

# Review: The Crystallisation of Cordierite Glass

## Part 1 *A Review of Glass Crystallisation theory with particular reference to Glass-Ceramics from the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System*

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A study has been made of the crystallisation of a glass near the cordierite composition ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) using the techniques of differential thermal analysis and multiple attenuated total reflectance infra-red spectrophotometry. An extensive review of the theoretical aspects of glass crystallisation, and in particular the crystallisation of cordierite-type glasses, was undertaken and is presented as part 1 of this work.

The present paper is the first of a series covering an extensive study of the crystallisation of a cordierite-type glass. A comprehensive literature review was undertaken which included the development of the present state of understanding of the crystallisation processes for  $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  glasses. The literature was drawn from a wide range of sources which included results from mineralogical, chemical and technological research programmes to bring together all the data available for use in glass-ceramic research. Subsequent papers will deal with the experimental techniques that were adopted and the results of the study.

### 1. Introduction

The development of glass-ceramics has promoted renewed interest in the study of the basic principles of glass crystallisation. The volume of literature concerned with theories of nucleation and crystallisation of glass has increased significantly in recent years and although much valuable data has been presented a complete and consistent theory is still lacking.

Several authors [1-7] have discussed these theoretical aspects in terms of the classical theories of homogeneous and heterogeneous nucleation and have shown that such treatments can be successfully applied to practical glass-ceramic systems. Modified treatments have also been developed to account for difficulties that arise through consideration of complex glass-

forming systems [8-10].

Glass-ceramic research has emphasised the importance of glass-in-glass separation as an initiating step for controlled crystallisation. Many authors have discussed the importance of this phenomenon both in classical terms [11-18] and in terms of spinodal decomposition [6, 7, 19-25]. Electron microscope and low-angle X-ray diffraction studies have been developed to obtain direct experimental evidence of the effects. In particular the recent studies of MacDowell and Beall [26] and James and McMillan [27] have given examples of the use of advanced techniques for the determination of the nature and role of metastable phase separation in glass crystallisation. Blinov [28] has postulated that the initiating stage of the process could be due in some cases to the precipitation of crystalline compounds which are isomorphous with the primary crystallisation products of certain glass-ceramics.

The theoretical concepts outlined above must be supplemented by a detailed review of the phase relationships and properties of the glass-forming system prior to any study of glass-ceramic production. In the present work a glass from the primary crystallisation field of cordierite was studied. The literature on the polymorphism of cordierite, the patent literature and previous investigations of glass-ceramic formation in the  $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  system were reviewed and are presented in the following sections.

## 2. The Polymorphism of Cordierite

There have been several important studies of cordierite polymorphism. The early workers Rankin and Merwin [29] and Geller and Insley [30] identified a stable high-temperature form and a metastable low-temperature form. These were classified as  $\alpha$ - and  $\mu$ -cordierite respectively.

Extended studies by Karkhanavala and Hummel [31], based on earlier work [32-35], showed the existence of a stable low-temperature polymorph which was called  $\beta$ -cordierite. These investigators found that the  $\alpha$ -modification was readily formed by the devitrification of glass at temperatures in the range 1050 to 1450°C. By contrast, the  $\mu$ -form could only be obtained by devitrification of very finely-ground glass (–350 mesh) at temperatures in the 800 to 900°C range using heat treatments of long duration. The low-temperature  $\beta$ -form could only be produced hydrothermally below 830°C. Both  $\beta$ - and  $\mu$ -forms readily converted to the stable  $\alpha$ -form in the temperature range 830 to 1050°C when heated in air.

Detailed studies of different natural cordierites were subsequently undertaken by several workers [36-41] and their results indicated that certain ordered forms were sufficiently different from the less ordered forms to justify the designation of the former as a new mineral species which they called indialite. The classification of cordierites and indialites was based on X-ray criteria developed by Miyashiro [42]. A comprehensive classification of the stable and metastable polymorphs was presented by Tyrrell, Gibbs and Shell [43] and the nomenclature used by Eitel [44] in his summary was based on the Miyashiro distortion index ( $\Delta$ ). An excellent summary of the phase relations has been given by Toropov and Barzakovskii [45].

