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Phase evolution by thermal treatment of equimolar cobalt–magnesium cordierite glass powders

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Abstract

The structural evolution with annealing time at temperatures between 900 and 1100 °C of loosely compacted equimolar cobalt–magnesium cordierite glass powder was reported. The glass, with composition $MgCoAl_4Si_5O_{18}$, was prepared by melting a glass precursor, previously synthesized by a semiwet method, at 1650 °C. Field emission scanning electron microscopy (FESEM) of isothermally heated glasses at 900 and 950 °C revealed increased phase separation with thermal treatment. X-ray diffraction (XRD) results of these powders indicated that the first crystalline phase formed was μ cobalt-containing cordierite which transformed to α cordierite with longer annealing. At the beginning of the μ to α transformation, mullite and cobalt–magnesium aluminate spinel were detected but on further annealing they disappear. Infrared (IR) spectroscopy after long annealing at 1100 °C showed that some ordering for aluminium and silicon in tetrahedral sites had taken place, indicating some transformation to the orthorhombic crystalline form, β, of cordierite. FESEM examination revealed that the μ-cordierite grew by a dendritic mechanism along the particle surface and that the nucleation and growth of α-cordierite occurs within the μ-cordierite dendrites. Finally, after short annealing at 1100 °C the fully crystallized microstructure developed was α-cordierite with columnar or linear features.

Keywords: Cordierite; Crystallization; Glass powder; Microstructure; $MgCoAl_4Si_5O_{18}$

1. Introduction

Cordierite based materials are very important because of their very outstanding thermal, chemical and electrical properties.[1,2] As a consequence, they have been widely used as a material in kiln furniture, carriers of purifying exhaust emission, heat exchanger for gas turbine engines and partial electronic components.

The mineral cordierite ($Mg_2Al_4Si_5O_{18}$) usually contains other cations in solid solution, which either substitute for Mg^{+2}, Al^{+3} or Si^{+4} or are inserted in the channel sites of the cordierite framework.[3,4] Also a considerable number of papers have been concerned with synthesis, characterization and measurement of properties in substituted cordierites. Thus, reported results on cordierites in which Mg^{+2}, Al^{+3} and Si^{+4} have been substituted by Mn^{+2}, Ga^{+3} and Ge^{+4}, respectively, indicate some modifications of the thermal expansion behaviour in high temperature cordierite.[5] The introduction of other cations with different chemical states in the high cordierite structure, such as Ca^{+2}, Cu^{+2}, Eu^{+3} has been also carried out.[6–8]

Recently, we have reported results on the synthesis and characterization of cobalt and nickel cordierites by crystallization of parent glasses at around 1100 °C.[9,10] In the cobalt-containing cordierite system μ- and α-cordierites were prepared with compositions $Co_2Al_4Si_5O_{18}$ and $MgCoAl_4Si_5O_{18}$. The pure cobalt phases with the structure of μ- and α-cordierites were also characterized by infrared and ultraviolet–visible spectroscopies. Microscopic examination by field emission scanning electron microscopy (FESEM) did not reveal defined morphologies for these phases.

From our view it would be interesting to make cobalt-containing μ- and α-cordierite based materials, from some compositions in the $CoO–MgO–Al_2O_3–SiO_2$ quaternary system, because of potential applications as ceramic pigments and luminescent materials. However, there is not enough information on the details of the reaction sequence for heating loosely pressed glass

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powder with these compositions. Therefore, the main purposes of this paper are: (i) to establish the complete mechanism of crystallization of equimolar magnesium and cobalt cordierite glass powder and compare with the one observed for pure magnesium cordierite glass and (ii) to follow the microstructural evolution during isothermal treatments at different temperatures from the glass precursor up to the final cordierite phase.

2. Experimental procedure

2.1. Preparation and thermal treatment of glasses

Glass with stoichiometric composition $MgCoAl_4Si_5O_{18}$ was prepared by a previously reported semiwet method.[9] The $Mg_2Al_4Si_5O_{18}$ glass was synthesized as a reference. Its synthesis and crystallization path have been reported elsewhere.[9,11–14]

Glass precursor for cobalt–magnesium glass specimen, thereafter COMG, was prepared by the following procedure. Appropriate amounts of reagent-grade $Al(NO_3)_2{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in distilled water at 80 °C with vigorous stirring. To the resulting dissolution the required loads of SiO_2 and $MgCO_3$ were added. The dispersion was then heated until dryness followed by drying in an oven at 110 °C for one day. The resultant powder was ground and calcined at 1000 °C for 2 h to remove nitrate, and after regrinding it was melted at around 1650 °C for 3 h. The glass was re-melted twice to increase the homogeneity and the last melt was poured into a brass mould to form glass rods.

After milling the glass rods to powder with particle sizes <30 μm, cylindrical pellets of glass powder were obtained by pressing at 5 MPa. The specimens were subsequently isothermally treated at temperatures between 900 and 1100 °C in an electric furnace during several time periods.

2.2. Characterization techniques

In order to follow the chemical and structural evolution of isothermally treated glasses conventional techniques of characterization have been used.

Differential thermal analysis (DTA) of the glass was performed using a Mettler Toledo TGA/SDTA 851^e equipment. Glass powders were heated in N_2 atmosphere from room temperature to 1100 °C with a heating rate of 10 °C/min.

Infrared transmittance spectra were obtained with a Nicolet Avatar equipment, in the range 1600–400 cm^{-1}, using the KBr pellet method. Powder X-ray diffraction (XRD) patterns were recorded using monochromated Cu K_α radiation with a Siemens D-5000 diffractometer, within the 2θ range 5–65° with a step size of 0.02° and a step time of 5 s.

Field emission scanning electron microscopy (FESEM) observations of fresh fracture surfaces of heat-treated specimens were made using a field emission Hitachi S-4100 microscope. The samples were chemically etched with 20% HF solution for 1 min to dissolve the glassy phase and to improve the observation.

Energy-dispersive X-ray analysis (EDS) was performed at 20 kV, using the above field emission scanning electron microscope equipped with a Rontec model EDR288 spectrometer. Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Quantitative analyses of specimens were made using software for oxide stoichiometries and normalized data.

3. Results and discussion

3.1. Characterization of glass powders

In a previous report,[9] TEM replica micrographs of the three as-prepared glasses indicated the presence of small droplets in the glass matrix. This feature is indicative of phase separation in these cooled glasses. The FESEM image (Fig. 1) of glasses heated at 900 °C for 55 min, for which the full crystallization is not reached, confirms the occurrence of phase separation as observed by TEM. The size of this separation increased with thermal treatment.

