Journal of the European Ceramic Society 22 (2002) 487–494

www.elsevier.com/locate/jeurceramsoc

Mechanism of crystallization of Co-cordierites from stoichiometric powdered glasses

Maria Angeles Villegas[a], Javier Alarcón[b,*]

[a]Instituto de Cerámica y Vidrio, CSIC, Antigua Ctra. Valencia Km. 24.3, 28500 Arganda del Rey, Madrid, Spain
[b]Department of Inorganic Chemistry, University of Valencia, Calle Doctor Moliner 50, 46100 Burjasot, Valencia, Spain

Received 11 January 2001; received in revised form 10 April 2001; accepted 21 April 2001

Abstract

The influence of cobalt, as a divalent cation, on the crystallization behaviour of the cordierite based glasses was studied. Powdered glass specimens of stoichiometric composition 2MO $2Al_2O_3$ $5SiO_2$ (M = Co and/or Mg) were obtained and thermally treated at several temperatures and times, and the sequence of crystallization and their microstructural evolution were analysed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Results on the crystallization sequence showed that the steps in the crystallization path are independent of the nature of the divalent cation. The first crystalline phase detected displayed the μ-cordierite structure, i.e. a solid solution with β-quartz structure. After further thermal treatment a phase with α-cordierite structure was formed. Cobalt μ- and α-cordierites were further characterized by infrared (IR) and UV–vis diffuse reflectance spectroscopies. The final morphology of cobalt-containing hexagonal cordierites depended on the densification degree of the precursor glass. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cordierite; Crystallization; Glass; Glass ceramics

1. Introduction

Cordierite ($Mg_2Al_4Si_5O_{18}$) as a ceramic material has a wide range of uses and applications for its low dielectric constant, high electrical resistivity and low thermal expansion. Magnesium cordierite exists under three polymorphic forms: a hexagonal high-temperature form, named indialite or α-cordierite (space group P6/mmc), an orthorhombic low-temperature form designated β-cordierite (space group Cccm) and a metastable form referred to as μ-cordierite, which is a solid solution with β-quartz structure.[1,2] The hexagonal and orthorhombic structures are characterized by their six-membered rings of tetrahedrally coordinated cations (T_2) perpendicular to the c axis. Alternate layers of the hexagonal rings structure are connected through Mg octahedra and T_1 tetrahedra. Silicon occupies mostly T_2 tetrahedra, and aluminum T_1 tetrahedra. Differences between high- and low-temperature cordierites lie in a greater or lesser degree of disorder between the aluminum and silicon atoms within T_1 and T_2 sites.[3,4] Most natural cordierites are not pure magnesium cordierites but contain other cations or molecules which either substitute for Mg^{+2}, Al^{+3} or Si^{+4} or are inserted in the channel sites of cordierite framework.[5,6] Several authors reported on the preparation of solid solutions containing several dopants and also the effect of substitution of different elements in the high cordierite lattice on the properties. Thus, modifications of the thermal expansion behaviour were observed in high temperature cordierite in which Mn^{+2}, Ga^{+3} or Ge^{+4} partly substitute for Mg^{+2}, Al^{+3} and Si^{+4}.[7] The introduction of other cations at several chemical states in the high cordierite structure, such as Ca^{+2}, Cu^{+2}, Eu^{+3} has been also carried out.[8–10]

As far as we know, the unique complete metal substitution occurs with cobalt in the solid solution $Mg_x Co_{2-x}Al_4Si_5O_{18}$ ($0 \leqslant x \leqslant 2$).[11] The use of Co-substituted cordierite ceramics as blue pigments has been described.[12,13] However, these products were not single phase but rather cordierite phase occurred in addition to mullite, cristobalite, spinel and glass. The monophasic cobalt-containing cordierite in the entire compositional range has been synthesized by crystallization of glasses

---

[*] Corresponding author. Tel.: +34-9-6386-4584; fax: +34-9-6386-4322.

E-mail address: javier.alarcon@uv.es (J. Alarcón).

PII: S0955-2219(01)00300-4

at temperatures between 1000 and 1100°C.[11] However, there have been no fundamental studies of the crystallization processes occurring in such compositions and little detailed scanning and/or transmission electron microscopy of the microstructural development. On the other hand, the crystallization of melt-derived stoichiometric magnesium cordierite has been extensively studied.[14] On devitrifying the glass at 980°C, the first phase to form is the metastable stuffed β-quartz structure (μ cordierite). After annealing at around 1000°C this transforms to the hexagonal form, which is then kinetically stable for indefinitely long periods of time and is retained on cooling to room temperature.

The main purpose of this work is, therefore, to enlighten on the mechanism of crystallization and phases involved in the formation of cobalt-derived cordierites, i.e. their stabilities and further spectroscopic characterization. The microstructural development over the temperature range up to 1300°C was also studied.

2. Experimental procedure

2.1. Preparation of samples

Specimens with stoichiometric compositions $Mg_xCo_{2-x}Al_4Si_5O_{18}$, with $x = 0$, 1.0 and 2 were prepared. The pure magnesium cordierite was synthesized as a reference and it will allow the comparison with cobalt-containing compositions.

The glass composition with magnesium cordierite stoichiometry, thereafter sample MG, was prepared using as starting materials $MgCO_3$ (Panreac), Al_2O_3 and SiO_2 (Aldrich).

