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TEM Investigation of Cordierite Crystallization from a Glass Powder with Composition $Mg_2Al_4Si_{11}O_{30}$

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Abstract

The crystallization of a glass powder with composition $Mg_2Al_4Si_{11}O_{30}$ to β-quartz$_{ss}$ and the transformation of β-quartz$_{ss}$ to α-cordierite were investigated by means of SEM and TEM. Crystallization of β-quartz$_{ss}$ starts at the surfaces of the glass grains. At first growth proceeds nearly isotropically, but due to mutual hindrance growth perpendicular to the surface is preferred when the β-quartz$_{ss}$ crystals impinge on each other. The transformation of β-quartz$_{ss}$ to cordierite starts at the surfaces of the β-quartz$_{ss}$ crystals. In a first stage the cordierite nuclei grow over long distances only along the grain boundaries of several β-quartz$_{ss}$ crystals. On prolonged annealing the cordierite rims grow dendritically into the cores of β-quartz$_{ss}$, maintaining the same crystallographic orientation.

1 Introduction

In recent years the fabrication and the properties of glass-ceramics based on cordierite ($Mg_2Al_4Si_5O_{18}$) have frequently been investigated due to the extraordinary combination of valuable properties of cordierite. The excellent electrical properties of cordierite such as high volume resistivity ($\approx 3 \times 10^{15}$ Ω cm) and low dielectric constant ($\approx 5{\cdot}3$ at 1 MHz) make it a promising material, especially for integrated circuit devices.[1,2] Moreover, cordierite glass-ceramics have a low thermal expansion coefficient (1–2×10^{-6}/K),[3,4] matching approximately that of silicon, a high deformation temperature, high chemical durability and high mechanical strength.

The double-ring silicate MAS osumilite ($Mg_2Al_4Si_{11}O_{30}$) is another compound from the system MgO–Al_2O_3–SiO_2 with structural and physical properties similar to those of cordierite.[5] This phase is metastable but endures extended heat treatments up to 1150°C. The similar thermal expansion behaviour to cordierite makes MAS osumilite ($\alpha_{25-600°C}$: $1{\cdot}1 \times 10^{-6}$/K) also very interesting for glass-ceramic applications. MAS osumilite crystallizes from glasses of a narrow compositional range in the system MgO–Al_2O_3–SiO_2 with BaO or SrO additions. The crystallization of MAS osumilite from glass proceeds via a complex mechanism involving nucleation of precursor Ba- or Sr-containing osumilite phases and a high quartz solid solution (β-quartz$_{ss}$, $MgAl_2Si_xO_{4+2x}$) which subsequently is transformed into MAS osumilite.[6]

However, when a glass of MAS osumilite composition itself without any additions is heat treated, MAS osumilite never crystallizes under any conditions. The glass crystallizes only to β-quartz$_{ss}$ and, at higher temperatures, the thermodynamically stable phases cordierite and α-quartz or cristobalite.

Depending on the glass composition, the sintering additives, nucleating agents and the crystallization temperature the crystallization sequence of cordierite-type glass powders and the microstructural development differ considerably.[7–11] The devitrification process of TiO_2- and ZrO_2-containing cordierite glasses usually involves phase separation in the liquid state. At low temperatures β-quartz$_{ss}$ always appears as a metastable precursor which transforms into cordierite after prolonged heating. At higher temperatures above about 1000–1200°C no β-quartz$_{ss}$ appears and cordierite crystallizes directly from the glass.