It is to be noted that X-ray powder diffraction of as-prepared cobalt-containing glass displays a trace revealing its amorphous nature.

3.2. Crystallization of glass powders

DTA traces for COMG as well as MG glasses heated up to 1200 °C have been shown elsewhere.[9] The two

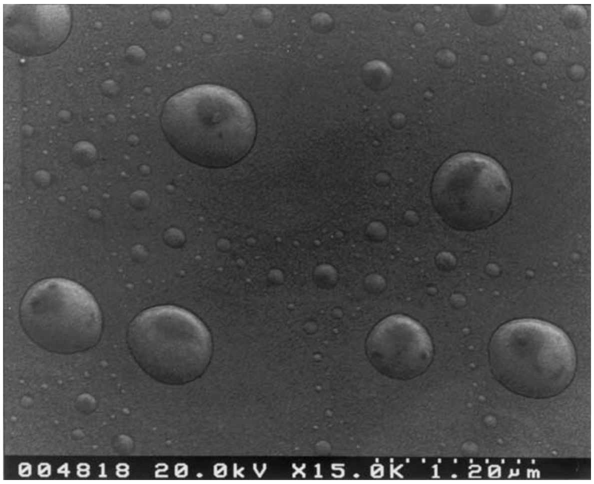

Fig. 1. FESEM micrograph of COMG glass isothermally treated at 900 °C for 55 min (bar = 1.20 μm).

glasses displayed two crystallization peaks representing μ- and α-cordierite crystallization on increasing the temperature and similar glass transition temperatures, at around 810 °C. In the MG glass an additional exothermic effect at around 1000 °C, was also associated with the crystallization of μ-cordierite.

However, a more careful observation of the DTA trace of COMG glass indicates the presence of other thermal effects which might be associated with compositional and/or structural changes.

Fig. 2 display more detailed DTA traces for the two glasses COMG and MG. In order to have a more complete picture of the crystallization process, different specimens were obtained by interrupting the heating in the DTA furnace at several temperatures and cooling down to room temperature, followed by XRD analysis. Specimens of COMG glass were analyzed after cooling in DTA from 920, 975, 1025 and 1100 °C, the XRD patterns of which are shown in Fig. 3. After the first exothermic effect, at 920 °C a phase with the structure of μ-cordierite forms. A hump in the range between 15 and 25° (2θ) as well as very weak peaks associated with α-cordierite are also displayed. The presence of this hump in the background indicates some glassy phase. The second exothermic effect is associated with further crystallization of μ-cordierite, as evidenced in the XRD pattern of the heated specimen at 975 °C. This conclusion is deduced by the disappearance of the hump in the background and almost no variation in the intensity of peaks associated to α-cordierite. Finally, the crystallization of α-cordierite is associated with the third exothermic effect as shown for specimens with interrupted heatings at 1100 °C. It is noted that mullite and spinel are present as very minority phases, also detected in magnesium cordierite glass–ceramics by Perham et al.[15] On considering these changes some questions can arise. It would be interesting to know the nature of the first crystalline phase appearing on heating, i.e. whether or not the μ-cordierite contains magnesium and cobalt.

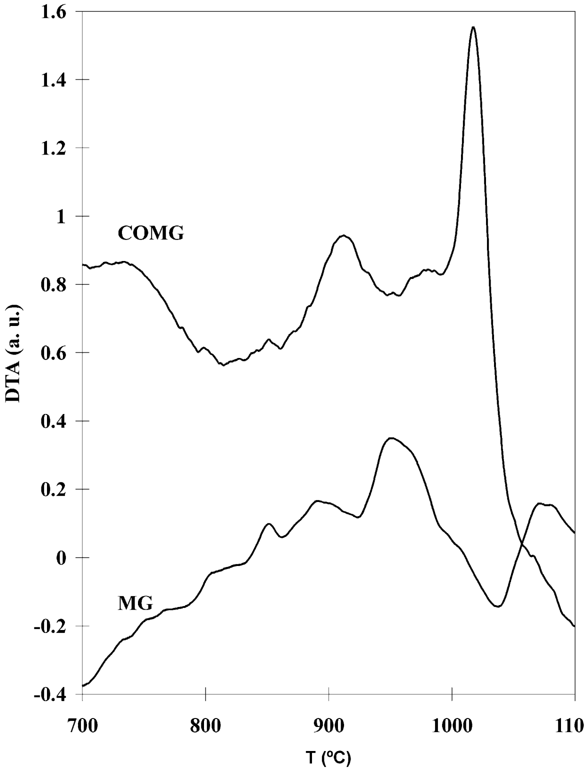

Fig. 2. DTA curves for glasses COMG and MG.

For comparison XRD patterns of MG samples cooled in DTA from 900, 960, 1000, 1050 and 1100 °C are shown in Fig. 4. As can be seen the magnesium μ-cordierite is the only crystalline phase present up to 1000 °C but when reaching 1050 °C the α-cordierite phase is detected. Finally at 1100 °C α-cordierite and a very small amount of mullite are detected.

In order to obtain a more complete picture of both the structural and microstructural changes in both specimens, they were submitted to isothermal treatments with increased annealing times. Figs. 5–7 display X-ray diffraction patterns of the isothermally heat-treated COMG specimens at 900, 950 and 1100 °C for several time periods. After heating at 900 °C for short time, XRD peaks at 25.72, 39.80 and 48.60° (2θ) are detected which are attributed to a phase with the structure of β-quartz solid solution, i.e. the so called μ-cordierite. After annealing longer at 900 °C, between 1 and 4 hours, the α-cordierite phase is fully developed and no significant change is produced even after further annealing up to more than 250 h. For isothermal treatment at 950 °C the α-cordierite phase is fully developed after annealing during 30 min and no further changes are detected even after annealing for more than 70 h. When the specimens are isothermally treated at 1100 °C the formation of α-cordierite phase is completed after holding for 5 min and the phase remains without changes after thermal treating for more than 220 h. From the Figs. 5–7 it can be noted that for the three isothermal treatments of COMG specimens very small amounts of mullite and cobalt–magnesium aluminate spinel are detected after the transformation from μ to α cordierite. This minority phases are almost undetectable for higher temperatures and longer annealing times.

The evolution of the pure magnesium cordierite glass on isothermal treatments has been reported in kinetic studies.[16–18] As can be seen in Fig. 8, the formation of α-cordierite occurs more slowly. Thus, after heating pellets of powder glass for more than 70 h at 900 °C only a small amount of α-cordierite is formed. At 950 °C for 10 h the formation of α-cordierite is not yet complete. In the case of the isothermal treatment at 1000 °C, the complete formation of α-cordierite is already detected after 15 min. For isothermally treated pure magnesium cordierite glass, mullite has also been detected as very minor phase.