The glass was obtained by weighing out sufficient reagents for ≈100 g of glass, mixing and blending with acetone slurry and drying under a heat lamp. The batch was melted in uncovered alumina crucible in a gas heated furnace at 1600–1650°C. The total duration of the high temperature melting period was 2 h. After remelting twice the final melt was quenched. Normal quenching of the melts was achieved by pouring them onto a cold brass mould.

The starting materials for cobalt-containing cordierite specimens, thereafter MGCO and CO for equimolar magnesium-cobalt and cobalt, respectively, were prepared by a semiwet method. Appropriate amounts of reagent-grade $Al(NO_3)_2\ 9H_2O$, $Co(NO_3)_2\ 6H_2O$ were dissolved in distilled water at 80°C with vigorous stirring. To the resulting dissolution the required loads of SiO_2 and/or $MgCO_3$ were added. The dispersion was then heated until dryness and then dried in an oven at 110°C for 1 day. The powder was ground and calcined at 1000°C for 2 h to remove nitrate and after regrounding the powder was melt in alumina crucible at around 1600°C for 3 h. The glasses were remelted twice for increasing the homogeneity and the last melt was poured into a brass mould to form glass rods.

After grounding the glass samples to powder with sizes < 30 μm, cylindrical pellets of powder glass were obtained by pressing at 0.5 MPa, which were subsequently fired in an electric furnace from 700 to 1400°C during several time periods.

2.2. Techniques of characterization

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

Differential thermal analysis (DTA) of the glass was performed using a Mettler equipment at a heating rate of 10°C/min with a sample weight around 15 mg.

Powder X-ray diffraction (XRD) data were measured using monochromated CuK_α radiation with a D-500 Siemens instrument.

Scanning electron microscopy observations of fresh fracture surfaces of heat-treated specimens were made using a field emission Hitachi S-4100 equipment. The samples were first etched using 20% HF for 60 s to dissolve the glass phase and to improve the observation.

Transmission electron microscopy observations of the three obtained glasses were performed with a Hitachi 7000 microscope, samples were etched with 5 vol.% HF for 20 s and then simple carbon replicas of the surfaces were prepared.

The thermal expansion coefficient of as-prepared glasses and crystallized specimens after thermal treatment was determined on a dilatometer Netzsch model 402 EP on rods of the samples. The average linear expansion coefficient from 300 to 500°C was calculated following the usual method.

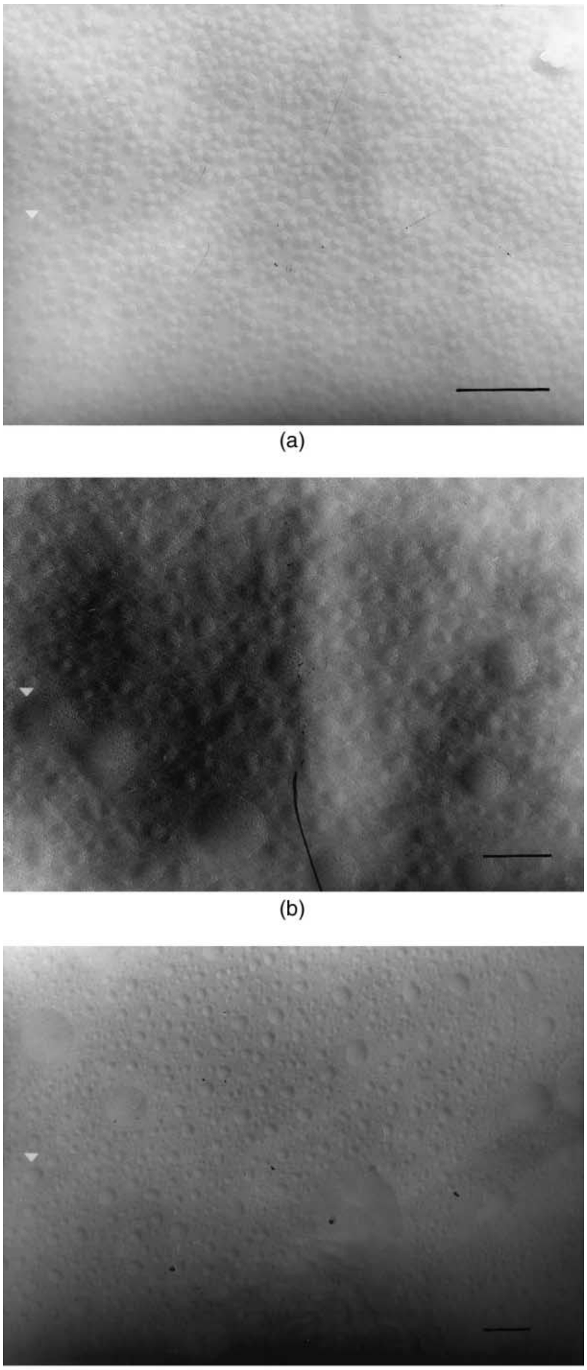
3. Results and discussion

3.1. Characterization of glasses

Fig. 1 (a)–(c) shows replica transmission electron micrographs of the textures of normally quenched glasses containing magnesium, magnesium-cobalt and cobalt, respectively. The pits or depressions represent the location of tiny dispersed droplets of glass, which were apparently less resistant to the hydrofluoric etch preceding replication than the glass matrix. From Fig. 1 note that for all the three quenched glasses by pouring in air a glass-in-glass phase separation is displayed.

