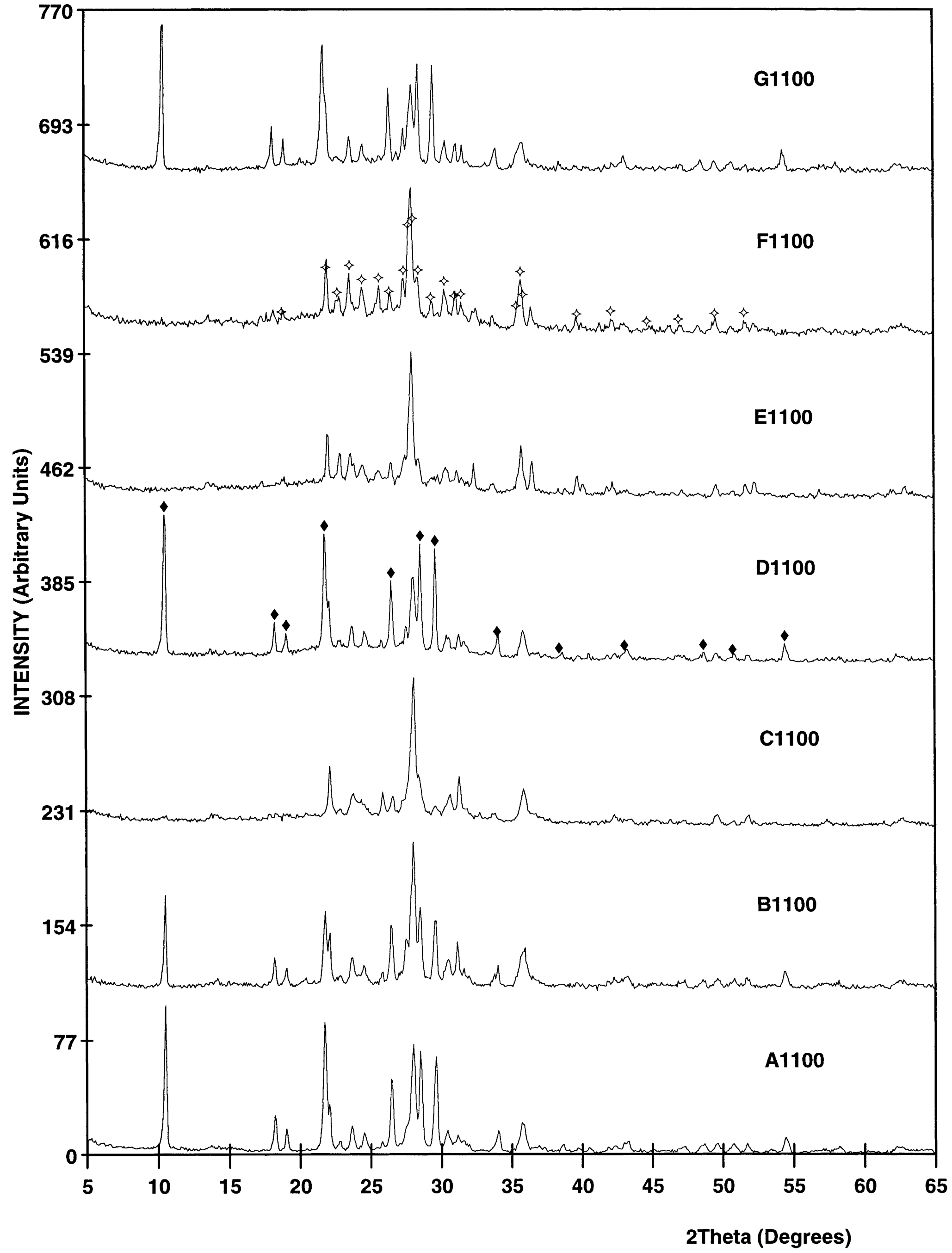

Fig. 4. XRD pattern of glasses A–G thermally treated at 1100 °C for 3 h (◇ is anorthite and ◆ is α-cordierite).

at higher temperatures. The two-step heating programs, hereafter TT1–TT4, included the heating of specimens up to 775 °C and holding at this temperature (which can be considered as the nucleation temperature) and further heating to 1100 °C (the growth temperature) and keeping at this several times. A summary of the holding times for the tested two-step thermal treatments is displayed in Table 2. The heating rate for both steps is 25 °C/ mm.

Table 2
Holding times (in min) for the two step thermal treatments

Thermal treatment	Time at 775 °C	Time at 1100 °C
TT1	30	5
TT2	120	5
TT3	5	30
TT4	5	120

The two one-step thermal treatments, hereafter TT5 and TT6, included a heating rate of 25 °C/min up to the end temperature of 1100 and 1160 °C, respectively, and holding for 5 min at this temperature. Fig. 5 displays the XRD patterns of glass G submitted at the above different thermal treatments. As can be seen for the heating schedules attempted when increasing the end temperature at 1160 °C for the one-step heating a glass ceramic containing cordierite as one crystalline phase is formed. For the other thermal treatments certain amount of anorthite is also detected. It is to be noted that the firing time for the thermal treatment TT6 takes less than 50 min, so it can be considered as a fast single thermal treatment.

