

# Crystal morphologies on a cordierite glass surface

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*With suitable thermal treatments, a nearly stoichiometric cordierite glass (2MgO.2Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub>) shows a variety of crystal morphologies on the external surfaces: lozenges, regular and elongated hexagons, spherical and square shaped particles. We initially identified these morphologies through optical and scanning electron microscopy techniques. Their structural features were distinguished by x-ray diffraction patterns, infrared and Raman microprobe spectra. We concluded that there are close structural similarities for: lozenges and glass matrix; regular and elongated hexagons; spherical and square particles. The ordering degree increases in the following sequence: glass matrix, lozenges, hexagons, squares and spheres. The lozenge crystals are known as X-phase. The hexagons belong to the μ-cordierite (high quartz solid solution) metastable phase and the squares and spheres to the α-cordierite stable phase.*

Most glasses crystallise preferentially at the external surfaces, however, the surface nucleation mechanisms are not fully understood.<sup>(1)</sup> This is generally a problem to the glass industry that cannot avoid spontaneous devitrification of certain glasses. However, surface crystallisation can be advantageous in some technical applications such as toughening and hardening of glass articles<sup>(2)</sup> and in the production of sintered glass ceramics. These features lead the Technical Committee on nucleation, crystallisation and glass ceramics (TC7) of the International Commission on Glass to organise a round robin study which started in 1989 and is continued until now. The purpose of the round robin is to understand both qualitative and quantitative aspects of surface crystallisation of glasses. The TC7 members have chosen a cordierite (2MgO.2Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub>) glass, since it crystallises essentially on the surface, is chemically durable and has important commercial applications in the electronic industry.

Throughout these years we and several other TC7 members have observed that a rich variety of crystal morphologies can appear on cordierite glass surfaces through suitable thermal treatments.<sup>(3,4)</sup> The morpholo-

gies also depend strongly on the polishing powder used! The behaviour of CeO<sub>2</sub> polished specimens is described.

In the temperature range 850–980°C regular and elongated hexagonal crystals grow. These crystals easily produce a fully crystallised surface layer with a thickness of over 100 μm. For long thermal treatments a few spherical crystals appear on such crystallised surface. Scanning electron microscopy analyses revealed that lozenge shaped crystals, of about 1 μm, are formed together with the hexagonal ones.

At temperatures of about 1300°C square crystals grow and the small lozenge shaped crystals begin to acquire a spherical shape. With increasing treatment times the square crystals became spherical and finally the sample surface fully crystallises.

The objective of this paper is to characterise qualitatively the crystal structure of each morphology. That task was accomplished by analysing their infrared and Raman microprobe spectra, as well as x-ray diffraction patterns which enabled us to establish interesting structural similarities between some morphologies.

## Experimental

### Sample preparation

A cordierite glass, GM30870, having almost stoichiometric composition was supplied by Schott Glaswerke (Germany) to TC7 members as 2–3 mm thick plates. The glass was melted in a platinum–rhodium crucible without stirring. The chemical composition is presented in Table 1. Energy dispersive spectroscopy (EDS) measurements, performed on different points of several samples, have detected the presence of S, Ca, Ti, Cl and P with varying concentrations for different areas. More-

**Table 1.** Chemical composition of the GM30870 cordierite glass determined by Schott Glaswerke compared with its nominal stoichiometric composition

Oxides and elements	Schott (wt%)		Nominal (wt%)	
	(wt%)	(mol%)	(wt%)	(mol%)
SiO <sub>2</sub>	52.3	56.2	51.4	55.6
Al <sub>2</sub> O <sub>3</sub>	33.2	21.0	34.8	22.2
MgO	14.6	22.8	13.8	22.2
Li <sub>2</sub> O	< 2 ppm	–	–	–
Mn <sub>2</sub> O	300 ppm	–	–	–
Pt	2 ppm	–	–	–
Rh	< 5 ppm	–	–	–
K <sub>2</sub> O	60 ppm	–	–	–

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over, in some regions, the content of Al was quite high. These analyses indicate that there is some fluctuation in the glass composition.<sup>(4)</sup>

Specimens of about  $(5 \times 5)$  mm<sup>2</sup> were polished to an optical degree with cerium oxide (1  $\mu$ m) on a plane pitch tool. Thermal treatments with thermal stability of  $\pm 2^\circ\text{C}$  were performed in electric furnaces in air and in vacuum. The treated samples were etched with a 1 vol% HF solution to allow the observation of the crystals under the optical microscopes of the microinfrared and micro-Raman spectroscopy equipment.