Schreyer and Schairer [46, 47] reinvestigated the central part of the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, the polymorphism of cordierite and structural transformations and presented a revised nomenclature. This was also based on the Miyashiro distortion index ( $\Delta$ ). One of the important points was the finding that the structure of the metastable  $\mu$ -phase corresponded to a stuffed high-quartz phase. This phase, previously described as silica-O by Roy [48], is found as the first crystallisation product of a wide range of glass compositions in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, forming as a metastable product at sub-solidus temperatures. The extensive study of Schreyer and Schairer [46] clearly classified the

polymorphic forms and it is unfortunate that other authors, for example Eitel [44], did not adopt their nomenclature to avoid confusion.

More recent work by Gibbs [49] added refinements to the structure of low-cordierite and Fleischner [50] presented a useful summary of the devitrification products of cordierite glasses. Langer and Schreyer [51] subsequently presented an alternative method for the characterisation of the high- to low-cordierite transition; this was claimed to be a more sensitive X-ray parameter than the distortion index.

This section has briefly described the important papers which have led to the present state of knowledge concerning the products of devitrification of cordierite glasses. An understanding of crystallisation behaviour at low temperatures, which leads to the formation of the metastable quartz-like phase, is of importance for any discussion of catalysed crystallisation of these glasses. The influence of relatively low temperature heat treatments on the crystallisation characteristics of cordierite glass, particularly on the formation of this metastable phase, is discussed in the next section.

## 3. Cordierite Glass-Ceramics

The commercial value of high-strength, low-expansion cordierite glass-ceramics was recognised at an early stage in the development of these materials. It was established that TiO<sub>2</sub> could exert a marked influence upon the crystallisation of cordierite-type glasses and consequently many compositions in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system with TiO<sub>2</sub> additions were patented [52-55]. A wide range of compositions have also been nucleated by additions of P<sub>2</sub>O<sub>5</sub> and converted to successful glass-ceramic products. Both TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> have also been used in conjunction with transition metal oxides in different proportions as nucleating agents [56-58]. Other nucleating agents that have been employed include ZrO<sub>2</sub> [59], LiF [60] and Li<sub>2</sub>O in conjunction with oxides of tungsten, molybdenum and vanadium [61, 62].

The early patents usually covered wide compositional limits and involved fairly complex heat treatments for the development of the nucleation and crystallisation stages of the conversion. Other batch additives were used to improve the melting and annealing properties of the parent glasses and the permissible limits for such "impurities" were given in the patents.

More recently a process for the production of

a transparent sintered glass-ceramic with cordierite as the major phase has been developed [63]. No additional nucleating agent was used in this process, the necessary control of the crystallite size being achieved by fine-grinding the parent glass, forming by pressing with an organic binder and finally heat treating to produce a sintered body with cryptocrystalline particles. A nucleating stage was included during the crystallisation process and it was claimed that an improved product was obtained by introduction of an intermediate holding stage during the heat treatment. The transparency of the product was closely dependent upon the composition and the limits of extraneous oxides added to the batch to improve melting characteristics, chemical durability and other properties were given.

Apart from the literature available in the form of patents there was, until quite recently, very little information available on catalysed crystallisation of cordierite-type glasses. The most important papers are discussed in this section and have been arranged in roughly chronological order. In most of the studies the compositions investigated included  $\text{TiO}_2$  as a nucleating agent. One of the most fruitful sources of additional information has been the Soviet research literature.

Maurer [14] used light scattering to study the mechanism of crystal nucleation in a  $\text{TiO}_2$ - $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  glass in an attempt to explain the role of  $\text{TiO}_2$  in promoting the devitrification process. From the measurements made it was found that isotropic scattering centres were becoming anisotropic during the initial stages of crystal formation from the glass. This was interpreted in terms of the crystallisation of  $\text{TiO}_2$ -rich regions from an emulsion within the vitreous body. These observations were in good agreement with the theories of glass-in-glass separation that were described earlier [11-25]. It is worth noting that fairly long annealing times were employed and could have had a significant effect upon the development of the dispersed phase. The study is important in the respect that it described a direct method for investigation of immiscibility effects and thus offered a useful complementary technique to the electron microscopy methods mentioned previously.