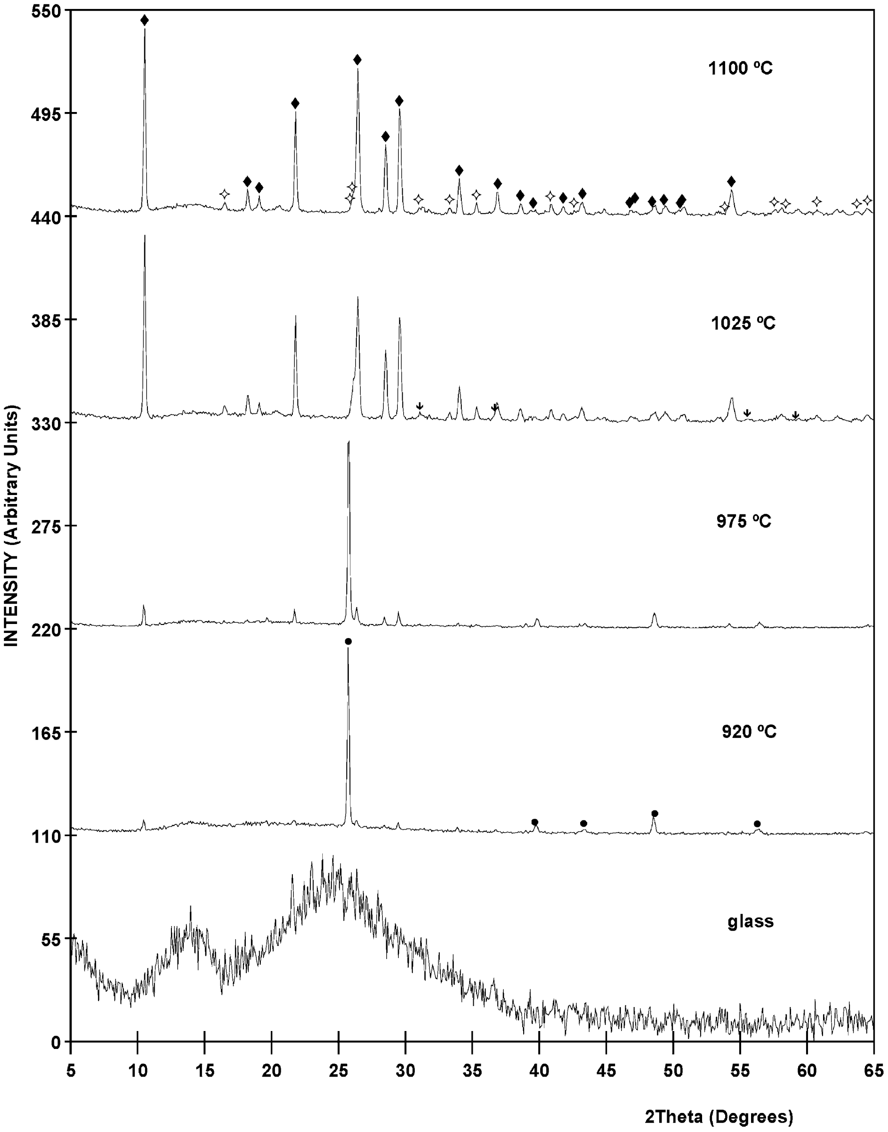

Fig. 3. XRD pattern of as-prepared COMG glass and cooled in DTA from different temperatures (● μ-cordierite, ↓ spinel, ✧ mullite and ◆ α-cordierite).

From the earlier results it seems clear that the formation of the phase with μ-cordierite structure occurs at lower temperature for the equimolar cobalt–magnesium cordierite glass than for the pure magnesium cordierite glass. Some reasonable explanation for this fact can be argued from structural considerations. The idealized β-quartz structure comprises a framework of interlinked helixes of SiO_2 tetrahedra in which distorting tetrahedral cavities capable of being occupied by small cations are located between the two helixes.[19] When Al^{+3} replaces Si^{+4} in the quartz tetrahedral sites the charge balance can be maintained by monovalent or divalent cations. In the MgO–Al_2O_3–SiO_2 ternary system neutrality is reached by occupying the Mg^{+2} cation octahedral sites between the two tetrahedral sites, giving rise to the so-called μ-cordierite.[20] From our results these octahedral sites can also accept other cations such as Co^{+2}. It seems that the occupancy of this octahedral position by Co^{+2} is the most favourable when comparing with Mg^{+2}. Also the more favorable crystallization of cobalt-containing μ-cordierite may be influenced by easier diffusion of Co^{+2} than Mg^{+2}.

The formation of α-cordierite from glass precursor in the MgO–Al_2O_3–SiO_2 ternary system occurs by transformation of the μ-cordierite crystalline form and/or by direct crystallization. Similar mechanisms appear to lead to the formation of α-cordierite from the equimolar cobalt–magnesium glass. From our results, the incorporation of Co^{+2} in the α-cordierite form is also favorable with respect to the Mg^{+2}. This fact, however, may

