

CRYSTAL MORPHOLOGIES AT THE SURFACE OF A CORDIERITE GLASS

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ABSTRACT

With suitable thermal treatment conditions, a nearly stoichiometric cordierite glass ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) shows different crystal morphologies: lozenges, regular and elongated hexagons, spherical and square shaped particles. These morphologies were initially identified through optical and scanning electron microscopy techniques. Their structural features were distinguished by their X-ray diffraction patterns and by infrared and Raman microprobe spectra. The results obtained allow to conclude that there are close structural similarities for: (a) lozenges and glass matrix, (b) regular and elongated hexagons, and (c) spherical and square particles. Additionally, the crystalline ordering degree increases in the following sequence: lozenges, hexagons, squares and spheres. It was also concluded that the lozenges and hexagons belong to the μ -cordierite metastable phase and the squares and spheres to the α -cordierite stable phase.

1. INTRODUCTION

Most glasses crystallize preferentially at the surface. This is generally a problem to the glass industry, but can be advantageous in some technical applications [1]. These features lead the Technical Committee No 7 (TC7) of the International Commission on Glass to organize a round-robin study. The present purpose of the TC7 is to study the qualitative and quantitative aspects of surface crystallization of glasses in a more systematic way than has been done so far. The TC7 members have chosen a cordierite glass, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$, for these studies, since this glass composition crystallizes essentially on the surface and has important commercial applications.

Since 1989, the authors observed that several crystal morphologies can occur on the cordierite glass surface through suitable thermal treatment conditions [2,3].

Between 850 and 980°C, regular and elongated hexagonal crystals grow. These crystals can produce a fully crystallized surface layer with a thickness over 100 μm . For longer thermal treatments, a few spherical crystals appear on such crystallized surface. Under scanning electron microscope analysis it was observed that lozengular crystals, with about 1 μm in size, are formed together with the hexagonal ones in the early times of thermal treatments.

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

Qualitative informations about the structure of each morphology were obtained by analyzing their infrared and Raman microprobe spectra. These spectra enable the observation of important structural similarities of some morphologies as well as to accompanying their structural modifications. Conventional X-ray diffraction

measurements were performed on special thermally treated samples with the main purpose to determine the crystal structure of each morphology.

2. EXPERIMENTAL

Sample Preparation

A cordierite glass having almost stoichiometric composition ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) was supplied by Schott Glaswerke (Germany) to the TC7 members as 2-3 mm thick plates, with label GM30870. The glass was melted in a platinum-rhodium crucible, without stirring. The chemical composition of this glass, presented in Table 1, was furnished by Schott Glaswerke. However, energy dispersive spectroscopy (EDS) measurements, performed on different points of several samples, show also the presence of S, Ca, Ti, Cl and P, with concentrations that varies for different microareas analyzed. Moreover, in some areas the content of Al was quite high. These analysis indicates that there is a fluctuation in the glass composition [3].

Samples of about $(5 \times 5) \text{ mm}^2$ were polished to an optical degree with cerium oxide ($1 \mu\text{m}$) on a plane pitch tool. Thermal treatments, with thermal stability of about $\pm 2^\circ\text{C}$, were performed in electric furnaces in air and in vacuum.

TABLE 1. Chemical composition of the GM30870 cordierite glass as determined by Schott Glaswerke, compared with its nominal stoichiometric composition.

oxides and elements	SCHOTT		nominal % mol
	% wt.	% mol	
SiO_2	49.1	52.3	51.4
Al_2O_3	34.6	33.2	34.6
MgO	14.6	14.2	13.8
Li_2O	< 2 ppm		
Mn_2O	300 ppm		
Pt	2 ppm		
Rh	< 5 ppm		
K_2O	60 ppm		

The thermally treated samples were etched with a 1% vol. HF solution to allow the observation of the crystal morphologies in the optical microscopes of the infrared and Raman spectroscopy equipments.

For X-ray diffraction measurements, higher surface area samples were prepared, in massive or powdered forms. These samples were submitted to choosed thermal treatment conditions so that no more than two distinct morphologies occurs simultaneously.

Instrumental Techniques

Observations of crystal morphologies were made trough optical microscopes, Jenapol and Jenavert, Carl Zeiss/Jena, with transmitted and polarized light.