3.2. Crystallization of glasses

The DTA curves in the various glass powder samples are shown in Fig. 2. The glass transition, T_g, appears around 810°C for glasses MG and COMG and at 720°C


(a)

(b)

(c)

Fig. 1. Replica TEM micrographs of quenched glass of (a) magnesium, MG (b) magnesium and cobalt, MGCO and (c) cobalt, CO (bar 250 nm).

for the CO. In the magnesium cordierite composition (sample MG) the DTA curve displays three distinct exothermic peaks at around 960, 1000 and 1100°C. On the basis of XRD data, the former two broad peaks were assigned to crystallization of high-quartz solid solution, i.e. μ-cordierite, whereas the latter peak was assigned to the transformation from the μ to α-cordierite and/or from direct crystallization of α-cordierite.

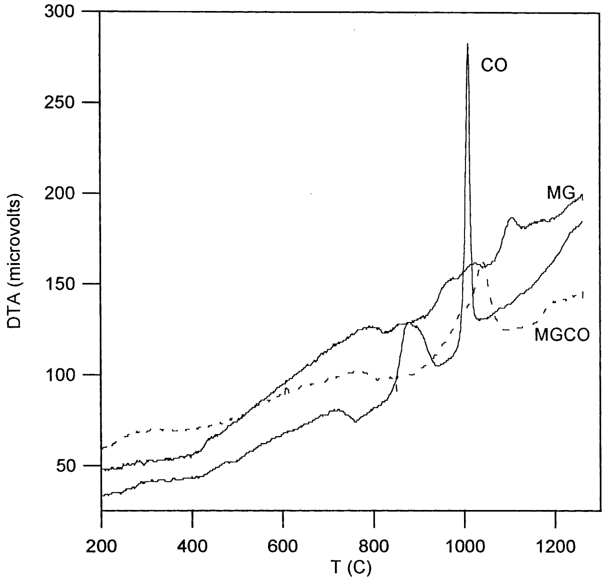


Fig. 2. DTA curves of the starting glasses.

The crystallization temperatures for μ and α-cordierite are seen to decrease with increasing cobalt content in the stoichiometric cordierites. Two exothermic peaks around 870 and 1000°C are shown for CO glasses whereas only one exothermic peak around 1050°C with a shoulder at 1000°C is displayed by the COMG glass. Comparing the DTA response of MG, MGCO and CO glasses suggests that the cobalt oxide component decreases the temperature of formation of both μ and α-cordierites. Since the glass transition temperature is quite close to the starting crystallization temperature in the CO specimens it can be predicted that sintering will not be completed at low temperatures. As it is well known that in order to reach densified bodies a full densification must occur prior to the crystallization start. The last process competes for mass transport with viscous flow. Thus, shortening the range of temperatures between the glass transition and crystallization prevents the densification at low temperatures.

Fig. 3 shows the X-ray diffraction patterns of the glass and the thermally treated specimens in the magnesium cordierite system. The specimens heat-treated below 800°C remain amorphous to X-ray diffraction. Peaks at 19.80, 25.96, 34.60, 40.12 and 43.64 (2θ) attributable to β-quartz solid solution, i.e. μ-cordierite, are detected after heating at 900°C. On heating at 1000°C peaks associated with the metastable α-cordierite as well as the β-quartz solid solution are displayed. Further heating at 1100°C gives rise to an increase of the intensity of peaks associated with the α-cordierite phase and to decrease of peaks corresponding to μ-cordierite. Heating to 1300°C produces α-cordierite phase as the only crystalline phase.

Fig. 4 shows the variation of X-ray diffraction patterns with heat treatment temperature in the cobalt cordierite system. Peaks at 25.56, 39.64, 48.20 and 56.4

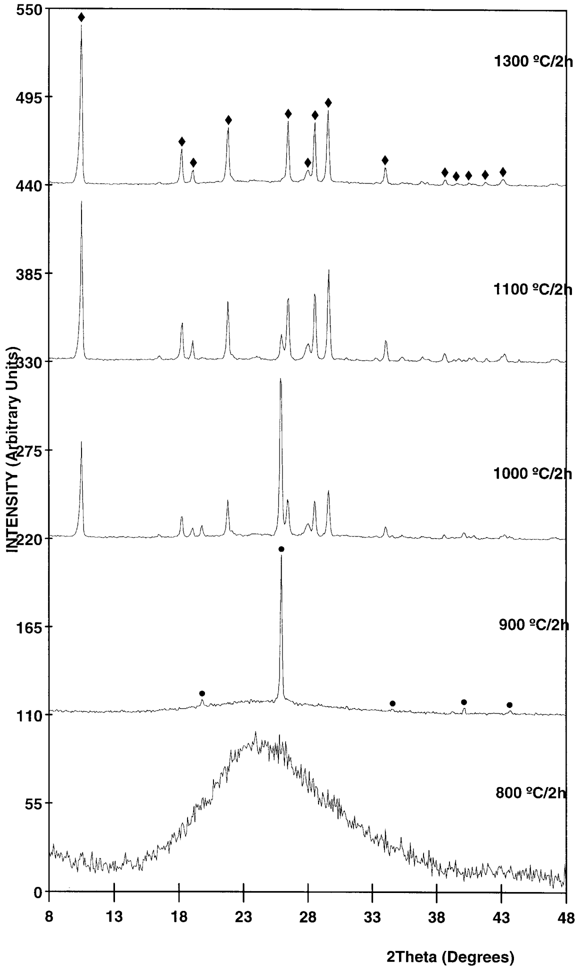


Fig. 3. X-ray diffraction patterns of glass MG heated at several temperatures for 2 h (● μ-cordierite and ◆ α-cordierite).