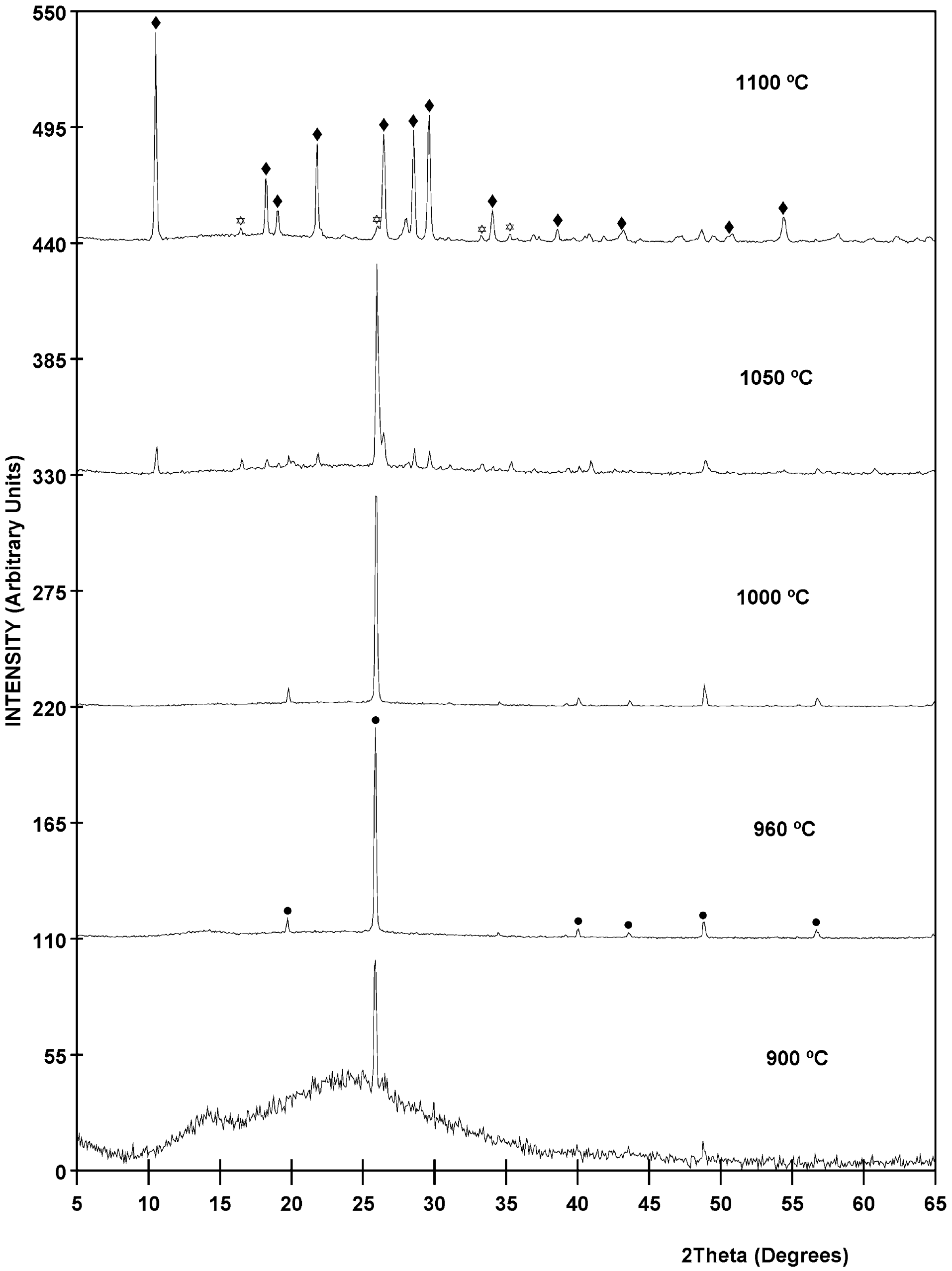

Fig. 4. XRD pattern of MG glass cooled in DTA from different temperatures (● μ-cordierite, ✧ mullite and ◆ α-cordierite).

be due to other factors such as a favourable microstructural development during crystallization.[14,21]

3.3. *Infrared spectroscopy*

Infrared spectra of both as-prepared equimolar cobalt–magnesium glasses and after thermal treatment at several temperatures and holding times are shown in Figs. 9 and 10. In Fig. 9, bands at 418, 443, 929 and 1090 cm^{-1} appear in the glass. Also a very weak band is detected at 799 cm^{-1}. All these bands are observed at similar energies for either pure magnesium or cobalt cordierites..[9,11] For the glass heated at 950 °C for 5 min, in which μ-cordierite was the only crystalline phase detected, an intense band appears at 720 cm^{-1}. In addition the band at 1090 cm^{-1} in the glass is split in two at 996 and 1115 cm^{-1}. For specimens with longer annealings, up to 75 h, in which only the structure of α-cordierite was detected by XRD, the whole spectrum is similar but shifted to higher energies.

In Fig. 10 are shown the spectra of glasses annealed for several times at 900 and 1100 °C. The spectra for glasses heated at 900 °C for 1 h 55 min and 264 h, which contain μ- and α-cordierite as only crystalline phase,