Infrared spectra of areas as small as about $(80 \times 80) \mu\text{m}^2$ were measured with a Perkin Elmer 16PC FT-IR spectrometer. The small areas on the samples of interest were selected with the help of a Cassegrain type optical

microscope. The infrared radiation incides onto the selected micro-region through the adjustable rectangular slit of the microscope. Spectra were obtained by reflection.

Microprobe Raman spectra were measured with a Dilor XY Confocal Laser Raman spectrometer with a Gold array detector (1024 diodes). The optical microscope objective enables to obtain a focal cylinder with diameter of about 1 μm and focal depth of the order of 0.7 μm . This focal cylinder was positioned on the crystal from which the spectrum would be measured. As exciting radiation, it was used the 514.5 nm line of a Coherent Innova 70-2 argon ion laser, with power of about 100 μW . An interference filter for this wavelength was used to avoid spurious scattered light, mainly due to the laser plasma lines. Spectra were measured by backscattering geometry.

X-ray diffraction measurements were performed on crystallized surfaces of massive samples and also in powder samples using the copper $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a nickel filter in a Rigaku Rotaflex diffractometer, operating at 40 kV and 20 mA.

3. RESULTS AND DISCUSSION

Optical Micrographs

The micrographs of Figure 1 show the several crystal morphologies which occur on the cordierite glass surfaces after particular thermal treatment conditions. The size of each crystal is large enough for measuring the infrared and Raman microprobe spectra of only one crystal at a time.

Infrared Microprobe Spectroscopy

Figure 2 shows the infrared microprobe spectra of each morphology which appears in the micrographs of Figure 1. It was impossible to measure the spectrum of only one lozenge due to the small dimensions of these crystals. Spectrum (b) in Figure 2 was obtained by framing the microscope slit on a surface region with a high numerical density of lozenges and having a small glass matrix area fraction. The regular and elongated hexagons have essentially the same spectra (Fig. 2 (c)). Very similar spectra were also observed for different spherical crystals (Fig. 2 (f)).

In infrared spectra, the narrower the bands, the higher is the ordering degree of the material analyzed. In glasses some interatomic distances and the angles of these interatomic bonds have a broad distribution. In crystals these distributions are narrower, and their infrared bands are narrow too. These features can be seen in the spectra of Figure 2, where the bands became narrower along spectra (a) to (f). Other aspect to be noted in these spectra is the shift of all bands to higher frequencies due to the increase of the force constant of the bond between neighbor atoms. Since the interatomic distances are smaller in crystalline phases than in the corresponding glassy phases [4], these force constants are stronger in the crystalline materials. Changes in the intensity of a particular band is due to the changes in the variation of the induced electric dipole moment during the molecular vibrations [4]. From the infrared spectra shown in Figure 2 it can be concluded that the glass matrix, the lozenge and hexagon crystals have a similar structure; the same should occur with the square and sphere crystals. Additionally, according the spectra obtained, from all morphologies observed the structure of the spherical crystals seems to have the higher ordering degree.

Raman Microprobe Spectroscopy

Raman microprobe spectra are shown in Figure 3. The intensity of Raman bands are related to the change of the polarizability of molecules during vibration [4, 5]. Generally, symmetric molecules have a high change in its polarizability and are Raman active, but are infrared inactive. Spectra (a) to (c) are poor in terms of number of bands in the high frequency region, which can be explained by the high number of tetrahedra interlinked by Si-O-Al bonds, or by the high distortion of the AlO_4 and SiO_4 tetrahedra, as in vitreous silica [6, 7].

There are no significant differences in the spectra of regular and elongated hexagons (Fig. 3 (c)), as also observed in their infrared spectra.

In infrared spectroscopy and also in Raman spectroscopy the width of the bands reflect the structural ordering of the material under study. Only for spectra (d) of the fully crystallized surface layer a narrowing of the bands initiates at about 160 and 500 cm^{-1} . This narrowing is not observed in the spectra of individual hexagons (spectrum (c)) since they have a low degree of crystallization for shorter times of thermal treatment, as was observed for HF etched samples in scanning electron microscopy [3].