Kumar and Nag [64] presented a paper on the internal stress in crystallised glasses of the cordierite type. Samples containing  $\text{TiO}_2$  as the nucleating agent were crystallised at different temperatures in the range 825 to 1225°C and

the products of crystallisation were determined by X-ray diffraction. The relationships between stress, thermal expansion and density were measured. The conclusions drawn were that compressive stress developed in the glass with certain heat treatments, because of the higher expansion and density of the crystalline phases, and resulted in increased strength of the products. These effects were only beneficial up to temperatures at which the formation of cordierite and cristobalite were detected, the critical temperature being 1025°C. It was considered unlikely, however, that the marked decrease in strength following this could only be conditional on the formation of these phases. A complementary effect could be the development of cracks which occurred either within the crystals or at the crystal-residual glass interfaces which would release the compressive stress and thus decrease the strength. It was envisaged that the results of this study should be utilised for determination of optimum heat treatment conditions for mechanically strong glass-ceramics.

Kalinin and Podushko [65] also studied glass from the  $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system with additions of  $\text{TiO}_2$  nucleating agent. Variation in the nature of the crystallisation of the glass was studied in relation to the  $\text{TiO}_2$  content and heat treatment. Low and high content  $\text{TiO}_2$  glasses were considered separately and a study of the effect of low-temperature heat treatments on the subsequent crystallisation behaviour was adequately demonstrated by differential thermal analysis and thermal expansion measurements.

Kitaigorodskii and Khodakovskaya [66] have also published a paper dealing with the principles of conversion of glass to glass-ceramic in the  $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system. They noted that most of the published work up to that time had been concerned with the effects of different heat treatments on the structure and properties of glass-ceramics. Studies concerned with phase transformations and crystallisation paths within the direct interval of maximum crystal growth rate had also been the subject of attention. The emphasis in their study was therefore placed on the effects of heat treatment in the "precrystallisation" region. The latter was defined as the interval of heat treatment in which there was no formation of crystalline phase detectable by X-ray diffraction within a set time. Unfortunately the set time was not defined and the definition was also conditional on the sensitivity of the

X-ray technique – quoted as “not exceeding one per cent”.

In common with other studies of the system, the glasses that were investigated contained substantial amounts of  $\text{TiO}_2$  as nucleating agent. The authors referred to an earlier study [67] which had indicated that the most influential factor on changes in the structure, phase composition and properties was preliminary heat treatment in the region of the glass softening point. They mentioned that such low-temperature heat treatments resulted in the shifting of the lower limit of visible crystallisation by up to  $150^\circ\text{C}$  because of the formation of transparent glass-ceramic material. The limiting temperatures for these effects were given as  $800$  to  $950^\circ\text{C}$ . The structure, phase composition and properties of these materials were reported to be markedly different from those of non-transparent glass-ceramics based on the same glasses. Samples which were not subjected to the preliminary heat treatments produced non-transparent glass-ceramics in the same temperature interval.

The ability to form transparent glass-ceramics was reported as being a specific property of compositions within the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system with high  $\text{TiO}_2$  content. The aim of the work was stated to be an investigation of the general principles of conversion of glasses in the system to glass-ceramics, particularly those glasses which did not produce transparent products. Glasses that were studied were therefore based on cordierite with additions of fluorides, stannic oxide and a reduced content of  $\text{TiO}_2$ .

The authors presented a brief description of sample preparation methods and analytical techniques. The glasses were initially heated to various temperatures in the range  $600$  to  $850^\circ\text{C}$  to determine the role of precrystallisation heat treatments. The samples were then quenched and reheated to the crystallisation range without any intermediate holding stages and were afterwards examined in a comparative manner. It was claimed that by using this programme the structural changes that had occurred at each temperature of the precrystallisation period would be fixed by quenching and the influence of the intermediate temperature interval was thus excluded.

The visual nature of the crystallisation was found to be dependent upon the precrystallisation heat treatment and a diagram was presented to illustrate this. The importance of the low-temperature heat treatments was emphasised by

the results of X-ray analysis, which indicated that completely different phases were formed under the modified conditions. Other physical parameters were also measured to show the magnitude of the effect of heat treatment on the final crystallisation products.