3.3. Microstructural characterization of glass-ceramic G

Specimens of composition G after the several thermal treatments considered in the above section were examined by FESEM. Figs. 6 and 7 show the representative crystal

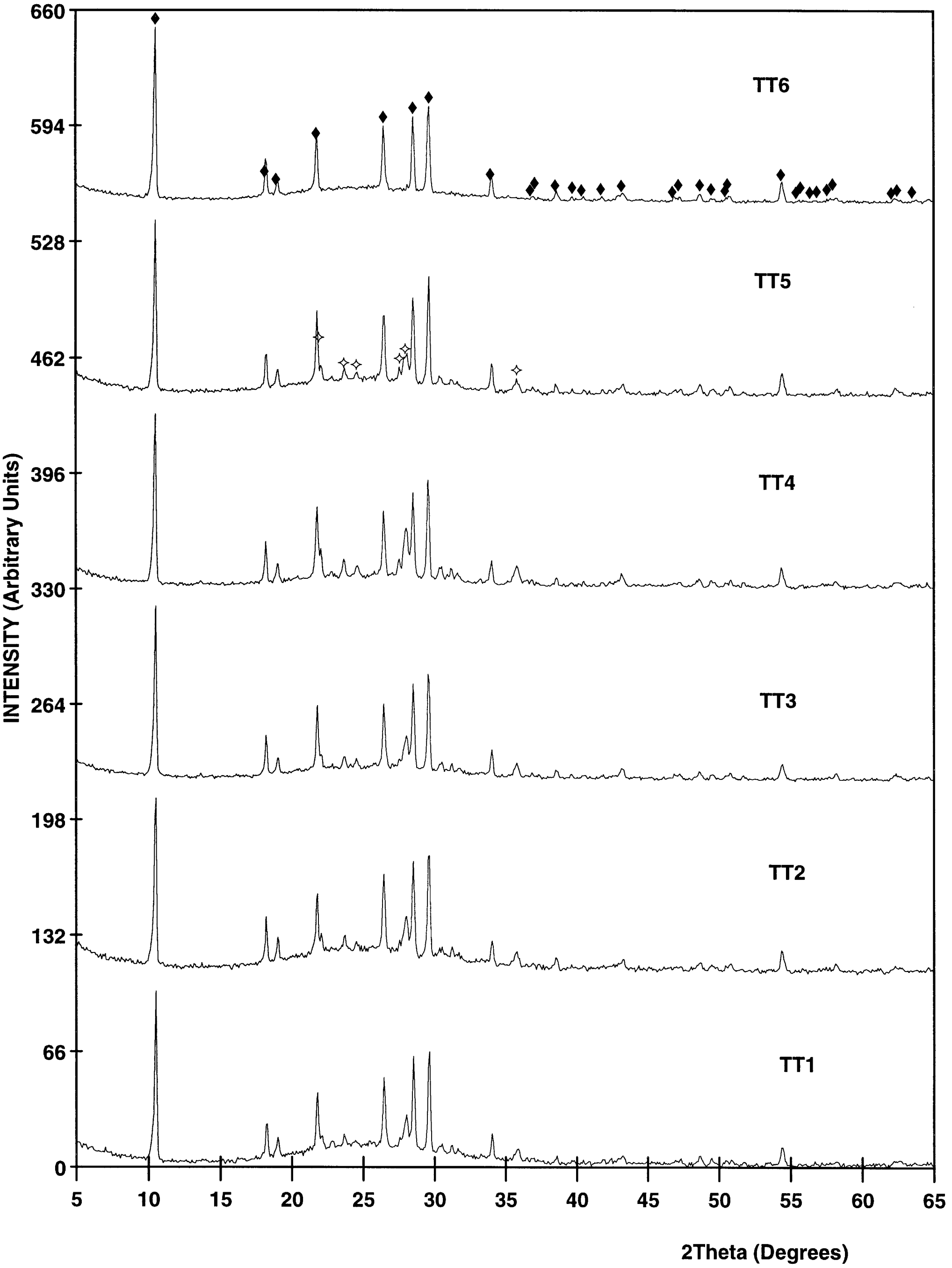

Fig. 5. XRD pattern of glass G after several thermal treatments (◇ is anorthite and ◆ is α-cordierite).

morphology developed after two-step and one-step thermal treatments TT1 and TT6, respectively. A more general view of the hexagonal prism arrangement for the treatment TT6 is shown in Fig. 8. As can be seen large crystals oriented in different directions, i.e. at random, display a well defined morphology of hexagonal prisms. Also from the micrographs it is inferred that these crystals are more defined after increasing either the nucleation and/or growth time in two-step heatings and by increasing the final temperature in one-step heatings.