The spectra of squares (e), and of spheres (f), are very similar, but show a drastic change in the vibrational structure with respect to the spectra of the other morphologies. This reflects a pronounced difference in the crystalline structures of the square and sphere crystal morphologies in relation to the lozenge and hexagon ones. The narrow bands of the former are explained by their higher crystalline structural ordering degree.

The Raman spectroscopy technique has an additional advantage with respect to infrared spectroscopy: the exciting laser light is polarized [8, 9]. This feature was exploited to verify to which degree the squares are single crystals, on the scale of the focus diameter of the laser radiation. Spectrum (e) shows that these crystals actually present properties that resemble those of single crystals. Independent of the exciting polarization direction, the spectra of different spherical crystals are essentially identical (Fig. 3 (f)), implying that they are polycrystalline.

X-Ray Diffraction

Figure 4 shows X-ray diffraction patterns of specially treated samples. The surface of the sample which exhibits pattern (a), treated at 819°C for 120h, is mainly covered by lozenge crystals, although some few hexagonal crystals are also present. Accordingly to the most recent literature, the lozenge crystals are denoted as X-phase [10-13]. The peaks of the pattern were well indexed with PDF #14-249 [14], which leads to conclude that the lozenge crystals belong to the μ -cordierite metastable phase, with hexagonal structure: $a = 5.200\text{\AA}$, $c = 5.345\text{\AA}$. Only the weak peaks at $2\theta \cong 25.0^\circ$ and between $2\theta \cong 10^\circ$ and 15° could not be identified. The broad background ranging from $2\theta \cong 15^\circ$ to 40° is characteristic of an amorphous sample and indicates that the surface of the sample has a relatively high vitreous area fraction.

Diffraction pattern (c) in Figure 4 was obtained for a fully crystallized powdered sample treated at 1370°C during 4 min, since no massive specimen could be obtained with this treatment condition. The reflection peak positions fit very well the results obtained by Schreyer and Schairer [15], with small differences in their intensities (see also File # 13-293 [14]). The observed reflections are indexed on the basis of a hexagonal unit cell: $a = 9.7698\text{\AA}$, $c = 9.3517\text{\AA}$, space group $P6/mcc$ (D_{2h}^2). Some synthetic and natural forms of cordierite present near 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 2θ between 29° and 30° , as shown by Miyashiro *et al.* [16] and Miyashiro [17]. This splitting should be related to structural distortion of cordierite minerals. The degree of distortion is measured by the distortion index, which is related to the 2θ differences of two to four reflections that can appear between 29° and 30° [17]. However this is not the case of the pattern (c) in Figure 4, where no splitting can be observed, possibly due to the compressed scale of the 2θ axis. It can then be concluded that the

distortion index of the studied sample is $\Delta = 0$, and that it is concerned with the α -cordierite phase, also denoted in the literature as indialite or high-cordierite [15-18].

A massive sample treated at 860°C during 67h gives the diffraction pattern (b) shown in Figure 4. It is essentially a matching of both (a) and (c) patterns, with predominance of the μ -cordierite (hexagonal morphology) due to the intense (101) reflection peak at $2\theta \cong 26^\circ$. Observation of this sample with optical microscope shows a fully crystallized surface, like that presented in micrograph (c) of Figure 1.

4. CONCLUSIONS

The observation of the thermally treated cordierite samples through optical microscopy shows that regular and elongated hexagons, and lozenges, appear simultaneously on the surface of samples treated between 850 and 980°C. The hexagons have a higher growth rate than lozenges and form a thick crystallized layer for longer treatments. Spherical crystals are formed during the growth of this layer. At 1370°C, for very short treatment times, nucleation and growth of lozenge and sphere crystals are observed, and they gradually acquire a spherical shape.

Infrared and Raman microprobe spectra show evidences of similarities between the crystalline structure of glass and lozenge, hexagons and crystallized surface layer, and squares and spheres. Additionally, the crystalline ordering degree have the following sequence: 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 geometries of Raman scattering spectra measurements [19-21].

From the X-ray diffraction patterns it is can be concluded that the morphologies concerned in the present work have hexagonal structures, but the sizes of the unit cells of lozenges and hexagons, of the metastable μ -cordierite phase, are smaller than that of the squares and spheres, of the stable α -cordierite phase.