X-ray diffraction measurements were performed in both monolithic and powdered specimens which were submitted to selected thermal treatment conditions so that no more than two distinct morphologies occurred simultaneously.

#### Instrumental techniques

Observations of crystal morphologies were made in two optical microscopes, Jenapol and Jenaval, Carl Zeiss/Jena, using polarised transmitted light.

Infrared spectra of areas as small as  $(80 \times 80)$   $\mu\text{m}^2$  were obtained with a Perkin Elmer 16PC FT-IR spectrometer. The small areas were selected with the help of a Cassegrain type optical microscope. In this arrangement, the infrared radiation illuminates the selected micro region through an adjustable rectangular slit. All spectra were obtained in the reflection mode.

Raman microprobe spectra were obtained with a Dilor XY Confocal Laser Raman spectrometer with a Gold array detector (1024 diodes). The optical microscope objective (Olympus, MS Plan, 100X, NA=0.95) enable a focal cylinder having 1.2  $\mu\text{m}$  diameter to be obtained and a focal depth of about 2.5  $\mu\text{m}$ . The focal cylinder was positioned on the crystal from which the spectrum would be measured. The 514.5 nm (green) line of a Coherent Innova 70-2 argon ion laser with output power of about 100 mW exciting radiation was used. An interference filter was used to avoid spurious scattered light mainly due to the laser plasma lines. Spectra were measured in the backscattering geometry.

X-ray diffraction measurements were performed on crystallised surfaces of monolithic and also in powdered samples using the copper  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) and a nickel filter, in a Rigaku Rotaflex diffractometer, operating at 40 kV and 20 mA.

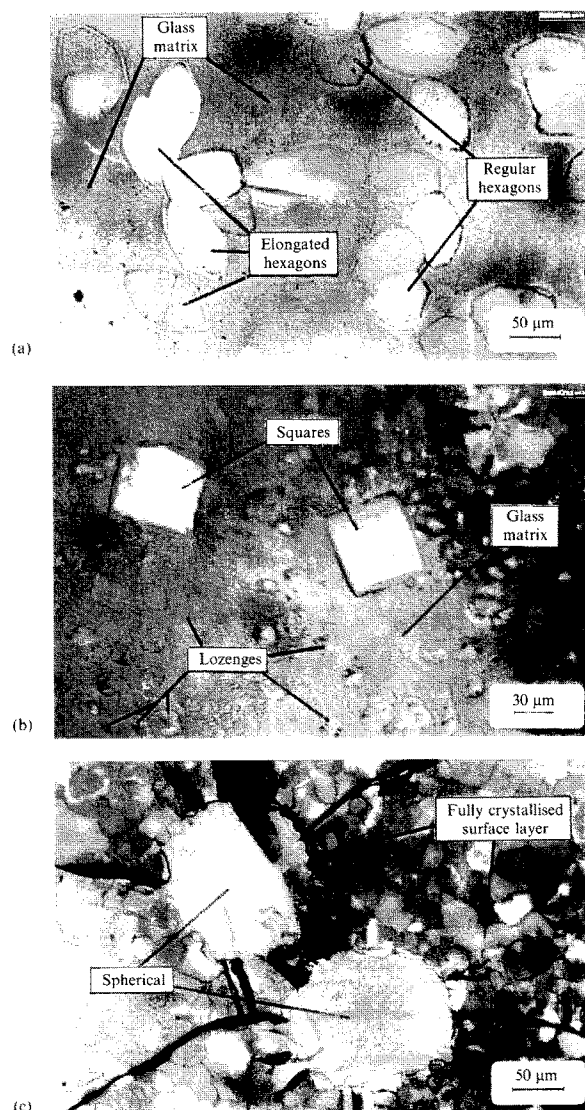
## Results and discussion

### Optical micrographs

The micrographs of Figure 1 show several crystal morphologies that occur on the cordierite glass surfaces after particular thermal treatment conditions. The size of each crystal is large enough for getting both infrared and Raman microprobe spectra of only one crystal at a time, except for the lozenge shaped crystals due to their reduced sizes.