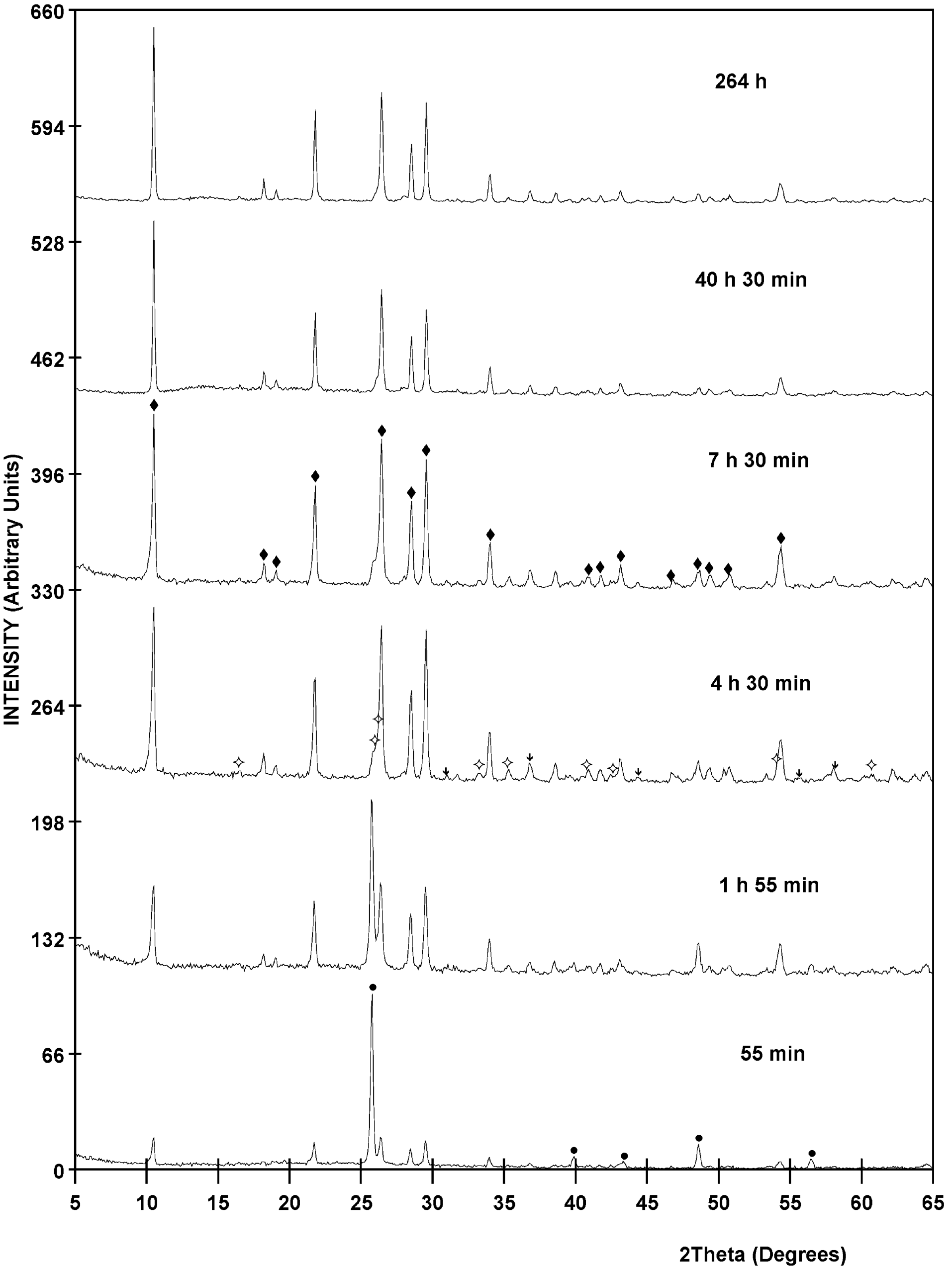

Fig. 5. XRD pattern of COMG glass isothermally treated at 900 °C for several time periods (● μ-cordierite, ↓ spinel, ✧ mullite and ◆ α-cordierite).

respectively, are similar to the ones corresponding to heated glasses at 950 °C displaying the same crystalline phase.

It is interesting to note the changes in the spectra of glasses annealed at 1100 °C. As it is also shown in Fig. 10 with long annealing, up to 220 h, an increasingly pronounced splitting of the bands is displayed, which can determine that some ordering for aluminium and silicon in tetrahedral sites has taken place.[22,23] This ordering would lead to the formation of the low temperature, orthorhombic form of cordierite, i.e. β-cordierite. However, results from X-ray powder diffraction do not reveal a clear splitting in peaks and even longer thermal treatments will be required for full formation of orthorhombic cordierite. It is also noted that evidence of the orthorhombic pure magnesium cordierite was only observed after glass annealing at 1400 °C.[22]

3.4. Microstructural characterization

The microstructural development of the COMG glass powder heated isothermally at 900 °C for increasing time periods, i.e. 55 min and 1 h 55 min, are very similar. The latter is represented in the FESEM micrograph

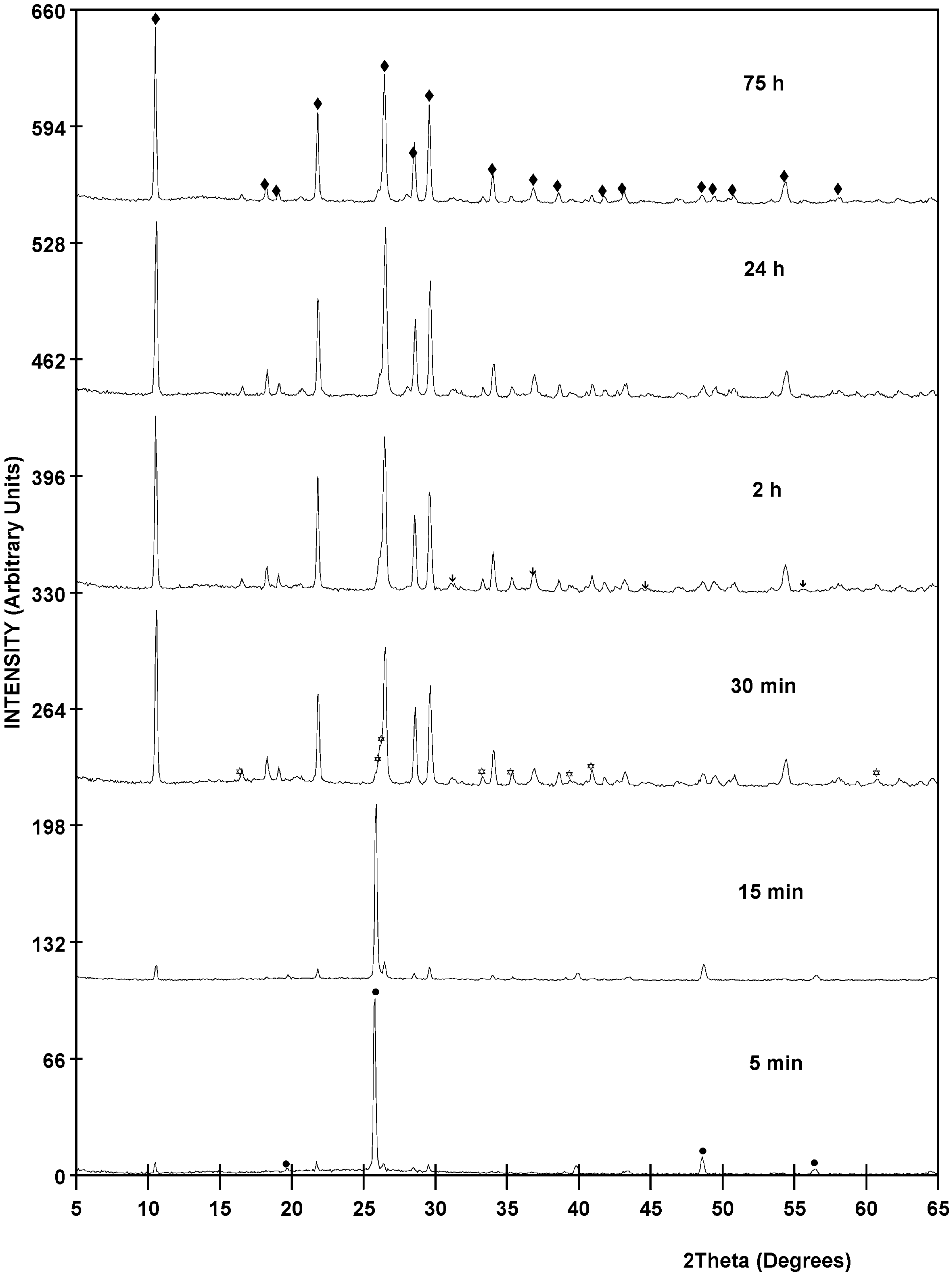

Fig. 6. XRD pattern of COMG glass isothermally treated at 950 °C for several time periods (● μ-cordierite, ↓ spinel, ✧ mullite and ◆ α-cordierite).