The morphology of the initial β-quartz$_{ss}$ varies greatly. In a sintered glass-ceramic with greater MgO and lower Al_2O_3 than stoichiometric

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cordierite with additions of P_2O_5 and B_2O_3 Bridge *et al.*[1] found roughly spherical crystals concentrating at the original boundaries of the glass particles. Rudolph *et al.*[12] examined a glass with a similar basic composition but without B_2O_3. They report a β-quartz$_{ss}$ skeleton forming along the original particle surfaces. In this thin β-quartz$_{ss}$ layer individual crystals could not be identified. Similar β-quartz$_{ss}$ boundary layers together with co-precipitated spherulitic ZrO_2 were observed by McCoy & Heuer[13] in a glass of similar composition containing 15 wt% ZrO_2. However, the ZrO_2 crystallites did not act as nucleation sites for the β-quartz$_{ss}$ crystals. In bulk glasses containing more SiO_2 and additions of ZrO_2, TiO_2 or CaF_2 Zdaniewski[8] observed spherulitic growth of β-quartz$_{ss}$.

Chaim & Heuer[14] studied the crystallization sequence of a glass with stoichiometric cordierite composition and an addition of 2 wt% BaO. In this glass the crystallizing β-quartz$_{ss}$ had a dendritic hexagonal morphology. BaO was rejected from the growing β-quartz$_{ss}$ and concentrated in an interdendritic amorphous phase. On the other hand, in the crystallization sequence of an MAS osumilite glass-ceramic from a similar BaO-containing glass but with higher SiO_2 content Winter *et al.*[6] found rounded and elongated non-dendritic β-quartz$_{ss}$ crystals nucleating at the original particle surfaces and growing perpendicular to the surfaces into the cores of the glass grains. BaO was rejected into an intergranular residual glass phase.

The microstructural evolution of a glass-ceramic during the transformation of β-quartz$_{ss}$ to cordierite and the mechanism of this process have been investigated by several authors. Watanabe *et al.*[15] described the variations in morphology of cordierite crystallizing both from β-quartz$_{ss}$ or directly from the glass as a function of crystallization temperature. Barry *et al.*[16] investigated the bulk crystallization of glasses of stoichiometric cordierite composition with various amounts of TiO_2 and ZrO_2. With increasing temperature these authors observed continuous exsolution of MgO and Al_2O_3 from β-quartz$_{ss}$ and formation of spinel and sapphirine. At temperatures above 1150°C the remaining SiO_2-rich β-quartz$_{ss}$ reacts with the exsolution products to form cordierite. Chaim & Heuer[14] showed that in BaO-containing compositions cordierite nucleates within the dendritic β-quartz$_{ss}$ grains or at the β-quartz$_{ss}$/glass interfaces. The morphology of cordierite also is dendritic and growth proceeds preferentially within the β-quartz$_{ss}$ grains.

The present paper presents a detailed study of the crystallization mechanism in a glass of composition $Mg_2Al_4Si_{11}O_{30}$ without any additives. The focus was mainly on the nucleation of cordierite and the transformation of the precursor phase β-quartz$_{ss}$ into cordierite. As already reported, the mechanisms of these processes are supposed to depend critically on the composition and the morphology of β-quartz$_{ss}$ and hence on the composition of the parent glass. In particular, an understanding of the present crystallization mechanism might also explain why MAS osumilite does not crystallize although the glass investigated is of MAS osumilite composition.

2 Experimental Details

The glass investigated has the composition of MAS osumilite ($Mg_2Al_4Si_{11}O_{30}$) (in wt%: 8·5 MgO; 21·6, Al_2O_3; 69·9 SiO_2). Stoichiometrically, this composition can be described as a mixture of 61·8% cordierite and 38·2% SiO_2.

A homogeneous glass was prepared from reagent grade Al_2O_3 and MgO from Merck AG (Darmstadt, Germany) and SiO_2 (Sipur, Bremthaler Quarzwerke, Usingen, Germany) by melting the constituents at 1550°C for 4 h in platinum crucibles and quenching the melt into cold water. After grinding the glass frit in an alumina ball mill to a grain size <63 μm samples for the crystallization process were cold-isostatically pressed. The 10 × 4 × 4 mm sized samples were put into a preheated furnace and crystallized isothermally at a temperature of 1150°C and various heating times.

The nucleation and crystallization sequence of the glass powder was studied by means of SEM and TEM.