In the discussion of results the optimum temperature of heat treatment in the precrystallisation period was related to thermograms of the original glasses. The most important correlation found was that the heat treatment exerting the most influence on the subsequent crystallisation occurred in the temperature interval of the endothermic effect. This was described as probably being the optimum interval for nucleation. Electron micrographs were also presented to show that the change in the appearance of the crystalline phase deposited during the final heat treatment might be directly related to a preliminary glass-in-glass separation.

The relationship between structure and properties of glass-ceramics of the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system was further studied by Bogdanova and Litvinov [68]. Glass of cordierite composition with additions of ceria and titania was studied. Density measurements were used as the major analytical technique, backed up by X-ray phase analysis and electron microscopy. A series of graphs was produced illustrating the relationship between density and crystallisation temperature for three different rates of heating. The general shapes of these curves were found to be the same for all three heating rates and were divided into sections corresponding to density changes of (a) steady increase, (b) rapid decrease and (c) constant density. The phase compositions were determined in an attempt to explain these effects. In particular the X-ray analyses of glass heated at  $120^\circ\text{C/h}$  were discussed. It was noted that crystals with  $d$ -spacings characteristic of quartz developed at the lower temperatures (at about  $820^\circ\text{C}$ ) and that as the crystallisation temperature was raised diffraction lines gradually appeared which were characteristic of phases with simpler structures than cordierite. The steady increase in density corresponded to the formation of these phases, and the maximum density product (formed at  $1060^\circ\text{C}$ ) was found to consist of spinel together with other phases identified as silica-O, rutile, mullite and an unknown phase referred to as the “x”-phase. The latter was suggested to be a compound of cerium and titanium, and separate experiments established that the principle  $d$ -spacings of this

“x”-phase corresponded to such a configuration.

The region of rapid decrease in density was shown to be correlated with the formation of cordierite from the spinel, silica-O and mullite. In the constant density region the composition of the glass-ceramic remained constant (1145°C and above) and only three phases were detected – cordierite, rutile and the “x”-phase. Electron micrographs were presented to show that heat treatments at higher temperatures merely increased the size of cordierite crystals that had grown from the intermediate phases. The optimum temperature for glass-ceramic formation was therefore taken to correspond to the point at which cordierite formation was complete. Further heating only caused enlargement of the crystals and slight disintegration of the material caused by cracking.

The usefulness of this paper lies in the fact that it illustrates the influence of nucleating agent on the course of crystallisation of the glass to glass-ceramic. Although the pattern of crystallisation was similar to that observed for cordierite glass containing  $\text{TiO}_2$  alone, the small amount of added ceria had a marked effect. The final product of the crystallisation process, cordierite, could only be formed through a whole series of intermediate compounds and the temperature of formation was of the same order as reported in the earlier studies.

A useful study was published by Toropov and Sirazhiddinov [69], also concerned with the topic of glass formation and crystallisation in the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system. Several glasses were examined and the experimental details included data on the raw materials and sample preparation techniques. Glasses were heat treated in the range 800 to 1300°C and examined by X-ray analysis, optical microscopy and differential thermal analysis.

Thermograms were presented for some of the glasses and the general features (illustrated in fig. 1a) were interpreted from X-ray analysis of the products. The primary phase of the low-temperature crystallisation was established as a metastable solid solution with a quartz-like structure. The first exothermic effect in the analysis was attributed to the formation of this phase. This conclusion was in agreement with data presented by earlier workers [44-46] although it was in disagreement with the earlier classification of the phase as  $\mu$ -cordierite [65]. The second, more intense peak was described as the main crystallisation peak on the thermogram.