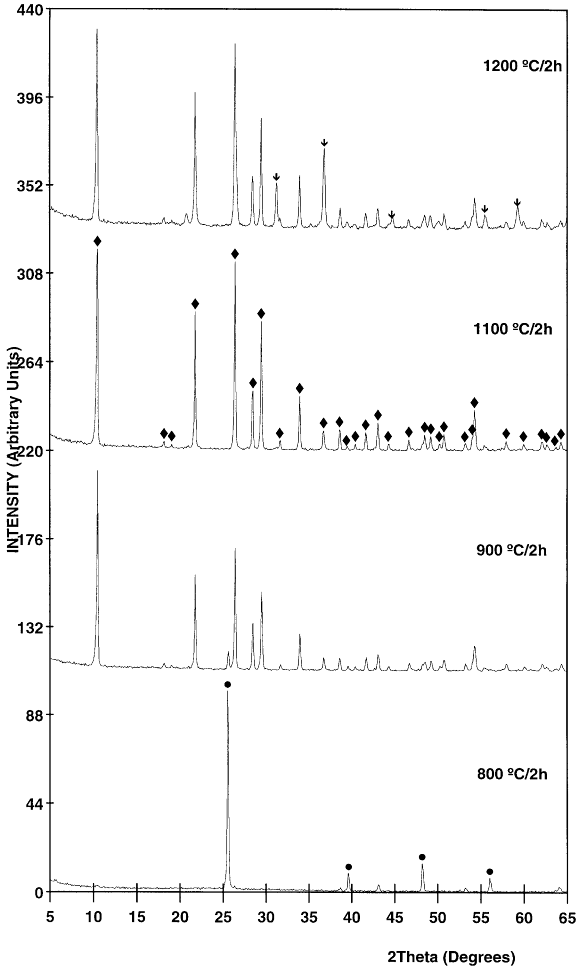


Fig. 4. X-ray diffraction patterns of glass CO heated at several temperatures for 2 h (● μ-cordierite, ◆ α-cordierite and ↓ $CoAl_2O_4$ spinel).

(2θ) associated with the β-quartz solid solution are displayed in the specimens heat-treated at 800°C. On heating specimens at 900°C, strong peaks associated with α-cordierite are displayed as well as weak peaks of μ-cordierite. The later minor phase disappears after heating at 1100°C. By further increasing of the temperature to 1200°C peaks at 31.24, 36.84, 44.68, 55.48 and 59.24 (2θ) attributed to $CoAl_2O_4$ spinel phase are detected.

Phase evolution of specimens in the equimolar magnesium–cobalt cordierite system are shown in Fig. 5. As can be inferred, the phase changes in these samples should be produced at intermediate temperatures on comparing with the end cordierite systems. Thus, peaks at 25.80, 33.96 and 48.68 associated with the β-quartz solid solution as well as weak peaks corresponding to the α form of cordierite are displayed in specimens heat-treated at 900°C. On heating at 1000°C the formation of α-cordierite is almost complete. It is noteworthy that this phase remains stable up to 1200°C/2 h.

From the above results it can be noted that in the three systems the whole crystallization process over the temperature range up to the crystallization of α-cordierite takes place in two steps. First, the β-quartz solid solution is formed on heating glasses. Second, further increase of the temperature causes the end α-cordierite phase to fully developed. As can be seen from Figs. 3–5, both steps are shifted to lower temperatures on increasing the amount of cobalt.

3.3. Thermal expansion of heated specimens

In Table 1 the measured thermal expansion coefficient of both as-obtained glasses and those thermally treated are summarized. After heating cobalt and magnesium–cobalt glasses at 950°C and magnesium glass at 1150°C all the specimens display relatively low polycrystalline linear thermal expansion (2.14×10^{-6} to 2.70×10^{-6}/°C from 300 to 500°C). These results suggest that for the cobalt-containing specimens a crystalline phase with the cordierite structure is formed and that the low thermal expansion is independent of the nature of the divalent cation in the cordierite structure.