Acknowledgments. The authors wish to thank Dr. E. da Silva and Dr. B. Roussel, of Dilor (France), and Prof. Dr. Marcos A. Pimenta and Ms. Maria S. Dantas of DF - UFMG for the Raman microprobe spectra measurements; M.Sc. Roberto A. M. Zocchetti, Valéria C. Barbosa and Prof. Dr. Ines Jockes of DQ - UNICAMP for help with infrared microprobe spectra measurements; Mr. J. A. L. Rocha and Mr. G. Catarino of IFSC - USP for help with the X-ray diffraction measurements.

Financial support: CNPq (Grant No 84.0117/92-2), CNPq/RHAE (Grant No 36.0062/90-0), and PADCT/CNPq (Grant No 62.0058/91-9).

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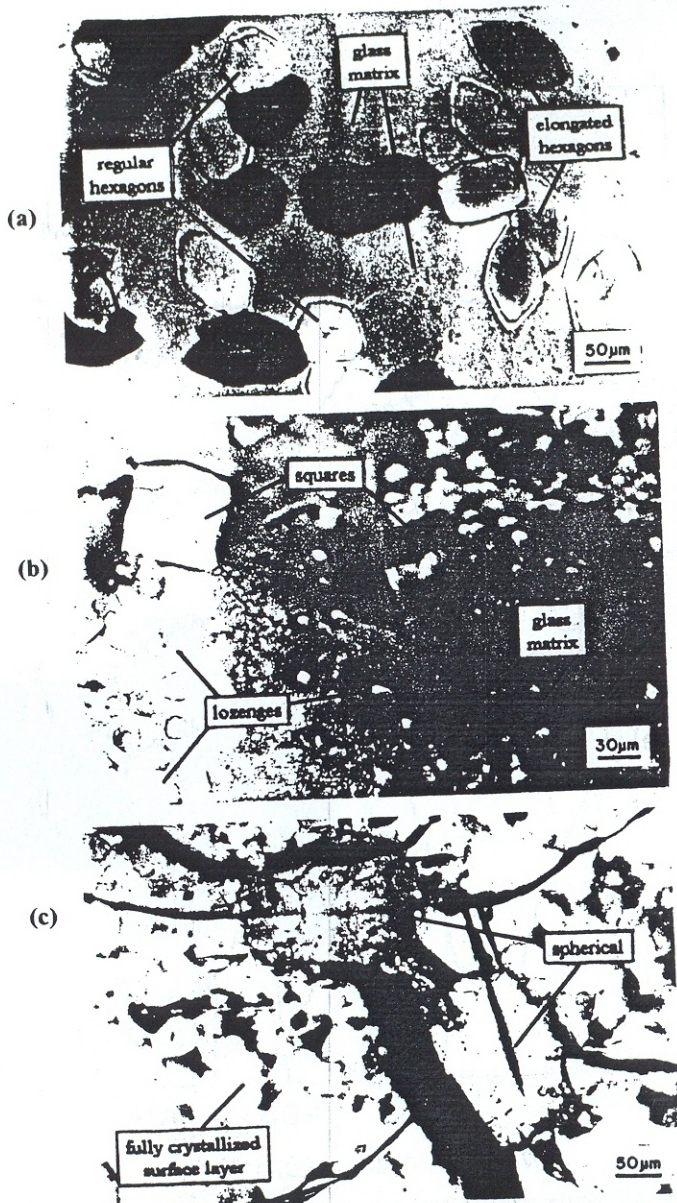


FIGURE 1. Optical micrographs (polarized transmitted light) showing the different crystal morphologies which occur on the surface of cordierite glass samples subjected to particular thermal treatments: (a) 950°C, 1h30min, in vacuum: glass matrix, regular and elongated hexagons; (b) 1370°C, 1min, in air: glass matrix, lozenges, and squares; (c) 910°C, 7h, in air: fully crystallized surface and spheres.