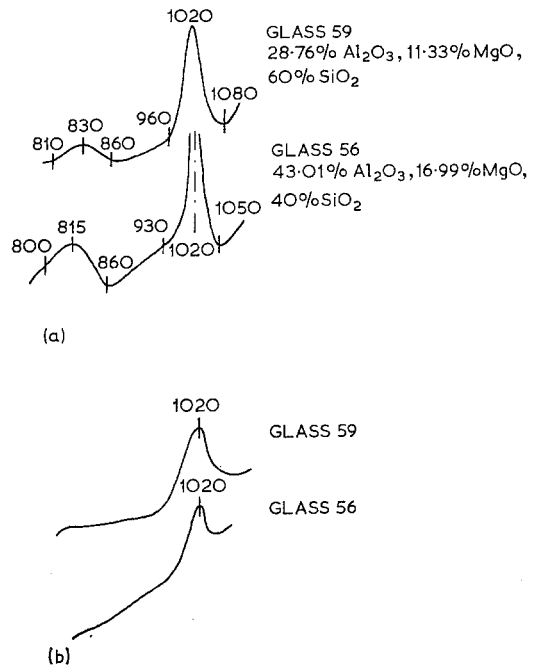


Figure 1 Differential thermal analysis curves from Toropov and Sirazhiddinov [69]: (a) original glasses (b) after heat treatment at 900°C for 5 h.

Glasses that had been heat treated at 900°C prior to differential thermal analysis did not give the low-temperature exotherm (fig. 1b). X-ray data was presented to show that the composition of the main crystallisation phase depended on the original glass composition.

The authors suggested that the formation of the metastable phases might be the result of chemical heterogeneity in the structure of the original glasses, although no details of any experimental evidence for this were given. Heat treatment above 1100°C caused decomposition of the metastable products of crystallisation and the crystallisation paths were described as following the course indicated by the equilibrium phase diagram.

Reference was made to the work of Filipovich [18] which indicated that microcrystallinity and heterogeneity were insufficient for formation of strong glass-ceramics. The crystals must be firmly bonded by direct intergrowth or through a thin bonding interlayer of residual glass. Consequently one of the prime factors for the production of a strong glass-ceramic must be the morphology of the crystalline phases and the ability to form bonds between crystals, especially

when several phases are present in the material. The authors therefore studied the changes that occurred in the external form and orientation of the crystals during extended heat treatments.

Photomicrographs were presented to illustrate the effects of composition, temperature and duration of heat treatment on the morphology of the crystals formed. Comparison of different compositions showed that melts with low  $\text{SiO}_2$  content could not be quenched to glasses and that the primary crystalline phase in these compositions was spinel. The products were relatively coarse-grained and the spinel crystals appeared to be oriented in definite crystallographic directions. A series of such quenched products showed that quenching from high temperature ( $1850^\circ\text{C}$ ) resulted in coarse irregular crystals which had formed near the liquidus. After heat treatment at  $900^\circ\text{C}$  these crystals formed into dendritic growths which were disoriented and grew towards one another. Further heat treatment at  $1000^\circ\text{C}$  caused much finer dendritic intergrowths.

By contrast the compositions which readily formed glasses differed in the sequence of crystal formation and growth rate. Low-temperature heat treatments were employed to nucleate the glasses and crystallisation to glass-ceramic products was achieved in the range  $800$  to  $1000^\circ\text{C}$ . Several different compositions were studied and the stages of crystal development through the various steps to the final recrystallisation and segregation of the equilibrium crystal phases were illustrated in detail.

This paper presented a most comprehensive study of the effects of heat treatment on crystallisation of cordierite glasses, the particular emphasis being on the ability to form fine-grained glass-ceramics without additional nucleating agents. It was shown that it was possible to induce volume crystallisation of some of the glasses by using low-temperature heat treatments. The mechanism of the whole process was then adequately explained in terms of intermediate steps through the metastable phases formed at low temperatures.