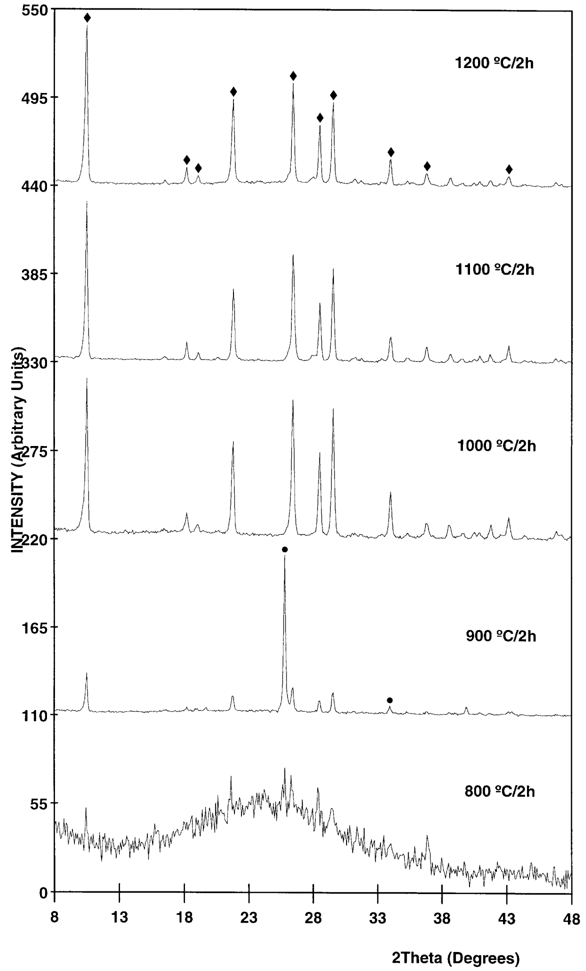


Fig. 5. X-ray diffraction patterns of glass MGCO heated at several temperatures for 2 h (● μ-cordierite and ◆ α- cordierite).

Table 1
Thermal expansion coefficient (°C^{-1}) in the temperature range from 300 to 500°C for as-obtained glasses and thermally treated cobalt-containing and pure magnesium at 950 and 1150°C for 6 h, respectively

Composition	As-prepared glasses	Thermally treated
MG	5.12×10^{-6}	2.61×10^{-6}
MGCO	5.35×10^{-6}	2.70×10^{-6}
CO	5.29×10^{-6}	2.14×10^{-6}

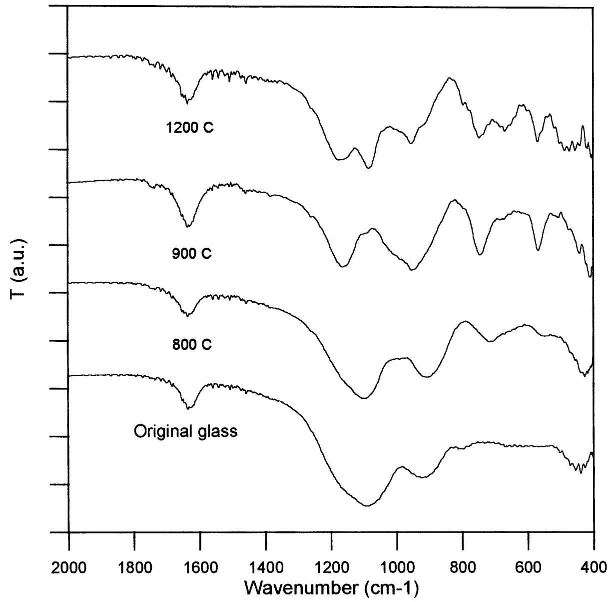


Fig. 6. Infrared spectra of CO glass as prepared and heated at several temperatures for 2 h.

3.4. Spectroscopic characterization of phases

IR spectra of the as-prepared glasses and those heated at the temperatures required to produce either high-quartz solid solution or α-cordierite monophasic specimens for CO glasses, which are displayed in Fig. 6, were similar to those of MG glasses.[14] Bands at 460, 620, 675 and 800 cm^{-1} are detected in both kinds of glass precursors. The band at 620 cm^{-1} is usually related to symmetric stretching vibration of Si–O bonds but may also be associated to octahedral absorption of $M^{+2}O_6$.[14,15] The band at 675 cm^{-1} has been attributed to aluminium in tetrahedral coordination.[16,17] The other two bands at 460 and 800 cm^{-1} are associated with bending modes of O–Si–O and Si–O–Si bonds, respectively.[14,16,18] In addition both glasses, MG and CO, display two strong bands peaked at around 955 and 1085 cm^{-1}.[14,19] The band peaked at 1085 cm^{-1} can be attributed to Si–O–Al bond stretching vibration modes.[20] This band is produced by the shifting of the band corresponding to the Si–O stretching vibration mode at 1100 cm^{-1} with the formation of Al–O–Si. Some ordering for aluminum and silicon in tetrahedral sites bring about this splitting.

As can be seen the IR spectra of specimens containing crystalline phases with either the structure of μ-cordierite or α-cordierite for both MG and CO compositions are quite similar.[14,19] In general, some splitting of bands is produced on forming the more ordered crystalline phase.

UV–vis diffuse reflectance characterization of the as-prepared CO glasses and the resulting crystalline phases on heating at 800, 900, 1100 and 1200°C for 2 h are displayed in Fig. 7. The spectrum of the glass manifests broad and unresolved bands, which is considered to reflect size-to-size variation of Co^{+2} ions in the glass. The broad absorption bands are observed at around 500 and 650 nm. These bands are attributed to six-coordinated and four-coordinated Co^{+2} ions, respectively.[21] In the spectrum of the specimen heated at 800°C/2 h, the intensity of the absorption around 650 nm is relatively weak, indicating that the Co^{+2} ions which occupy the tetrahedral sites move into the octahedral sites during crystallization of the cobalt-containing β-quartz solid solution. On heating at 900°C/2 h, in which the specimen is almost completely crystallized as cobalt α-cordierite as well as a small amount of cobalt μ-cordierite,