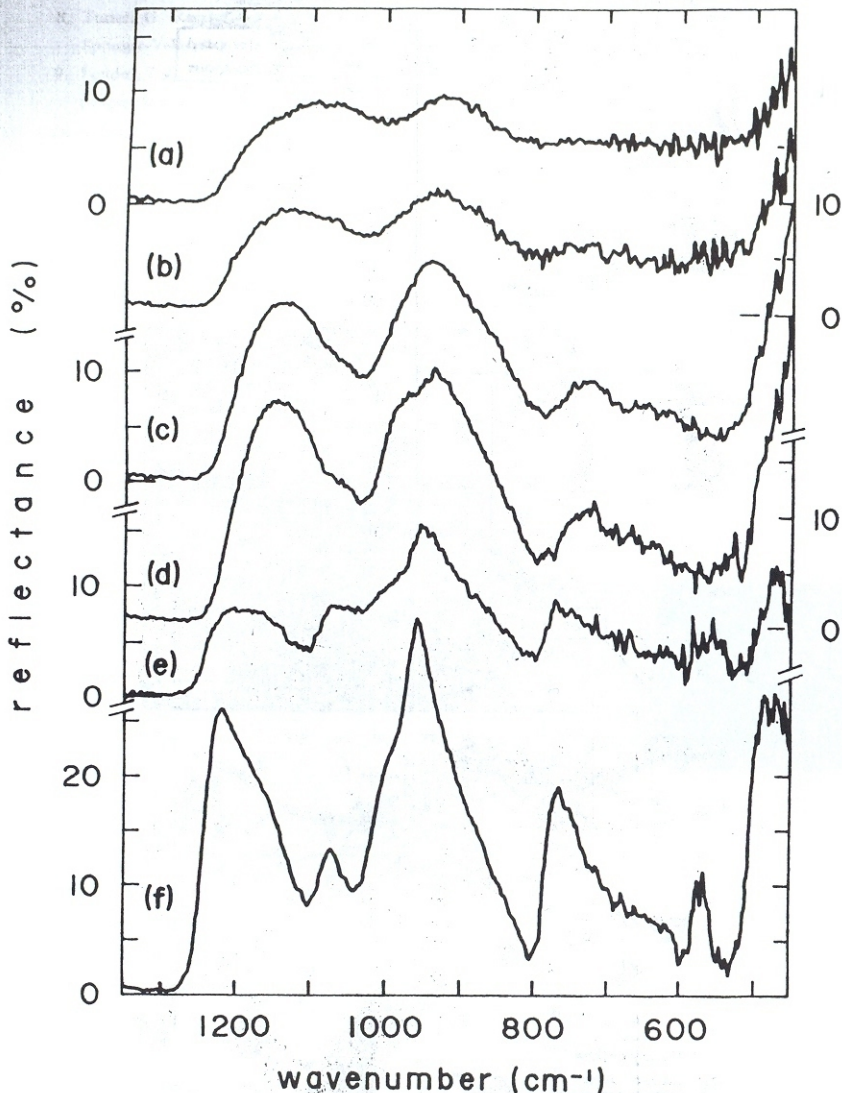


FIGURE 2. Fourier transform infrared microprobe reflection spectra of the crystal morphologies shown in Figure 1. All spectra were obtained after 100 scans: (a) glass matrix, slit area: $\cong (100 \times 100) \mu\text{m}^2$, (b) lozenges and glass matrix, slit area: $\cong (135 \times 135) \mu\text{m}^2$, (c) regular and elongated hexagons, slit area: $\cong (100 \times 100) \mu\text{m}^2$, (d) fully crystallized surface, slit area: $\cong (100 \times 100) \mu\text{m}^2$, (e) squares, slit area: $\cong (80 \times 80) \mu\text{m}^2$, (f) sphere, slit area: $\cong (100 \times 100) \mu\text{m}^2$.