This work was extended in certain areas by Toropov, Zhukauskas, and Aleinikov [70] who emphasised formation and recrystallisation of the quartz-like phases in the general scheme of crystallisation of glasses from the system. Several glasses with silica content ranging from 41 to 61 wt % were studied and were compared with glasses of similar base composition but

containing from 2 to 15 wt % added  $\text{TiO}_2$ . Differential thermal analysis and X-ray diffraction methods were used to determine the influence of  $\text{TiO}_2$  on the "temperature range of existence" and quantity of the metastable phase. Thermograms were presented which showed the characteristic two-stage crystallisation of the glasses and illustrated the effects of  $\text{TiO}_2$  on devitrification behaviour (fig. 2). Similarly, X-ray

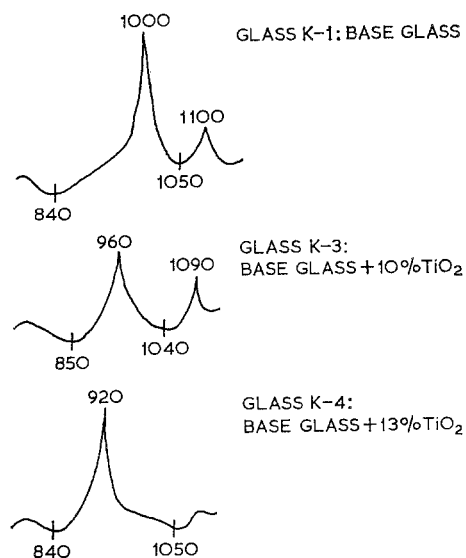


Figure 2 Differential thermal analysis curves from Toropov *et al* [70].

data was given which showed the dependence of the relative amount of the quartz-like phase on the silica content of the glasses which had been heat treated at various temperatures for a standard time of 2 h. This heat treatment schedule was described as a standard method for glass-ceramic production [71]. The results also showed that the decrease in content of the quartz-like phase at higher temperatures was accompanied by a gradual increase in the cordierite content of the product. The interrelationship of these two processes was obvious (fig. 3) and the authors described the process as a recrystallisation of the quartz-like phases to cordierite by rearrangement of the hexagonal structure of the metastable phase to the structure of hexagonal cordierite.

The addition of  $\text{TiO}_2$  to one of the glasses had a marked effect upon both the relative amount of quartz-like phase and the temperature interval of

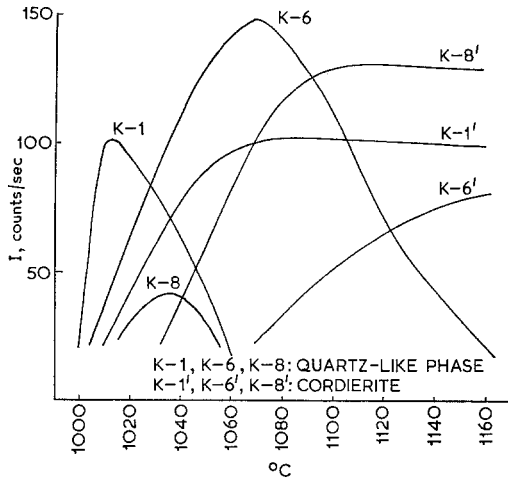


Figure 3 Dependence of relative amounts of quartz-like phase and cordierite on silica content of three glasses, from Toropov *et al* [70].

existence of this phase. Addition of up to 13%  $\text{TiO}_2$  resulted in an expansion of this interval of existence in the lower-temperature direction and an increase in the relative amount formed (fig. 4). Addition of 15%  $\text{TiO}_2$  caused a decrease in the amount of quartz-like phase and a narrowing of the "temperature interval of existence" which was claimed to be a result of the formation of substantial amounts of magnesium and aluminium titanates.

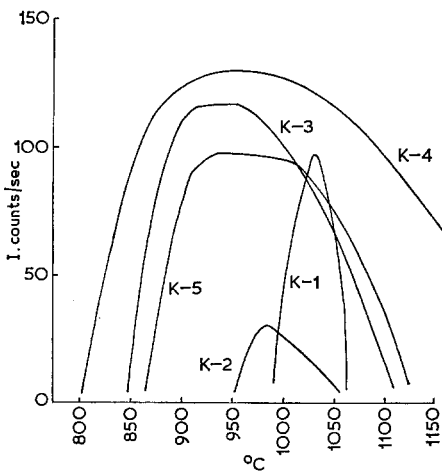


Figure 4 Effect of  $\text{TiO}_2$  on the quartz-like phase content of cordierite glass: K-1 base glass; K-2 base glass + 2%  $\text{TiO}_2$ ; K-3 base glass + 10%  $\text{TiO}_2$ ; K-4 base glass + 13%  $\text{TiO}_2$ ; K-5 base glass + 15%  $\text{TiO}_2$ . Data from Toropov *et al*. [70].