### Infrared microprobe spectroscopy

Figure 2 shows the infrared microprobe spectra of each morphology that appear in the micrographs of Figure 1. It was impossible to measure the spectrum of only one lozenge due to the small dimensions of these crys-

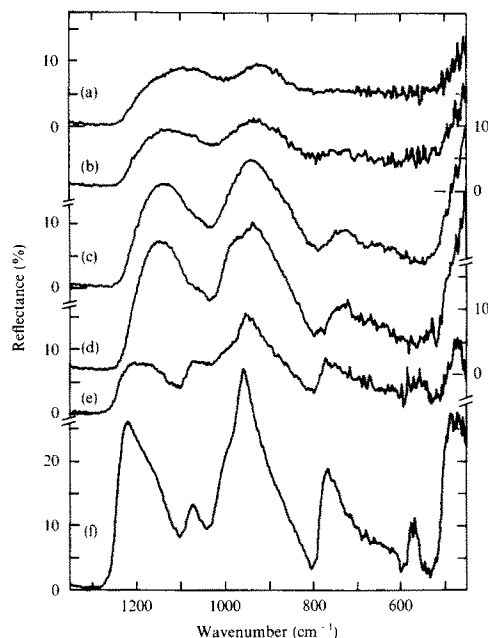


**Figure 1.** Optical micrographs (polarised transmitted light) showing the different crystal morphologies which occur on the surface of cordierite glass samples subjected to particular thermal treatments: (a)  $950^\circ\text{C}$ , 1h 30min, in vacuum: glass matrix, regular and elongated hexagons; (b)  $1370^\circ\text{C}$ , 1 min, in air: glass matrix, lozenges and squares; (c)  $910^\circ\text{C}$ , 7 h, in air: fully crystallised surface and spheres

tals. Hence, the spectrum (b) in Figure 2 was obtained by framing the microscope slit on a surface region having a high numerical density of lozenges, which contained only a small area fraction of residual glass.

The spectra for the regular and elongated hexagons are essentially the same, Figure 2(c). Very similar spectra were also observed for different squares, Figure 2(e) and spherical crystals, Figure 2(f).

In analysing the infrared spectra, it is well known that the narrower the bands the higher is the ordering degree of the material. Some interatomic distances and bond angles (for instance Si-O-Si) in glasses have a broad distribution while these distributions are narrower in most crystals and thus their infrared bands are narrower too. These features can be seen in the spectra of Figure 2 where there is a band narrowing along spectra (a)-(f). The other aspect to be noted is the shift



**Figure 2.** Fourier transform infrared microprobe reflection spectra of the crystal morphologies shown in Figure 1. All spectra were obtained after 100 scans: (a) glass matrix, slit area= $(100 \times 100)$  mm<sup>2</sup>; (b) lozenges and glass matrix, slit area= $(135 \times 135)$  mm<sup>2</sup>; (c) regular and elongated hexagons, slit area= $(100 \times 100)$  mm<sup>2</sup>; (d) fully crystallised surface, slit area= $(100 \times 100)$  mm<sup>2</sup>; (e) squares, slit area= $(80 \times 80)$  mm<sup>2</sup>; and (f) sphere, slit area= $(100 \times 100)$  mm<sup>2</sup>