For TEM preparation the crystallized samples were cut into thin sections which were ion thinned with a 5 kV argon beam. The TEM analyses were performed on a Philips CM12 microscope (Philips, Eindhoven, The Netherlands) equipped with an EDAX 9900 EDX device. Polished and HF-etched samples were studied with a Philips SEM500 scanning electron microscope.

3 Results

The first phase appearing in the crystallization sequence is β-quartz$_{ss}$ nucleating at the surfaces of the glass grains. Growth proceeds isotropically in a first stage, but due to mutual hindrance further growth proceeds preferentially perpendicular to the surface into the volume of the glass grains. Figure 1 shows a typical microstructure of an early growth stage with slightly elongated β-quartz$_{ss}$ crystals growing from the surface into the residual glass at the centre of the glass grain.

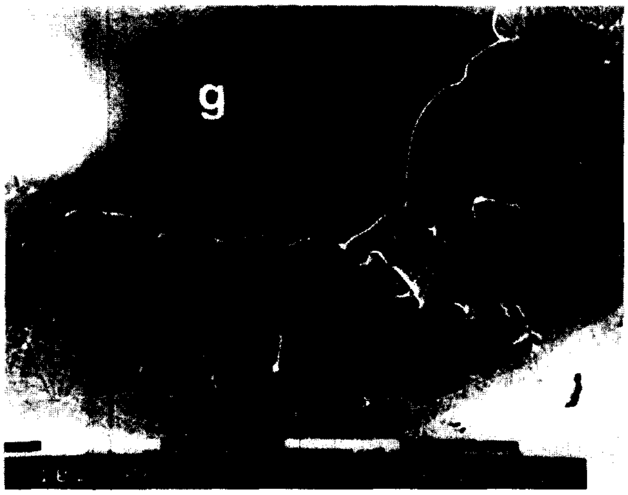

Fig. 1. SEM micrograph of several elongated β-quartz$_{ss}$ crystals growing from the surface (bottom) into the centre of a glass grain (g). Heat treatment: 1150°C, 2 min.

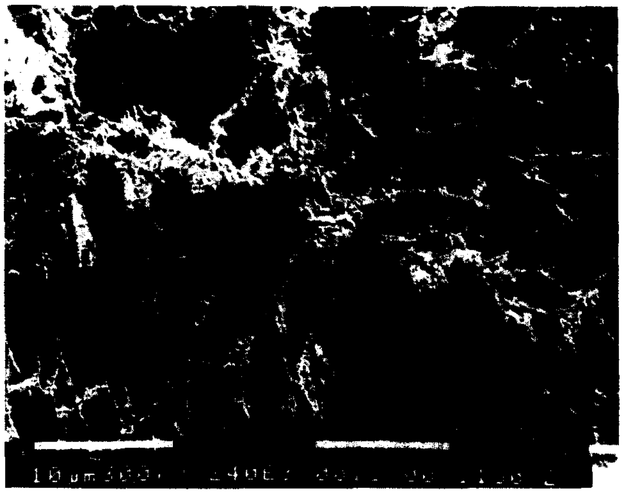

Fig. 3. SEM micrograph of the cordierite network (bright areas) around the β-quartz$_{ss}$ grains (dark areas) in the centre of a former glass grain. Heat treatment: 1150°C, 10 min.

EDX analysis confirmed that the composition of the β-quartz$_{ss}$ crystals corresponds to that of the parent glass which has the theoretical composition of the starting mixture. No residual glass phase could be found on the grain boundaries between adjacent β-quartz$_{ss}$ crystals by means of TEM (Fig. 2). EDX measurements suggest that the chemical composition is homogeneous within one β-quartz$_{ss}$ crystal and within the whole sample.