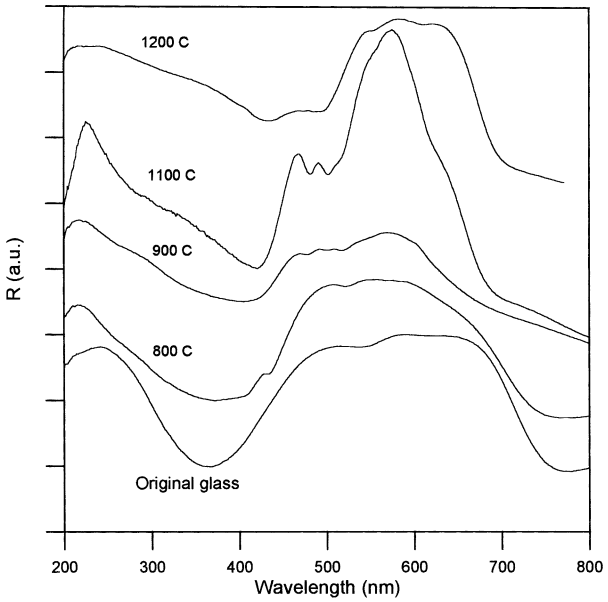


Fig. 7. UV–vis diffuse reflectance spectra of CO glass as prepared and heated at several temperatures for 2 h.

the spectrum does not change significantly but more defined absorptions are shown. The absorption spectrum of the specimen on heating at 1100°C/2 h, also containing cobalt α-cordierite phase as the only crystalline phase, shows the only difference is an increase in the band peaked at around 580 nm. Finally, the absorption spectrum of the specimen heated at 1200°C/2h, in which the spinel $CoAl_2O_4$ coexists with α-cordierite, bears a great resemblance to the absorption spectrum for the pure spinel $CoAl_2O_4$ as previously reported.[22]

3.5. *Microstructural evolution through the thermal treatment*

Fig. 8 shows the microstructural changes of cobalt glass pellets over the range of temperature up to the complete crystallization of the cobalt α-cordierite phase. It is to note that the pellets were formed at very low pressure, so that our specimens may be considered as loose powder. As was mentioned before the crystallization of CO glasses began after heating at 800°C. SEM images from the etched surfaces of specimens after annealing 2 h at 800°C, shown in Fig. 8(a), indicates that the µ-cordierite is present as dendritic-shape arms. After annealing at 1100°C, in which the predominant crystalline phase is α-cordierite, the morphology of crystals is similar but the size of the group of crystals is greater, as displayed in Fig. 8(b).

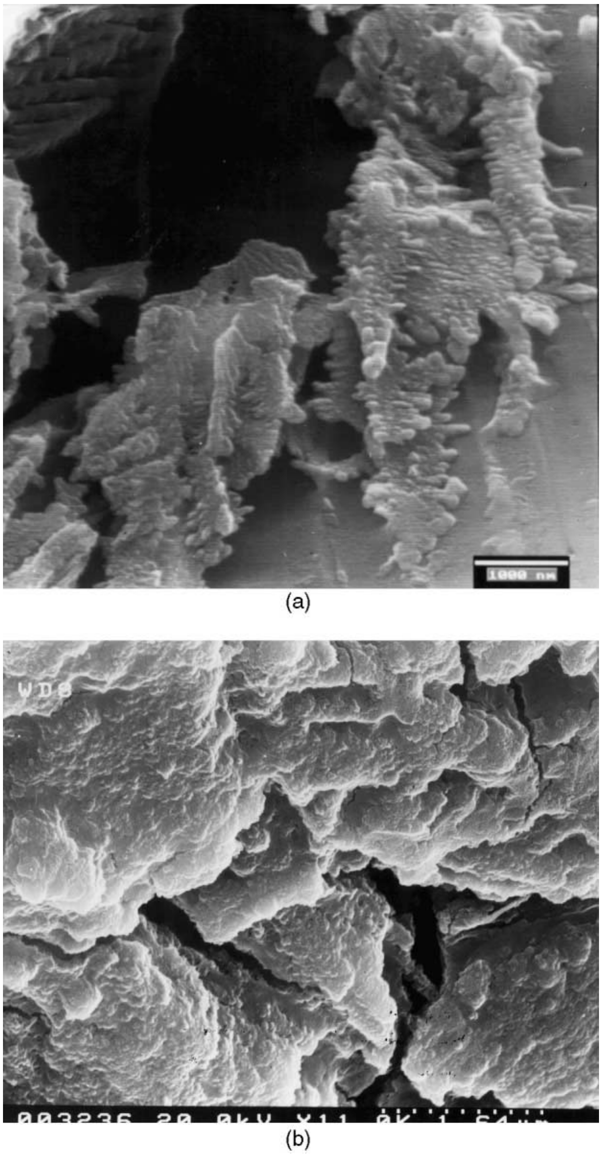
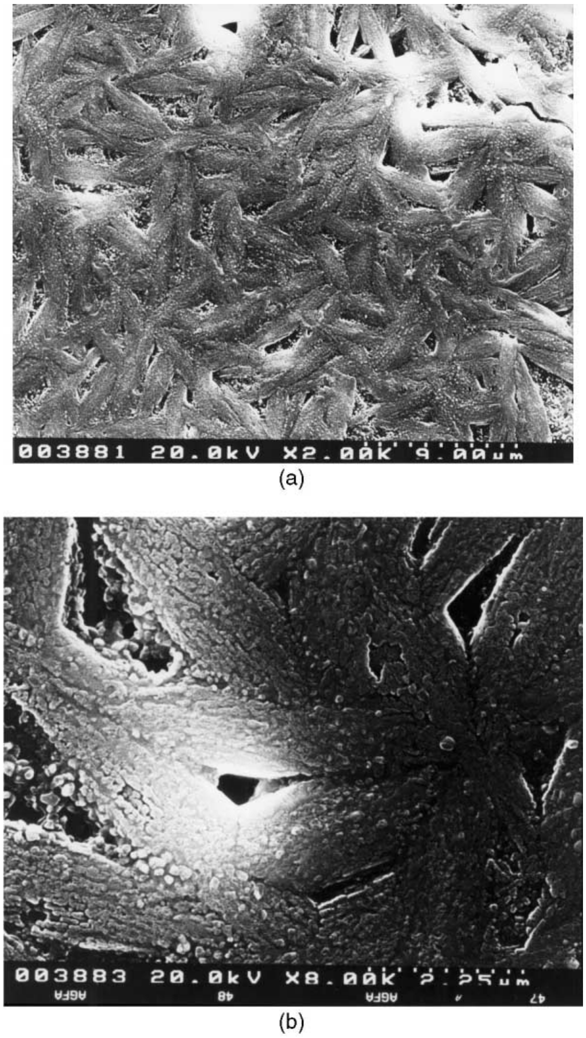