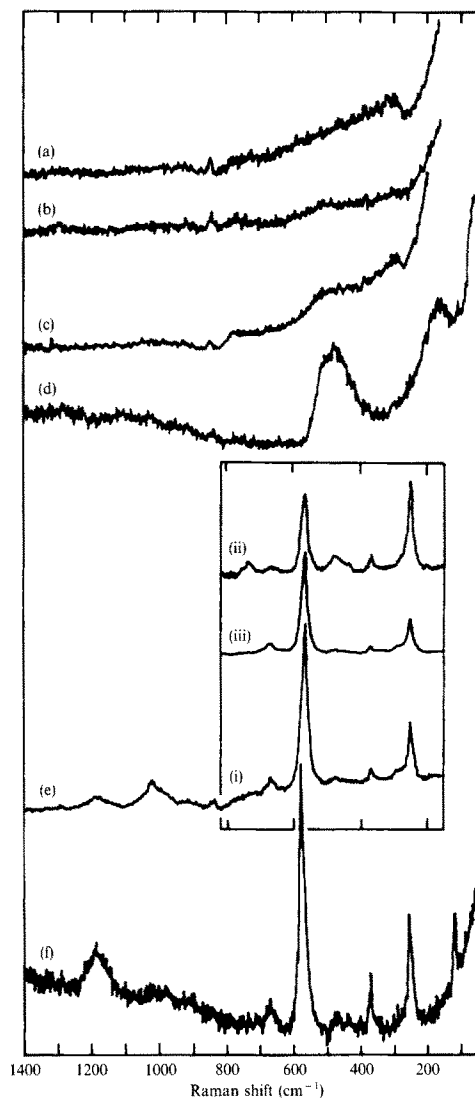
of all bands to higher frequencies due to the increase of the bonding forces. Since most interatomic distances are smaller in crystalline phases than in the corresponding glassy phases,<sup>(5)</sup> these force constants are stronger in the crystalline materials.

Changes in the intensity of a particular band are due to changes in the variation of the induced electric dipole moment during molecular vibrations.<sup>(5)</sup> From the infrared spectra shown in Figure 2 we can conclude that the glass matrix, lozenge and hexagon crystals have a similar structure. The same trend is observed for the square shaped and spherical crystals. Additionally, according the spectra obtained from all morphologies, the structure of the spherical crystals seems to be the most ordered.

#### Raman microprobe spectroscopy

Raman microprobe spectra are shown in Figure 3. The low intensity band at about 850 cm<sup>-1</sup> that appears in the main spectra is due to the resonant Raman effect of the anti-reflecting coating of the microscope objective.<sup>(6)</sup>

The intensities of Raman bands are related to the change of the polarisability tensor of molecules during their vibrations.<sup>(5,7)</sup> Generally, a high symmetric



**Figure 3.** Raman-Stokes microprobe spectra of the crystal morphologies shown in the micrographs of Figure 1. The spectra were obtained with about 20 scans: (a) glass matrix; (b) lozenge; (c) regular and elongated hexagons; (d) fully crystallised surface; (e) square: (i) spectrum taken with an random polarisation plane of the exciting light, (ii) spectrum taken with the polarisation plane parallel to the edge, (iii) spectrum taken with the polarisation plane 45° with respect to the edge; (f) sphere

interlinked by Si-O-Al bonds or by a significant distortion of the AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra, as in vitreous silica.<sup>(8,9)</sup> There are no significant differences in the Raman spectra of regular and elongated hexagons, Figure 3(c), as observed in their infrared spectra.

In Raman spectroscopy, analogous to infrared spectroscopy, the width of the bands reflects the structural ordering of the material under study. Only in spectrum

set of thin branches which seem to be glued by amorphous material.<sup>(4)</sup>

The spectra of squares (e) and of spheres (f) are very similar and display a distinct vibrational structure with respect to the other morphologies. This characteristic reflects a significant difference in the crystalline structures of these morphologies in relation to the lozenge and hexagon crystals. The narrow bands of the spheres and squares are explained by their high crystalline structural ordering degree.