Reported results in the literature on the crystallization of cordierite in bulk glasses with compositions in the $MgO–Al_2O_3–SiO_2$ ternary system revealed the formation of two kinds of morphologies.[13] For the first type, which is associated with the as-called primary cordierite, the shape of cordierite crystals is prismatic and is formed at low temperatures. Subsequent heating gives rise to the as-called secondary cordierite, which main feature is to be developed as well formed hexagonal prisms. The latter morphology has also been reported by other authors.[14,15]

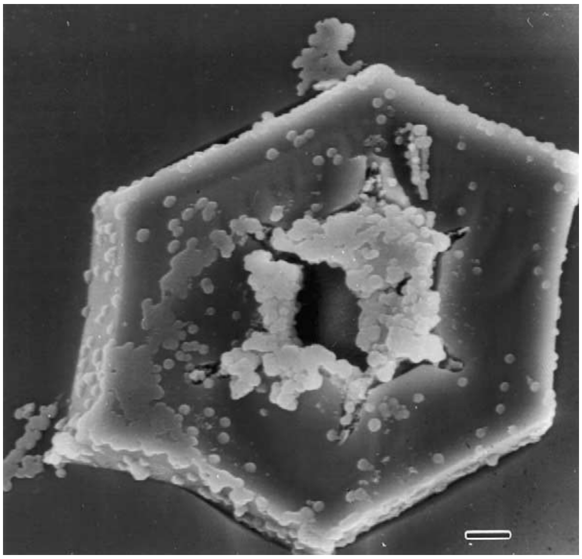
Fig. 6. FESEM micrograph of a hexagonal prism formed in glass G after thermal treatment TT1 (bar = 5 μm).

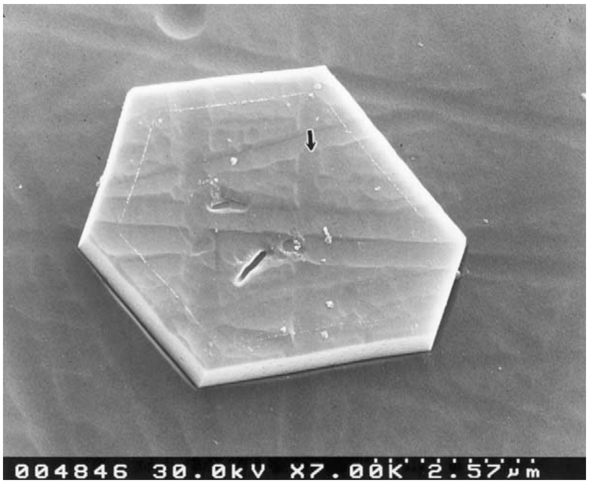

Fig. 7. FESEM micrograph of polished specimen showing a hexagonal prism formed in glass G after thermal treatment TT6 (bar = 2.5 μm).

The challenge of developing well shaped crystals of cordierite at temperatures lower than 1200 °C in loosely pressed powders only may be fulfilled by adding in the glass composition some fluxes and nucleants. Also, it would be advantageous to start from compositions in the $CaO–MgO–Al_2O_3–SiO_2$ quaternary system because the CaO plays the role of fluxing.[5,16,17] As far as we know until now there have been no reports on the crystallization of well formed crystals of cordierite hexagonal prisms in the quaternary system.

From the microstructure developed in these cordierite-based glass-ceramic glaze it would be worthy to consider that in the mechanism of crystal formation two facts have taken place. Firstly, the nucleation of cordierite nucleis occurring at low temperature is produced over all the glass specimen. Secondly, the growth of these metastable nucleis takes place at the higher temperatures when melting has been produced and there are favourable conditions for growing. It is, however, of note that it would be desirable to control the crystal growth to reach cordierite sizes around 1 μm.

One interesting feature to note in some hexagonal prisms is the fact that the inner central area in the prism is not fully developed, as shown in Fig. 9. It is formed by small particles which probably contain the components which only can enter into the cordierite phase in small amounts. So, they must be mainly secondary phases such as anorthite and/or glass particles rich in calcium oxide. EDX microanalysis results displayed in

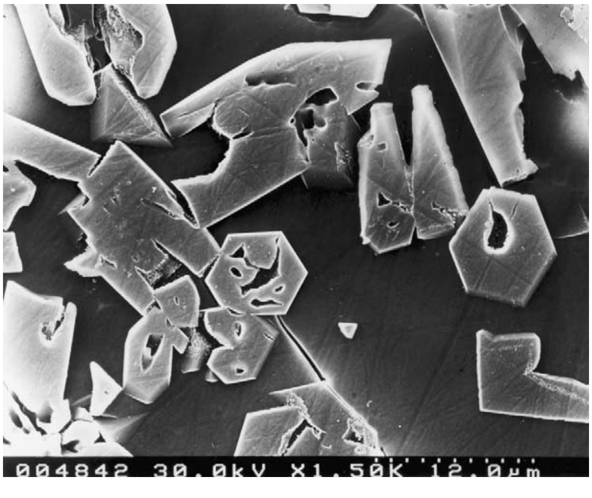

Fig. 8. FESEM micrograph of polished specimen showing a more large view of glass G after thermal treatment TT6 (bar = 12 μm).