Fig. 8. FESEM micrographs of pressed glass powder of CO sample heated for 2 h at several temperatures: (a) 800°C (bar = 1 µm); (b) 1100°C (bar = 1.64 µm).

The crystal morphology of magnesium α-cordierite obtained from bulk glasses has been the concern of several authors.[23–26] The crystallization in these glasses is initiated at the surface and the crystals grow from the glass surface toward the centre. Two techniques have been used to increase volume nucleation in cordierite melt-derived glass. The first is to add a range of nucleating agents to the bulk glass. In the second, the glass powder compacts are sintered and crystallized. A rich variety of crystal morphologies have been observed on the external surface of a cordierite glass through suitable thermal treatments: elongated hexagonal prisms, lozenges and square shaped particles. These well defined morphologies only have been detected in hot-pressed powdered glasses when some kind of additives were added to permit sintering to full density prior to any crystallization.[27,28]

In order to check the possibility of obtaining well defined morphologies of crystalline cordierite in thermal treated cobalt-containing glasses, monolithic CO glass was heated and examined by FESEM. The micrography



(a)

(b)

Fig. 9. FESEM micrographs of heated bulk CO glass sample at 1200°C/3 h: (a) (bar = 9.00 μm); (b) (bar = 2.25 μm).

Fig. 10. FESEM micrography of heated MGCO glass powder at 1100°C for 2 h (bar = 1.80 μm).

of the fracture surface of the bulk CO glass previously heated at 1200°C/2 h displayed in Fig. 9(a), shows that the pure cordierite specimen attains almost a dense sintered microstructure. A closer look at this sample reveals that the microstructure is characterized by well ordered areas formed by small-sized grains (<200 nm), with a uniform grain-size distribution [Fig. 9(b)].

Finally, it is remarkable that pressed pellets of MGCO glass thermally treated at 1100°C for 2 h (Fig. 10) present small acicular crystals which become faces of hexagonal shaped prisms, defining one of the morphologies previously reported in pure magnesium cordierite.

4. Conclusions

Glasses of stoichiometric composition 2MO $2\mathrm{Al}_2\mathrm{O}_3$ $5\mathrm{SiO}_2$ (M=Co and/or Mg) were obtained by the melting of starting mixtures prepared by a semi-wet method. Powdered and bulk glass specimens were thermally treated at several temperatures and times and the sequence of crystallization and their microstructural evolution were analysed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Results on the crystallization sequence in all glasses showed that the first crystalline phase detected displayed the μ-cordierite structure, i.e. a solid solution with β-quartz structure. At higher temperatures a phase with α-cordierite structure was formed. IR spectra of cobalt μ- and α-cordierites, formed during the reaction sequence of cobalt-containing glasses, were similar to the ones previously reported for the magnesium phases. UV–vis diffuse reflectance spectra of cobalt-containing samples show that the Co^{+2} ions, which occupied the tetrahedral sites in glasses, moved into the octahedral sites during crystallization. The final morphology of cobalt-containing hexagonal cordierites depended on the reached sintering degree of the precursor glass before starting crystallization. In the case of equimolar cobalt-magnesium cordierites well defined morphologies were attained.