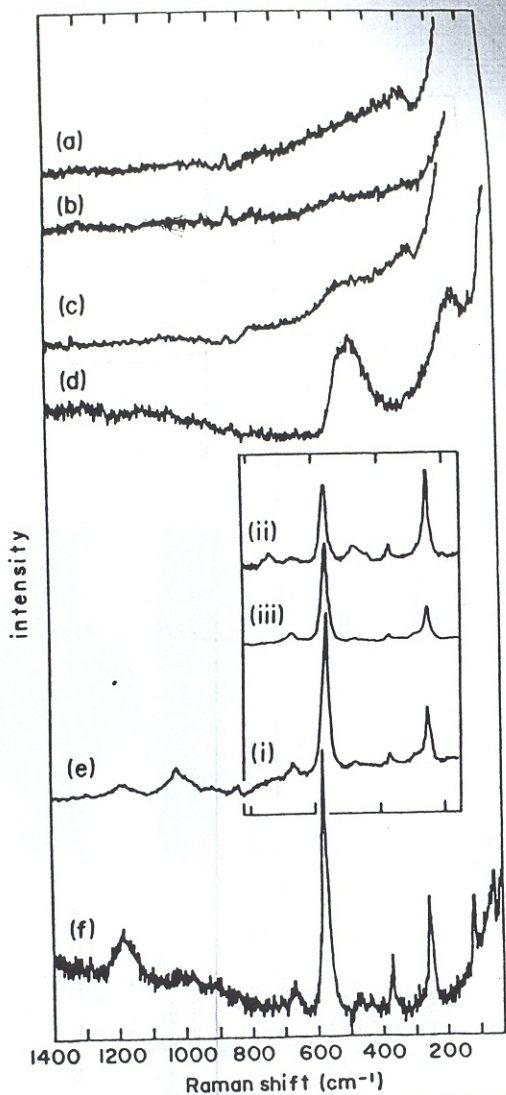


FIGURE 3. Raman-Stokes microprobe spectra of the crystal morphologies shown in the micrographs of Figure 1. The spectra were obtained with about 20 scans: (a) glass matrix; (b) lozenge; (c) regular and elongated hexagons; (d) fully crystallized surface; (e) square: (i) spectrum taken with aleatory polarization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

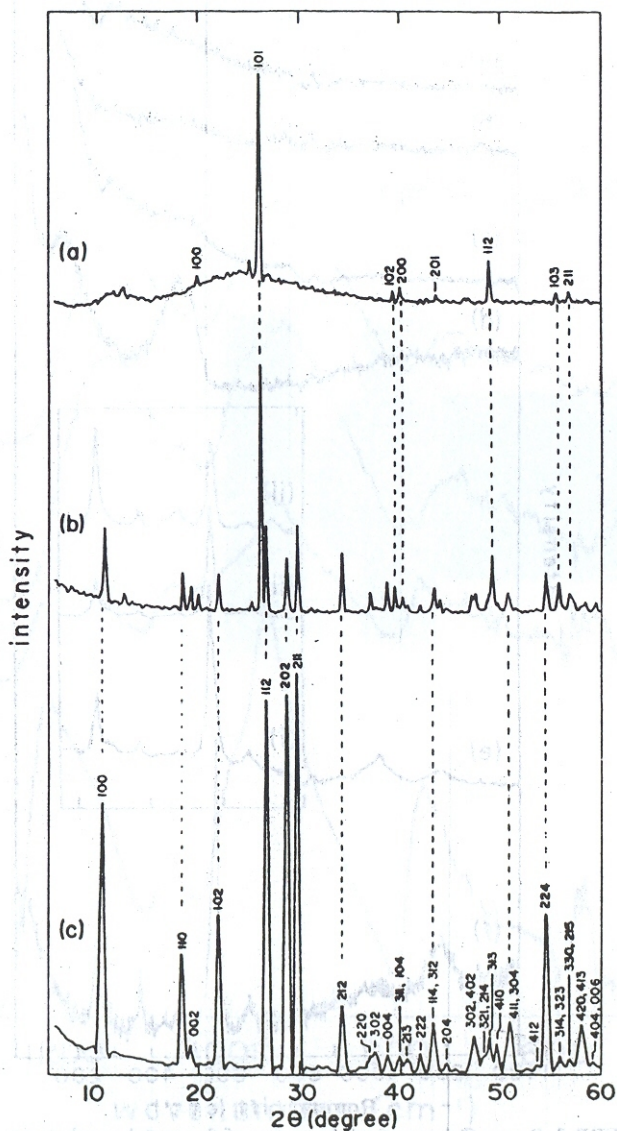


FIGURE 4. X-ray diffraction patterns of crystal morphologies grown on the surface of the GM30870 cordierite glass samples subjected to thermal treatments in air: (a) 819°C, 120h, massive; (b) 860°C, 67h, massive; (c) 1370°C, 4min, powder.