The Raman spectroscopy technique has an additional advantage with respect to infrared spectroscopy, i.e. the exciting laser light is polarised.<sup>(7,10)</sup> This feature was exploited to verify whether the squares are single or polycrystalline on the scale of the laser (focal cylinder) diameter. Spectrum (e) shows that the square crystals have properties that resemble those of single crystals. On the other hand the spectra of different spherical crystals are essentially identical, independently of the polarisation direction, Figure 3(f), implying that they are polycrystalline (spherulitic like).

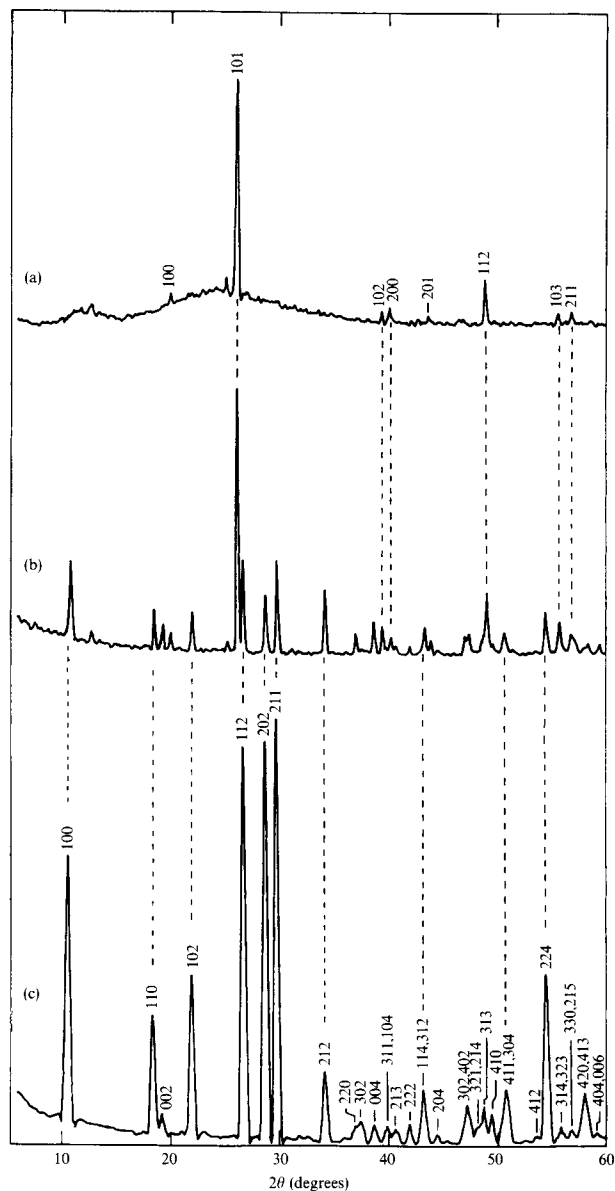
#### X-ray diffraction

Figure 4 shows some x-ray diffraction patterns of selected specimens. The surface of the sample that exhibits pattern (a), treated at 819°C for 120 h, is mainly covered by small lozenge crystals although some (large) hexagonal crystals are also present. According to recent literature the lozenge crystals are denoted as X-phase,<sup>(11-14)</sup> a magnesium petalite like solid solution.

Most XRD peaks were well indexed with PDF14-249<sup>(15)</sup> which leads us to conclude that the hexagonal crystals belong to the  $\mu$ -cordierite metastable phase, that has an hexagonal structure with  $a=5.200\text{Å}$  and  $c=5.345\text{Å}$ . The weak peaks at  $2\theta\approx 25.0^\circ$  and between  $2\theta\approx 10^\circ$  and  $15^\circ$  could not be identified but are probably due to the X-phase.

It should be emphasised that a layer of about 120  $\mu\text{m}$  is responsible for most of the diffracted x-rays intensity. Thus, the broad background, ranging from  $2\theta\approx 15$  to  $40^\circ$  is due to the relatively high fraction of residual glass.