Toropov, Zhukauskas, and Aleinikov [72] also studied the high-temperature structural transformations of synthetic cordierite in detail. They described earlier results and criticised the existing data as inadequate in spite of the extensive range of these studies. X-ray diffraction had been used previously to study the processes involved and the authors felt that more direct experimental methods were required. They also pointed out that most studies had used impure natural cordierites and that no detailed studies had been made of synthetic material. Cordierite was accordingly synthesised by devitrification of three different glasses using a fairly complex thermal treatment and the crystalline products were examined by X-ray diffraction, electron diffraction and electron microscopy. Although the authors emphasised the need for an investigation of pure synthetic cordierite they added up to 15 wt %  $\text{TiO}_2$  to the base glass to facilitate the observation of formation and growth of cordierite crystals using electron microscopy.

Results of the investigation were in general agreement with previous work [37, 38, 42] concerned with the order-disorder processes which occurred in specimens heat treated in the 1400 to 1460°C range. Electron microscopy confirmed X-ray diffraction results and established that lengthy heat treatment at 1400°C caused a polymorphic transition from a hexagonal to an orthorhombic form. This process was also shown to be accompanied by a partial conversion of the hexagonal structure into an amorphous form – described as occurring "at a high rate in a narrow temperature range". Further heat treatment at 1460°C caused a gradual disordering of the orthorhombic cordierite structure back to the hexagonal form prior to incongruent melting.

Electron diffraction patterns were recorded from the whole available surface of thin sections and from individual crystals at various stages in their development. Identification of the polymorphs was very difficult because of limitations in the resolving power of the instrument that was used. The accumulated evidence was taken to confirm the results of other studies but did not add much to the existing state of understanding of the processes involved in the structural transformations of cordierite at high temperatures. The electron micrographs were interesting in that they showed something of the morphological features of the polymorphs. Although three glass compositions were used, the results

that were discussed in any detail related to the stoichiometric composition alone and it was not clear whether these results related to the base glass or to glass with  $\text{TiO}_2$  additions.

Toropov and Sirazhiddinov [73] had previously described a study of the phase transformations of natural cordierites from Finland. In addition to data which illustrated the effect of temperature on the distortion index from X-ray measurements and on refractive index they also presented the infra-red absorption spectrum of their material. The results of this study were in good agreement with those of the Japanese workers [37, 38] and the authors concluded that this was an indication that mineral species from different locations had been formed under very similar geological conditions.

One of the most useful papers from the Soviet literature which dealt with the stable and metastable phases in the crystallisation of cordierite glass was published by Sirazhiddinov [74]. The crystallisation of glass with the cordierite stoichiometry was studied by X-ray diffraction, optical microscopy and differential thermal analysis. No additions of catalyst were made to the glass and the course of the crystallisation was followed through the various intermediate stages.

The data presented included X-ray measurements which showed that the  $d$ -spacings of the quartz-like phase corresponded to so-called  $\mu$ -cordierite. The disappearance of the quartz-like phase and the gradual appearance of hexagonal cordierite was noted. The critical temperature was found to be  $1000^\circ\text{C}$ , and the author stated that cordierite formed at this relatively low temperature was of non-stoichiometric composition with an anomalous value of refractive index. A few crystals of the true cordierite stoichiometry were also identified and it was inferred that these had developed from the intermediate phases. Parts of the X-ray diffraction traces were reproduced as evidence for this development process. An exothermic effect obtained in the differential thermal analysis at  $1015^\circ\text{C}$  was reported to correspond to this transformation.

Optical and electron microscopy were used to examine the products of crystallisation from samples heated for 5 h at  $1000^\circ\text{C}$  and it was found that crystals had developed in discrete clusters with distinct boundaries between them. The electron microscope gave more detailed information. It was possible to deduce the

existence of at least two varieties of cordierite from the nature of the distribution of the microcrystalline product. One variety was concentrated in spherical clusters and the other, which was more finely divided, was distributed in between the clusters.