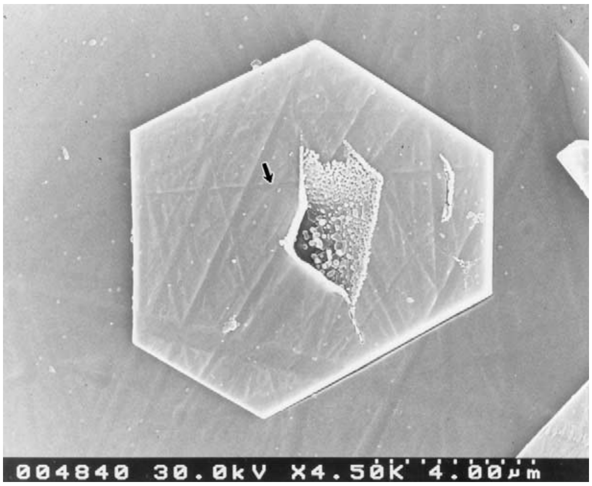

Fig. 9. FESEM micrograph of polished specimen showing a not fully developed hexagonal prism formed in glass G after thermal treatment TT6 (bar = 4 μm).

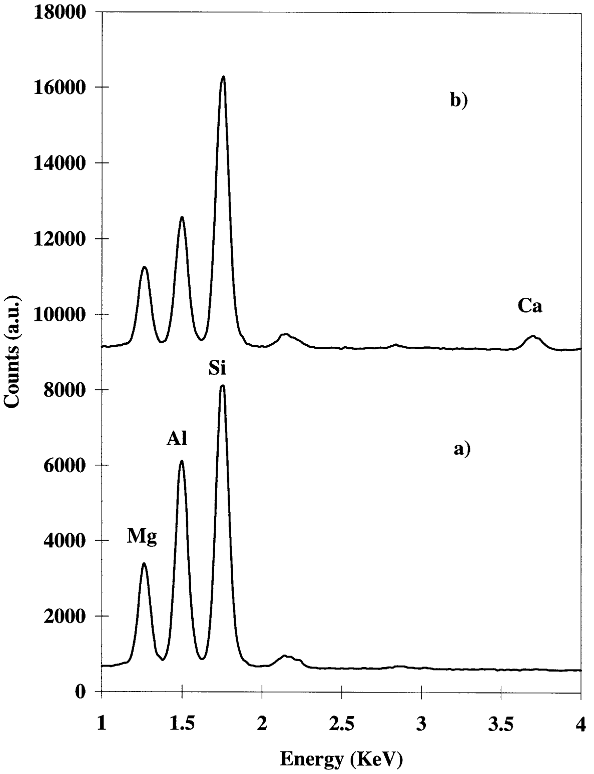

Fig. 10. EDX microanalysis of hexagonal prism formed in glass G after thermal treatment TT6: (a) completely developed (shown in Fig. 7), and (b) not fully developed (shown in Fig. 9).

Fig. 10 show differences in the composition of two similar points (indicated with an arrow) on the surface of both hexagonal prisms, i.e. completely and not fully developed, shown in Figs. 7 and 9. As can be seen it confirmed the increase of Ca content in the crystal which is not completely formed.

4. Conclusions

The effect of several additives such as fluxes and/or nucleants on a parent glass with composition located in the primary field of cordierite within the CaO–MgO–Al_2O_3–SiO_2 quaternary system has been examined. The crystallization behaviour and the microstructural evolution of the several glasses in the series were followed by thermal analysis, X-ray powder diffraction, field emission scanning electron microscopy and energy-dispersive X-ray microanalysis.

The results obtained indicated the feasibility of the proposed guideline to obtain a well developed cordierite-based glass-ceramic glaze from a cordieritic glass in the quaternary system CaO–MgO–Al_2O_3–SiO_2 and additional amounts of B_2O_3, as flux, and TiO_2, as nucleant. Furthermore, extended crystallization of cordierite as the only crystalline phase in fast single firing processes was achieved. Also a well defined morphology of the cordierite crystals was developed within the glass matrix.

Acknowledgements

The authors thank IMPIVA and SALONI for financial support of this work.

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