of Fig. 11. The XRD pattern of the heat-treated samples (Fig. 6) displayed the formation of μ-cordierite as the main crystalline phase with a very small amount of α-cordierite, and the amount of the latter increases when extending the annealing time to 1 h 55 min. The FESEM micrographs suggest that the μ-cordierite forms by dendritic growth of faceted crystals that have nucleated heterogeneously on the particle surfaces. It appears from the earlier Fig. 11 that the growth is extended from the particle surface to the inner to consume the glass. This fact indicates that the crystallization in this system occurs by a surface controlled nucleation mechanism. With respect to the composition of the μ-cordierite dendrites, EDS results for the specimen annealed for increased times are shown in Table 1. For the specimen annealed at shorter time, i.e. 55 min, the analysis has been made on the μ-cordierite dendrite arms and the amorphous phase. The obtained results show the presence of Co and Mg in the dendrites. It is also evidenced that the μ-cordierite is richer in Al_2O_3 and consequently poorer in SiO_2 than the glass matrix. It is quite uncertain to make measurements at the interdendritic glass because

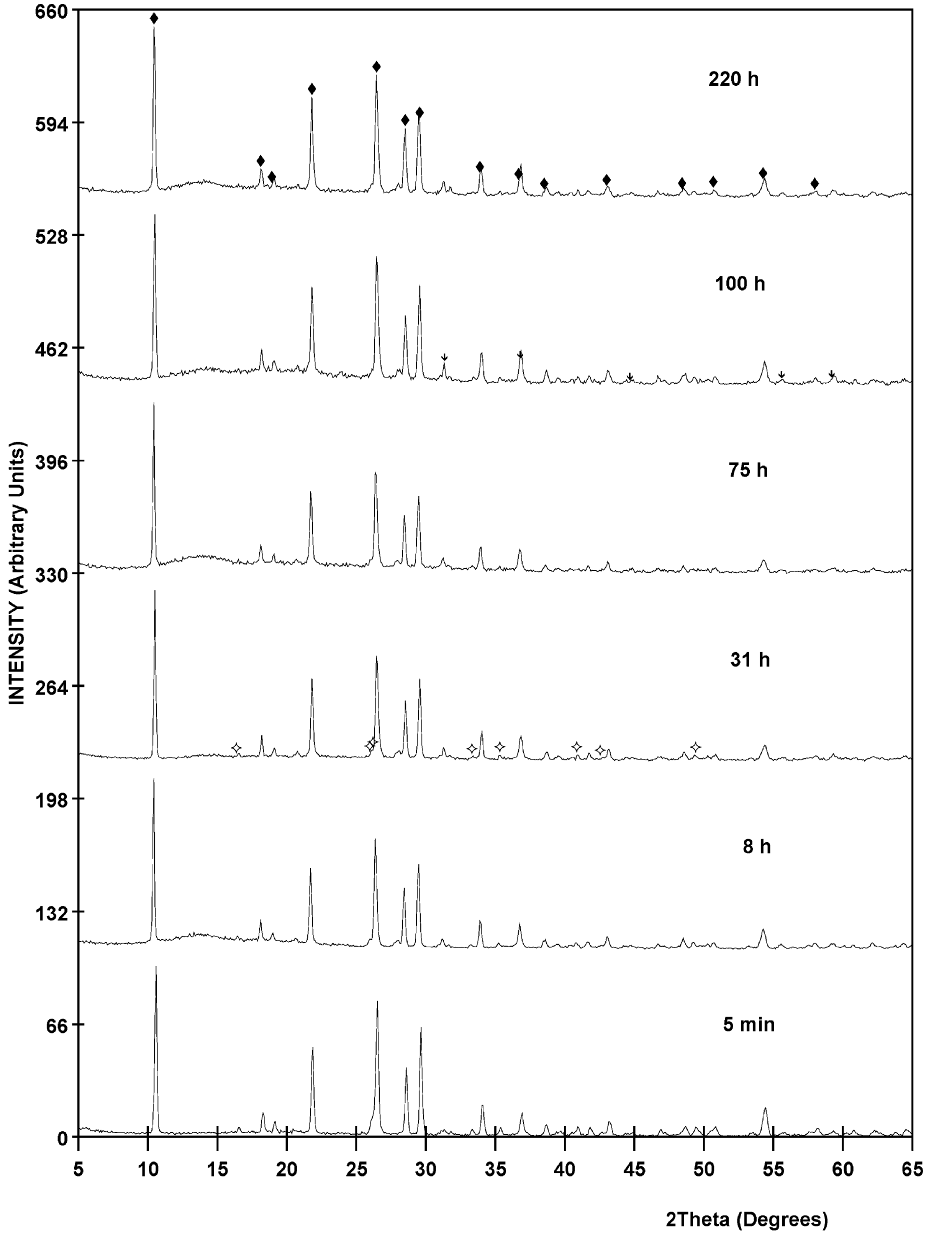

Fig. 7. XRD pattern of glass COMG isothermally treated at 1100 °C for several time periods (● μ-cordierite, ↓ spinel, ✧ mullite and ◆ α-cordierite).

of the limited spatial resolution of the EDS. Thus, it is difficult to detect whether chemical segregation ahead of dendritic growth occurs. After longer annealing at 900 °C, i.e. 264 h, at which the only crystalline phase detected is α-cordierite, the particles still contain an arrangement of primary and secondary dendrites. This fact is shown in Fig. 12 suggests that the α-cordierite has nucleated on the μ-dendrites and that the growing α consumes the μ-cordierite in which it forms. In addition, this Fig. 12 exhibits that the α-cordierite dendrites have a hexagonal morphology, which its probably due to the shape of its precursor phase, i.e. μ-cordierite. The composition of the α-cordierite phase in the specimen annealed for 1 h 55 min and 264 h at 900 °C is also shown in Table 1. It should be noted that its composition is in agreement with that expected from the stoichiometric glass $MgCoAl_4Si_5O_{18}$. It can be, therefore, assumed that a equimolar magnesium and cobalt α-cordierite solid solution has been obtained. In general, two techniques have been used to increase volume nucleation in melt-derived glasses.[12,13,24,25] Firstly, a range of nucleating agents such as TiO_2 or ZrO_2 have been added to bulk glasses. The other one was to sinter and crystallize glass powder compacts. In our case the