The diffraction pattern of Figure 4(c) was obtained from a fully crystallised powdered sample, treated at 1370°C for 4 min, because no massive specimen could be prepared with this treatment condition. The reflection peak positions agree very well with the results obtained by Schreyer & Schairer<sup>(16)</sup> with small differences in intensities (see also File 13-293<sup>(15)</sup>). The observed reflections can be indexed on the basis of a hexagonal unit cell:  $a=9.7698\text{Å}$ ,  $c=9.3517\text{Å}$ , space group  $P6/mcc$  ( $D_{2h}^2$ ). Some synthetic and natural forms of cordierite present almost identical patterns to that shown in Figure 4(c). The most notable differences are the splitting of some reflection peaks specially that in the range of  $2\theta$  between  $29$  and  $30^\circ$  as shown by Miyashiro *et al*<sup>(17)</sup> and Miyashiro.<sup>(18)</sup> This splitting should be related to structural distortion of cordierite minerals. The degree of distortion is measured by the distortion index,  $\Delta$ , which is related to the  $2\theta$  differences of two to four reflections that can appear between  $29$  and  $30^\circ$ .<sup>(18)</sup> However, this is not the case of



**Figure 4.** X-ray diffraction patterns of crystal morphologies grown on the surface of the GM30870 cordierite glass samples subjected to thermal treatments in air: (a) 819°C, 120 h, massive; (b) 860°C, 67 h, massive; (c) 1370°C, 4 min, powder

pattern (c) in Figure 4 where no splitting can be observed possibly due to the compressed scale of the  $2\theta$  axis. It can then be concluded that the x-ray pattern it is related to the  $\alpha$ -cordierite phase, also denoted in the literature as indialite or high cordierite.<sup>(16-19)</sup>

A monolithic specimen treated at 860°C during 67 h gives the diffraction pattern (b) shown in Figure 4. It is essentially a matching of both (a) and (c) patterns with predominance of the  $\mu$ -cordierite (hexagonal morphology the  $\mu$ -cordierite phase is also labeled as high quartz solid solution by some authors) due to the intense (101) reflection peak at  $2\theta\approx 26^\circ$ . Observation of this sample with optical microscope shows a fully crystallised surface, similar to that presented in micrograph (c) of Figure 1.

A final observation is that the mass densities and

**Table 2.** Densities and refractive indexes of glass,  $\mu$  and  $\alpha$  cordierite<sup>(20)</sup>

	Glass	$\mu$ -cordierite	$\alpha$ -cordierite
Density, $\rho$ (g/cm <sup>3</sup> )	2.60	2.59	2.51
Refractive index, $n$	1.55	1.55	1.53–1.54

refractive indexes of three phases confirm the similarities and differences discussed in this work. These properties are summarised in Table 2 and reinforce the conclusion that the glass structure is more similar to the  $\mu$  phase than to the  $\alpha$ -cordierite.

### Conclusions

Optical microscopy analysis of a thermally treated, almost stoichiometric, cordierite glass shows that regular hexagons, elongated hexagons and lozenges appear simultaneously on the surface of samples treated between 850 and 980°C ( $T_g \sim 820^\circ\text{C}$ ). The hexagons have a much higher growth rate than lozenges and form a thick crystallised layer for long treatments. Spherical crystals are also formed during the growth of this layer. For short treatment times at 1370°C, nucleation and growth of lozenge and square crystals are observed and they gradually acquire a spherical shape.

Infrared and Raman microprobe spectra have shown evidences for remarkable similarities between the structures of: (1) glass, lozenges, hexagons and fully crystallized surface layer; and (2) squares and spheres. The following sequence of crystalline ordering degree is observed: lozenges, hexagons, squares and spheres. Some of these conclusions agree with those obtained by early infrared absorption spectra and by the conventional 90° and glancing angle geometry of macro Raman scattering spectra.<sup>(21–23)</sup>

From the x-ray diffraction patterns we conclude that the crystal phases (morphologies) described in the present work have hexagonal structures, but the sizes of the unit cells of hexagons, which belong to the metastable  $\mu$ -cordierite phase, are smaller than that of the squares and spheres of the stable  $\alpha$ -cordierite phase. It should be emphasised, however, that the observed morphologies in glass GM 30780 might not be equal to those observed in stoichiometric cordierite glasses.

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