The transformation of β-quartz$_{ss}$ to α-cordierite starts at the grain boundaries of the β-quartz$_{ss}$ crystals. In a first stage the cordierite nuclei always grow along β-quartz$_{ss}$ grain boundaries. Figure 3 shows a typical cordierite network around the β-quartz$_{ss}$ crystals in the centre of a former glass grain. TEM diffraction analysis shows that this network typically consists of cordierite crystals forming rims of the same orientation over large areas and surrounding numerous β-quartz$_{ss}$ grains. Figure 4 shows an example with cordierite in an $[0\bar{2}1]$ orientation. Only a slight rotation around the $[0\bar{2}1]$ zone axis is observed during growth over about 4 μm along the grain boundaries of several adjacent β-quartz$_{ss}$ grains.

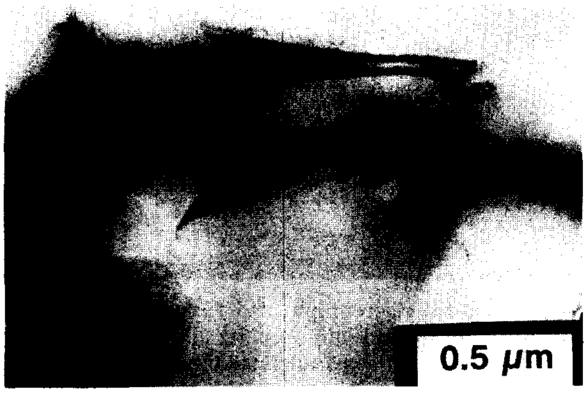

Fig. 2. TEM micrograph of grain boundaries between β-quartz$_{ss}$ crystals. Heat treatment: 1150°C, 2 min.

The dark field photograph of another locality of the sample shows that the cordierite rims along the β-quartz$_{ss}$ grain boundaries have a dendritic spinal-type microstructure with an interspatial amorphous phase (Fig. 5). The volume of this phase is too small for an EDX analysis but as the β-quartz$_{ss}$ crystals are much richer in SiO_2 than cordierite a second phase with a relatively high SiO_2 concentration must be formed during the β-quartz$_{ss}$ to cordierite transformation.

Starting from the β-quartz$_{ss}$ grain boundaries the cordierite rims begin to grow into adjacent β-quartz$_{ss}$ grains. Frequently, preferred growth planes of cordierite are observed. The bright and dark field photographs of Fig. 6 show a cordierite crystal with pronounced lamellar growth along (100) planes. These growth planes are preferred probably due to their high atom occupancy. It was frequently observed that starting from the same cordierite rim crystal the (100) planes grow into different β-quartz$_{ss}$ crystals without changing

Fig. 4. TEM BF micrograph of the first stage of cordierite growth along grain boundaries of several β-quartz$_{ss}$ grains. Heat treatment: 1150°C, 60 min.

Fig. 5. TEM (100) DF micrograph of the spinal morphology of the cordierite rims on the β-quartz$_{ss}$ grain boundaries. Heat treatment: 1150°C, 60 min.

Fig. 7. BF micrograph of the dendritic growth of cordierite in a highly transformed β-quartz$_{ss}$ crystal. Orientation of cordierite is [001] parallel to the electron beam. {100} faces are preferentially formed. Heat treatment: 1150°C, 60 min.

their orientation. This suggests that the transformation does not proceed along distinct directions of the β-quartz$_{ss}$ structure. Hence, it is not of a topotactic nature. The orientation of cordierite growth within a β-quartz$_{ss}$ crystal depends only on the orientation of the cordierite seed crystals.

In Fig. 7 a β-quartz$_{ss}$ grain is penetrated completely by a cordierite dendrite in a more advanced stage of the transformation process. The cordierite crystal maintains its orientation over the whole former β-quartz$_{ss}$ grain with the [001] zone axis parallel to the electron beam as can be seen from electron diffraction (SAD). This orientation shows, that preferentially hexagonal prismatic {100} planes are formed. Since the transformation of β-quartz$_{ss}$ into cordierite is not an isochemical reaction again an SiO_2-rich amorphous phase develops within the cordierite dendrites.