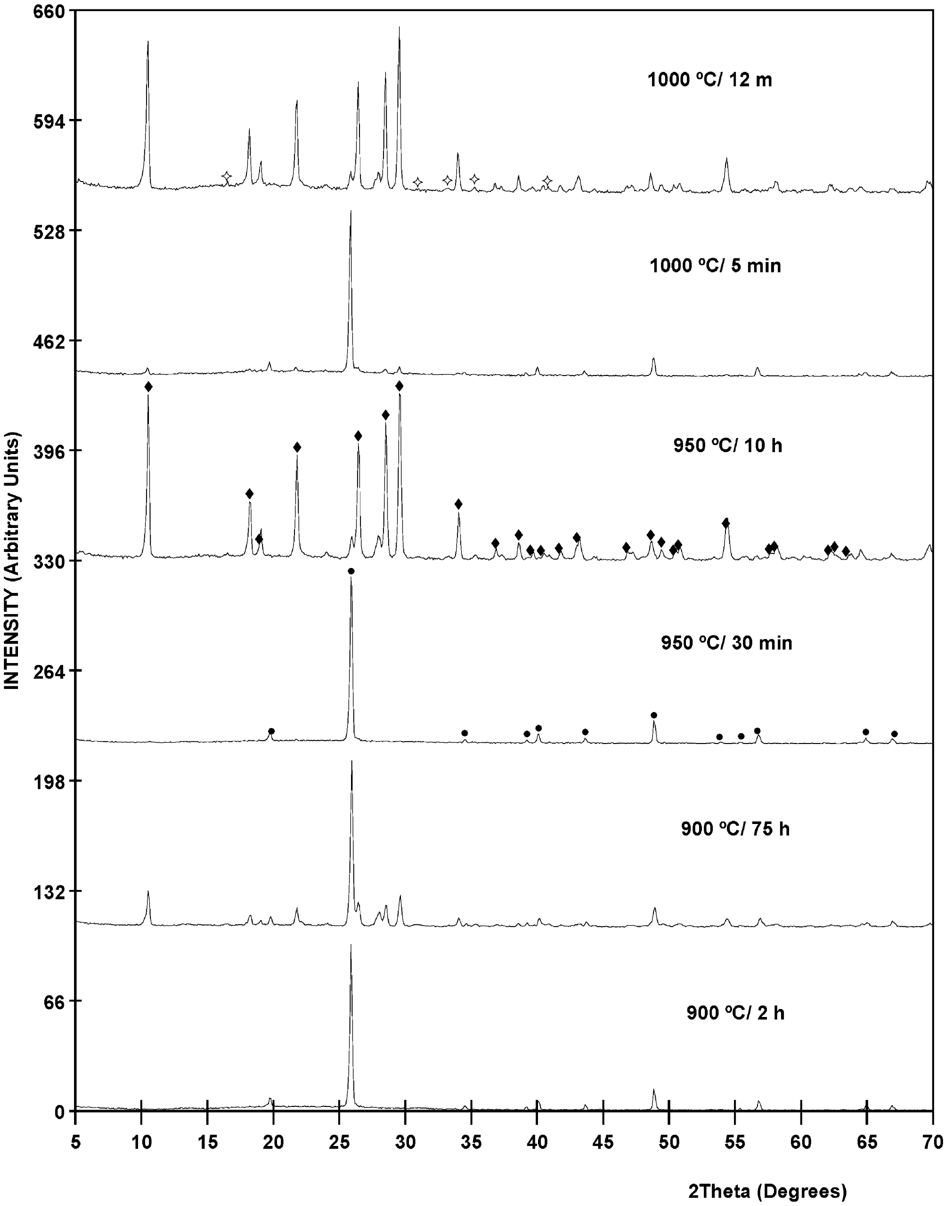

Fig. 8. XRD pattern of MG glass isothermally treated at 900, 950 and 1000 °C for several time periods (● μ-cordierite, ↓ spinel, ✧ mullite and ◆ α-cordierite).

almost loose glass powder crystallizes before densification and consequently the process of crystallization takes place by a dendritic growth from the particle surface to the inside.

For specimens isothermally treated at 1100 °C, the whole picture is different but the microstructural changes are also observed at the particle level. After annealing the specimen long times, up to 220 h, at 1100 °C some changes are observed in the particle. Fig. 13, corresponding to the specimen annealed for 8 h, shows the morphology developed by α-cordierite in the original particle. Two types of cordierite crystals, depending upon the size and morphology of crystals, have been described in the literature dealing with the crystallization of nearly stoichiometric cordierite glass.[26,27] The first are acicular prismatic grains elongated on the *c*-axis and the second regular or elongated hexagonal shaped prisms. Prism faces also show a variation in their surface roughness, i.e. smooth, stepped or columnar. The occurrence of one type of surface roughness on different parts of the same crystal may reflect different growth mechanisms. The irregular appearance observed in Fig. 13, results from different terminations on elongated pseudohexagons, which grow side by side vigorously in the direction of the *c*-axis, to show columnar or linear features. From the earlier micrographs it can also be drawn that a certain degree of densification can be reached after heating at temperatures higher than 1100 °C.

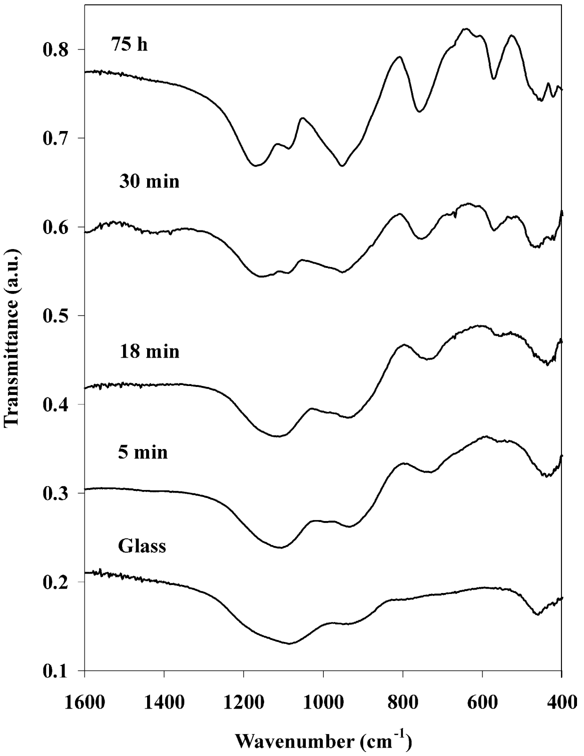

Fig. 9. Infrared spectra of COMG glass as prepared and isothermally treated at 950 °C for different time periods.