Heat treatment at  $1100^\circ\text{C}$  caused the crystalline material to homogenise to the cordierite stoichiometry, and complete conversion to ordered low-cordierite was achieved by heat treatment in the range  $1200$  to  $1400^\circ\text{C}$ . The distortion index was used as a measure of the order of the structure. Electron microscopy was used to measure the size of the crystals and the structure of the product was shown by infra-red spectroscopy to be identical with that of natural low-cordierite, as illustrated in fig. 5.

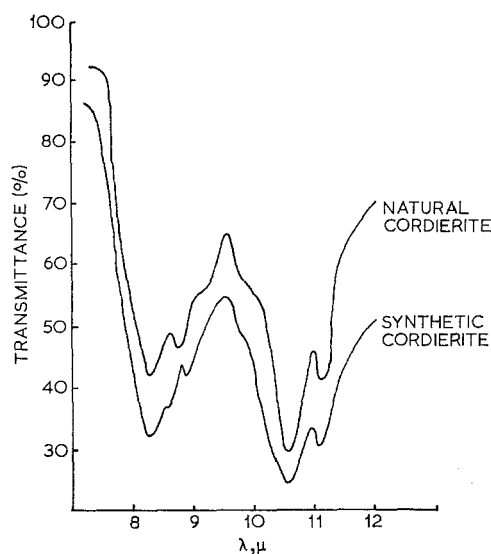


Figure 5 Infrared analysis from Sirazhiddinov [74].

More recently a very useful publication by De Vekey and Majumdar [75] has dealt with an extensive study of nucleation and crystallisation of glasses based on cordierite. Analytical techniques that were used included dilatometry, differential thermal analysis, optical and electron microscopy. Several different glasses were analysed and various oxide nucleating agents were evaluated. These authors found that  $\text{TiO}_2$  and a mixture of  $\text{TiO}_2$  and  $\text{ZrO}_2$  in amounts ranging from 10 to 12 wt % could be employed to produce good quality glass-ceramics. The phenomenon of glass-in-glass separation as a



precursor to controlled crystallisation was established by electron microscopy. The crystallisation course, determined by differential thermal analysis and X-ray diffractometry, was in agreement with other workers' results and confirmed the sequence of cordierite formation through the metastable quartz-like phase at lower temperatures.

Differential thermal analysis was also used to show the effect of  $\text{TiO}_2$  additions on the kinetics of crystallisation and a limited study of the effect of heat treatment in the precrystallisation range was made. Data were also presented on the physical properties of some of the glass-ceramic products.

#### 4. Conclusions

The papers described in this review represent the development of the present state of knowledge of the processes of crystallisation of cordierite glasses. The most important points which are of relevance to any study of glass crystallisation in the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system are summarised below:

The crystallisation usually progresses through intermediate metastable stages during heat treatment and the final composition of the crystallised product will depend upon the following factors:—

- (i) the chemical composition of the parent glass;
- (ii) the thermal history of the sample; and
- (iii) the addition of small amounts of nucleating agents.

A general conclusion is that detailed analyses of the fundamental structural changes which occur during the heat treatment of these glasses are still fragmentary although much useful information has been gathered. Many of the studies reported have concentrated on what may best be described as the technologically important aspects of the processes, particularly those which have utilised  $\text{TiO}_2$  additions to the base glass to promote crystallisation. Comprehensive studies of the effects of other nucleating agents for this system are lacking, and some of the work dealing with the "pure" system must be open to criticism of the experimental conditions. More attention must be paid to the sample preparation techniques so as to ensure reliable results and some of these aspects have been mentioned in the course of the literature review.

The aim of the present work was to investigate the crystallisation behaviour of one representative glass in the cordierite system. The crystal-

lisation of the base glass, without any added nucleating agent, was studied first employing several complementary analytical techniques. Attempts were made to ensure strict control of experimental conditions and each analytical method was carefully checked for accuracy and reproducibility. Further experiments were then performed to determine the effect of certain oxide nucleating agents on the crystallisation behaviour of the base glass. The products were then examined and analysed and the crystallisation sequence determined. This part of the work will be reported in later publications.

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