After about 3 h at 1150°C, the amorphous SiO_2-rich phase between the cordierite dendrites has crystallized to β-quartz. The α-quartz crystals can reach the size of a former β-quartz$_{ss}$ grain, show-

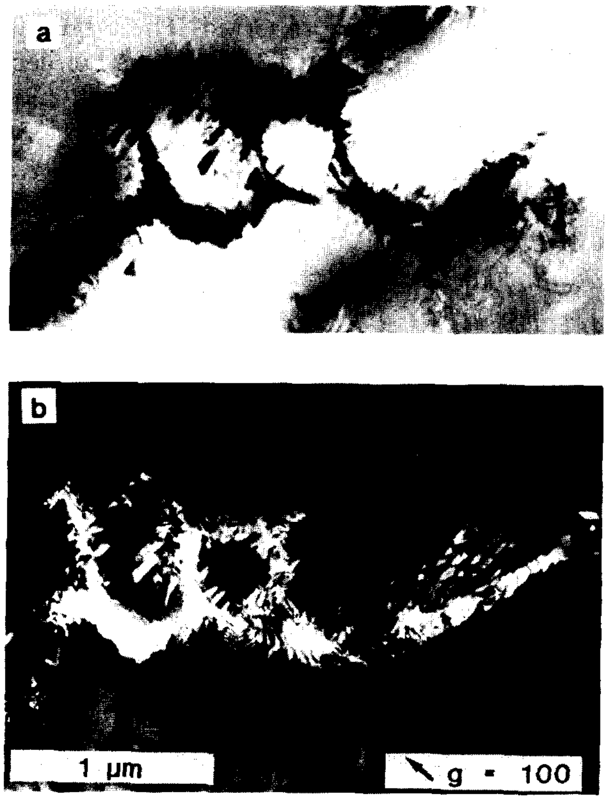

Fig. 6. (a) TEM BF micrograph, (b) TEM (100) DF micrograph of the preferred growth of cordierite along (100) planes into neighbouring β-quartz$_{ss}$ grains. Heat treatment: 1150°C, 60 min.

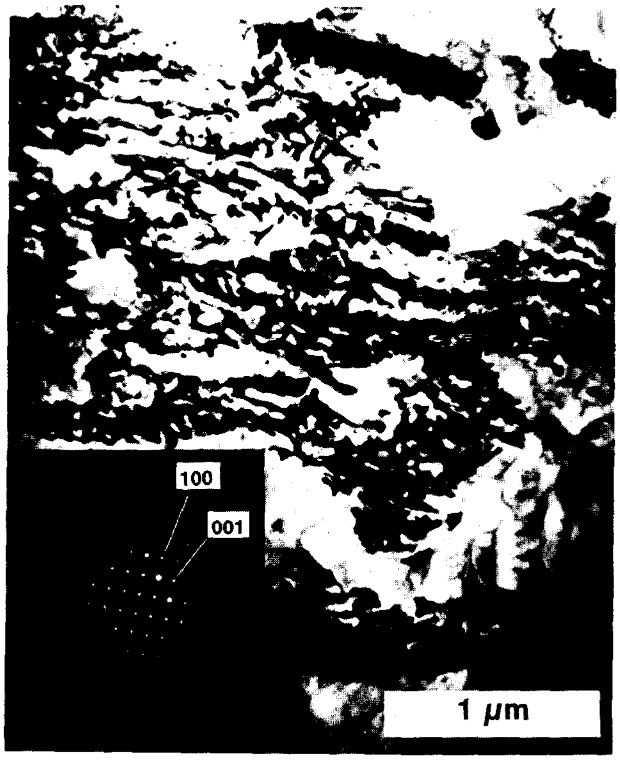

Fig. 8. TEM BF micrograph of a former β-quartz$_{ss}$ crystal completely transformed into α-quartz and cordierite. α-Quartz with orientation $[0\bar{1}0]$ parallel to the electron beam. The forbidden reflections $00l$ with $l = 3$ result from dynamical interaction of $h00$ and $h0l$ reflections. Heat treatment: 1150°C, 60 min.

ing a dendritic morphology that is finely interlaced with the cordierite dendrites (Fig. 8).