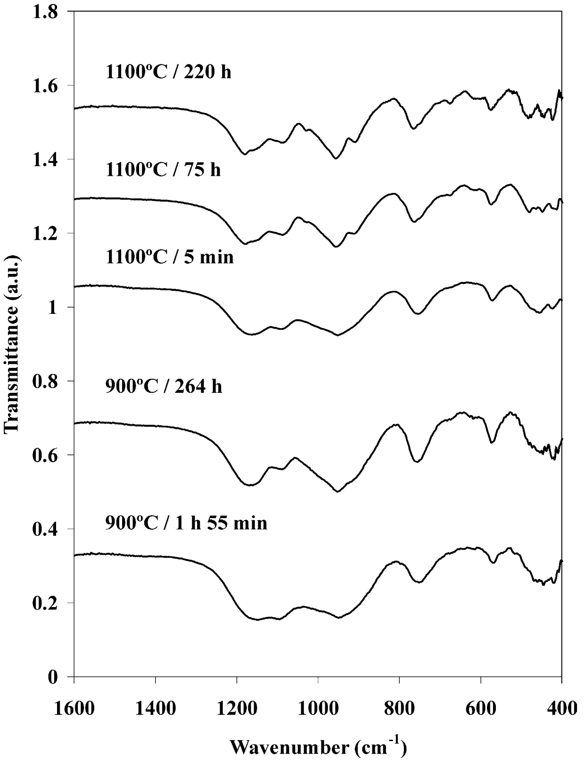

Fig. 10. Infrared spectra of COMG glass isothermally treated at 900 and 1100 °C for several time periods.

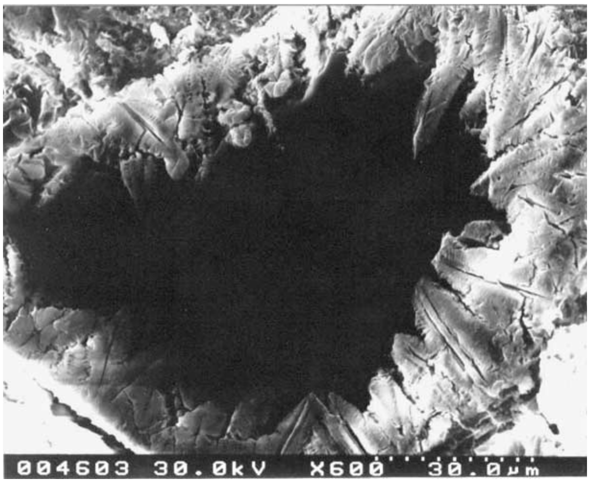

Fig. 11. FESEM micrograph of COMG glass isothermally treated at 900 °C for 1 h 55 min (bar = 30 µm).

Table 1
EDS microanalysis results[a] of COMG glass isothermally treated at 900 °C for several time periods

Time period	Analysed feature	Composition (wt.%)			
		SiO_2	Al_2O_3	MgO	CoO
55 min	µ-Cord dendrites	41.4±1.2	42.6±1.1	7.9±0.4	8.2±0.5
	Amorphous phase	50.8±0.8	34.6±0.7	4.6±0.2	10.0±0.5
1 h 55 min	µ-Cord dendrites	41.1±1.2	44.4±1.1	6.6±0.8	8.0±0.9
	α-Cord dendrites	48.4±0.6	33.6±0.4	5.6±0.2	12.4±0.9
	Amorphous phase	50.9±0.8	35.3±0.7	4.8±0.2	9.0±0.6
264 h	α-Cord dendrites	49.0±0.6	33.6±0.7	5.7±0.5	11.7±0.6

[a] Averaged at least over five-point analyses.

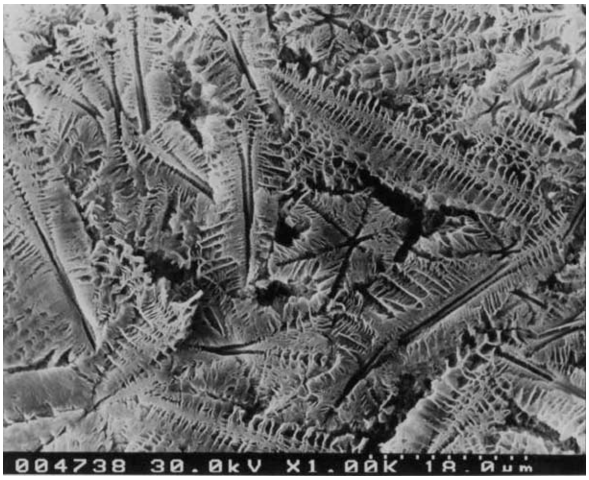

Fig. 12. FESEM micrograph of COMG glass isothermally treated at 900 °C for 264 h (bar = 18 µm).

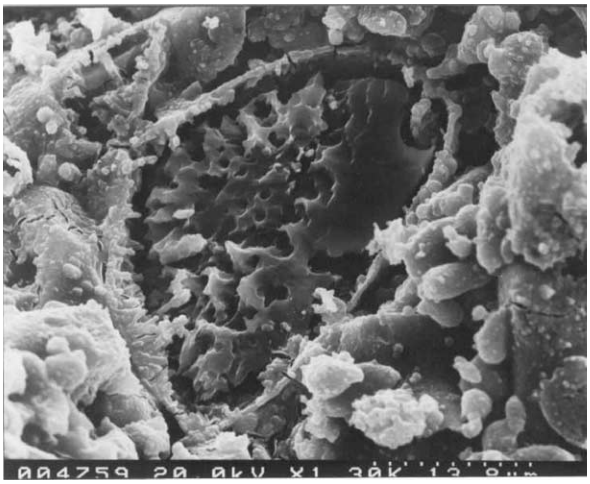

Fig. 13. FESEM micrograph of COMG glass isothermally treated at 1100 °C for 8 h (bar = 13.8 μm).

4. Conclusions

The crystallization behaviour of loosely compacted glass powder with chemical composition $MgCoAl_4Si_5O_{18}$ was investigated. Glasses were prepared by cooling melted glass precursor at 1650 °C. During isothermal treatment at 900 and 950 °C for increasing holding times, the size of phase separation, in glassy areas of the original particles, increased with thermal treatment. The glass first crystallized to form β-quartz solid solution (μ-cordierite) and then transformed to high-cordierite (α-cordierite). Very small contents of mullite and magnesium–cobalt aluminate spinel were detected during the transformation from μ to α, but they disappeared with heat treatment. On isothermal heating at 1100 °C the formation of α-cordierite was very fast. In this case the crystalline form of μ-cordierite was not detected. Infrared spectra of specimens heated at 1100 °C for more than 75 h revealed transformation to the β-cordierite orthorhombic form.

Field emission scanning electron microscopy revealed that the μ-cordierite grew by a dendritic mechanism with a very close packing of dendrites attained by further heating. Finally, after short annealing at 1100 °C the fully crystallized microstructure cordierite contained α-cordierite with columnar or linear features.

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