References

1. Karkhanavala, M. D. and Hummel, F. A., The polymorphism of cordierite. *J. Am. Ceram. Soc.*, 1953, **36**, 389–392.
2. Gibbs, G. V., The polymorphism of cordierite: I. The crystal structure of low cordierite. *Am. Mineral.*, 1966, **51**, 1068–1087.
3. Putnis, A., The distortion index in anhydrous Mg-cordierite. *Contrib. Mineral. Petrol.*, 1980, **74**, 135–141.
4. Meagher, E. P. and Gibbs, G. V., The polymorphism of cordierite: II. The crystal structure of indialite. *Can. Mineral.*, 1977, **15**, 43–49.
5. Goldman, D. S., Rossman, G. R. and Dollase, W. A., Channel constituents in cordierite. *Am. Mineral.*, 1977, **62**, 1144–1157.
6. Selkregg, K. R. and Bloss, F. D., Cordierites: compositional controls of Δ, cell parameters, and optical properties. *Am. Mineral.*, 1980, **65**, 522–533.
7. Ikawa, H., Otagiri, T., Imal, O., Suzuki, M., Urabe, K. and Udagawa, S., Crystal structures and mechanism of thermal expansion of high cordierite and its solid solutions. *J. Am. Ceram. Soc.*, 1986, **69**, 492–498.

8. Sundar, S., Vepa, V. S. S. and Umarji, A. M., Effects of substitution of Ca on thermal expansion of cordierite ($Mg_2Al_4Si_5O_{18}$). *J. Am. Ceram. Soc.,* 1993, **76**, 1873–1876.
9. Chen, Y. F., Rabu, P., Pourroy, G. and Vilminot, S., Phase evolution with thermal treatment in the system cordierite-CuO. *Eur. J. Solid State Inorg. Chem.,* 1995, **32**, 1065–1076.
10. Piriou, B., Chen, Y. F. and Vilminot, S., Unusual luminescent properties of Eu^{+3} in α cordierite. *Eur. J. Solid State Inorg. Chem.,* 1995, **32**, 469–481.
11. Wandscheneider, P. and Seifert, F., The system magnesium cordierite-cobalt cordierite. *J. Am. Ceram. Soc.,* 1984, **67**, C163–C164.
12. Cherepanina, L. I., Pyrkova, V. P., Vizir, L. A. and Denisov, A. N., Cordierite-type ceramic pigments of the system MgO–CoO–Al_2O_3–SiO_2. *Steklo Keram.,* 1978, **12**, 27–28.
13. Pyrkova, V. P., Cherepanina, L. I., Denisov, A. N. and Vizir, L. A., Soldatova, Cordierite-type ceramic pigments. *Steklo Keram.,* 1981, **5**, 22–23.
14. Langer, K. and Schreyer, W., Infrared and powder X-ray diffraction studies on the polymorphism of cordierite. *Am. Mineral.,* 1969, **54**, 1442–1459.
15. Watanabe, K. and Giess, E. A., Crystallization kinetics of high-cordierite glass. *J. Non-Cryst. Sol.,* 1994, **169**, 306–310.
16. Sales, M. and Alarcón, J., Crystallization of sol-gel derived glass ceramic powders in the MgO–CoO–Al_2O_3–SiO_2 system. II. Cordierite. *J. Mater. Sci.,* 1995, **30**, 2341–2347.
17. Nogami, N., Ogawa, S. and Nagasaka, K., Preparation of cordierite-glass by the sol-gel process. *J. Mater. Sci.,* 1989, **24**, 4339–4342.
18. Roy, B. N., Infrared spectroscopy of lead and alkaline-earth aluminosilicate glasses. *J. Am. Ceram. Soc.,* 1990, **73**, 846–855.
19. Vila, J., Muñoz, M. C., Valentín, C., Sales, M. and Alarcón, J., Cristalización de cordierita a partir de geles y vidrios estequiométricos. Estudio comparativo. *Bol. Soc. Esp. Cerám. Vidrio,* 1999, **38**, 21–28.
20. Okada, K. and Otsuka, N., Characterization of the spinel phase from SiO_2–Al_2O_3 xerogels and the formation process of mullite. *J. Am. Ceram. Soc.,* 1986, **69**, 652–656.
21. Bates, T., Ligand field theory and absorption spectra of transition-metal ions in glasses. In *Modern Aspects of The Vitreous State*, Butterworths, UK, 1962, pp. 195–254.
22. Sales, M., Valentín, C. and Alarcón, J., Cobalt aluminate spinel-mullite composites synthesized by sol-gel method/contribution. *J. Eur. Ceram. Soc.,* 1997, **17**, 41–47.
23. Watanabe, K., Giess, E. A. and Shafer, M. W., The crystallization mechanism of high-cordierite glass. *J. Mater Sci.,* 1985, **20**, 508–515.
24. Chaim, R. and Heuer, A. H., Crystallization in a barium-containing magnesium aluminosilicate glass-ceramic. *J. Am. Ceram. Soc.,* 1992, **75**, 1512–1521.
25. Glendenning, M. D. and Lee, W. E., Microstructural development on crystallizing hot-pressed pellets of cordierite melt-derived glass-containing B_2O_3 and P_2O_5. *J. Am. Ceram. Soc.,* 1996, **79**, 705–713.
26. Winter, W., Sintering and crystallization of volume- and surface-modified cordierite glass powders. *J. Mater Sci.,* 1997, **32**, 1649–1655.
27. Giess, E. A., Fletcher, J. P. and Herron, L. W., Isothermal sintering of cordierite-type glass powders. *J. Am. Ceram. Soc.,* 1984, **67**, 549–552.
28. Watanabe, K. and Giess, E. A., Coalescence and crystallization in powdered high-cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$) glass. *J. Am. Ceram. Soc.,* 1985, **68**, C102–C103.