4 Discussion

In the crystallization sequence of the studied glass MAS osumilite did not appear, although the glass is of MAS osumilite composition ($Mg_2Al_4Si_{11}O_{30}$). This is in accordance with previous results about MAS-osumilite crystallization from BaO containing glasses[5,6] and can be explained in terms of the nucleation kinetics of the crystallizing phases. For the formation of MAS osumilite pre-crystallization of a stable osumilite-type phase such as Ba osumilite ($BaMg_2Al_6Si_9O_{30}$) is necessary on which it can nucleate epitactically. Even then MAS osumilite nucleation competes with the simultaneous epitactic nucleation of cordierite on Ba osumilite. However, the nucleation rate of MAS osumilite is higher than that of cordierite in this case. In a pure MAS osumilite glass the formation of a stable osumilite-type phase is not possible. Cordierite, on the other hand, can nucleate at the interfaces between the β-quartz$_{ss}$ crystals, but although the crystal structures are similar, cordierite does not supply suitable surfaces for epitactic nucleation of MAS osumilite. One reason for this is that the cordierite surfaces are enriched in SiO_2 and hence no longer of the MAS osumilite composition.

The second interesting observation concerns the differences in the growth morphologies between β-quartz$_{ss}$ and cordierite. The nucleation of both phases is interface induced. The interfaces of the glass grains and of the β-quartz$_{ss}$ crystals, respectively, represent the nucleation sites for β-quartz$_{ss}$ and cordierite.

Metastable β-quartz$_{ss}$ nucleates first, possibly because it has a closer relation with the glass structure than α-cordierite. In a first stage the growth of β-quartz$_{ss}$ is isotropic. When neighbouring crystals impinge on each other further growth is only possible perpendicular to the surface of the glass grains into their core and the β-quartz$_{ss}$ crystals become more elongated.

On the other hand, the first nucleating cordierite crystals show a preferred growth along the β-quartz$_{ss}$ surfaces. Thus, the β-quartz$_{ss}$ crystals are characterized by an isotropic three-dimensional growth while the first nucleating cordierite crystals show only two-dimensional growth. The differences in crystal growth morphology and orientation are supposed to depend on the transformation kinetics of the glass to β-quartz$_{ss}$ and the β-quartz$_{ss}$ to cordierite transformation, respectively. The decisive difference in the crystallization of β-quartz$_{ss}$ and cordierite in the present glass lies in the different chemical compositions. The glass to β-quartz$_{ss}$ transformation proceeds isochemically, whereas the β-quartz$_{ss}$ to cordierite transformation is of an allochemical nature. Hence, the latter process is diffusion controlled. Grain boundaries generally represent a defective crystal structure of a higher energy state than the perfect crystal. Hence, crystallization and growth of cordierite along the β-quartz$_{ss}$ grain boundaries provides both a fast reduction of stored energy and effective diffusion paths. The present results show that this leads to fast two-dimensional growth. Obviously, the growth rate of cordierite along the grain boundaries is very high in comparison to the nucleation rate. During growth into the cores of the β-quartz$_{ss}$ grains the diffusion rate probably limits the growth rate of cordierite. The necessity for the cordierite crystals to pierce through a simultaneously rejected SiO_2-rich layer during growth results in the formation of a dendritic morphology.

5 Conclusion

The present results suggest that in general the nucleation and growth kinetics and the morphology of cordierite during the β-quartz$_{ss}$ to cordierite transformation depend critically on the morphology and chemical composition of the β-quartz$_{ss}$ crystals. In the present case of diffusion-controlled cordierite crystallization from β-quartz$_{ss}$ of a different chemical composition two stages can be distinguished:

(i) fast two-dimensional growth along the β-quartz$_{ss}$ grain boundaries leads to formation of a cordierite network with relatively large areas of the same crystallographic orientation.

(ii) cordierite growth proceeds dendritically into the bulk of the β-quartz$_{ss}$ grains. Quartz crystallizes within the SiO_2-rich dendritical interspaces.

References

1. Bridge, D. R., Holland, D. & McMillan, P. W., Development of the alpha-cordierite phase in glass-ceramics for use in electronic devices. *Glass Technology*, **26**(6) (1985) 286–92.
2. Owate, I. O. & Freer, R., Electrical properties of some cordierite glass-ceramics in the system MgO–Al_2O_3–SiO_2–TiO_2. *J. Mater. Sci.*, **25**(12) (1990) 5291–7.
3. Lachman, I. M., Bagley, R. D. & Lewis, R. M., Thermal expansion of extruded cordierite ceramics. *Am. Ceram. Soc. Bull.*, **60**(2) (1981) 202–5.
4. Hirose, Y., Doi, H. & Kamigaito, O., Thermal expansion of hot-pressed cordierite glass-ceramics. *J. Mater. Sci Lett.*, **3**(2) (1984) 153–5.

5. Winter, W., Bogdanow, C., Müller, G. & Pannhorst, W., Crystallization sequence of Ba-osumilite and MAS-osumilite glass-ceramics with low thermal expansion. *Glastech. Ber.*, **66**(5) (1993) 109–17.
6. Winter, W., Berger, A., Müller, G. & Pannhorst, W., Crystallization mechanism of an MAS–osumilite with composition $Mg_2Al_4Si_{11}O_{30}$ from glass. *J. Am. Ceram. Soc.*, **76**(7) (1993) 1837–43.
7. Zdaniewski, W., Crystallization and structure of a MgO–Al_2O_3–SiO_2–TiO_2 glass-ceramic. *J. Mater. Sci.*, **8** (1973) 192–202.
8. Zdaniewski, W., Microstructure and kinetics of crystallization of MgO–Al_2O_3–SiO_2 glass-ceramics. *J. Am. Ceram. Soc.*, **61**(5–6) (1978) 199–204.
9. McCoy, M., Lee, W. E. & Heuer, A. H., Crystallization of MgO–Al_2O_3–SiO_2–ZrO_2 glasses. *J. Am. Ceram. Soc.*, **69**(3) (1986) 292–6.
10. Sue, Y. J., Shen, P., Chen, S. Y. & Lu, H. Y., Spherulitic growth from a phase-separated vitreous matrix in a cordierite-Y-stabilized zirconia glass-ceramic. *J. Am. Ceram. Soc.*, **74**(1) (1991) 85–91.
11. Lim, B. C. & Jang, H. M., Phase transformation in seeded monophasic cordierite gel. *Ceram. Trans.*, **22** (1991) 431–6.
12. Rudolph, T., Szabo, D. V., Pannhorst, W., Weisskopf, K. L. & Petzow, G., Microstructural development of a P_2O_5-modified cordierite glass ceramic during sintering. *Glastech. Ber.*, **64**(8) (1991) 218–24.
13. McCoy, M. A. & Heuer, A. H., Microstructural characterization and fracture toughness of cordierite–ZrO_2 glass-ceramics. *J. Am. Ceram. Soc.*, **71**(8) (1988) 673–7.
14. Chaim, R. & Heuer, A. H., Crystallization in a Ba-containing magnesium aluminosilicate glass-ceramic. *J. Am. Ceram. Soc.*, **75**(6) (1992) 1512–21.
15. Watanabe, K., Giess, E. A. & Shafer, M. W., The crystallization mechanism of high-cordierite glass. *J. Mater. Sci.*, **20** (1985) 508–15.
16. Barry, T. I., Cox, J. M. & Morrell, R., Cordierite glass-ceramics—effect of TiO_2 and ZrO_2 content on phase sequence during heat treatment. *J. Mater. Sci.*, **13** (1978) 594–610.