Nucleation and crystallization studies of some glasses in the CaO–MgO–Al₂O₃–SiO₂ system

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SUMMARY. Glass-ceramics based on the mineral cordierite have good mechanical and thermal properties. They can be easily prepared from glasses whose compositions lie in the primary phase field of cordierite on the 5 % CaO plane of the CaO–MgO–SiO₂–Al₂O₃ system. For uniform crystallization in the bulk, addition of a suitable nucleating agent is essential. The addition of 10–12 wt % of TiO₂ is considered to be suitable for both ternary and quaternary glasses. During controlled heat treatment of these glasses extensive phase separation occurs. The nucleation and crystallization processes that follow have been studied by differential thermal analysis, X-ray diffraction, and light and electron microscopy. Some of the physical and mechanical properties of these glass-ceramics have been measured.

THE high melting point and the very low thermal expansion coefficient of the mineral cordierite are two important properties that have been utilized in the development of industrial ceramic materials in which this phase is a major constituent. Although cordierite ceramics are commonly manufactured by a sintering process, the possibility of producing glass-ceramic materials based on cordierite has already been explored in several laboratories (e.g. British Patent 829,447). The thermal, electrical, and mechanical properties of such a material are considered to be satisfactory, but there are production limitations due to the high melting points and the high viscosity of ternary MgO–Al₂O₃–SiO₂ glasses even after the addition of suitable nucleating agents. The present work, of which this report is a preliminary account, is aimed at examining several quaternary glasses with compositions in the primary phase field of cordierite in the CaO–MgO–Al₂O₃–SiO₂ system with a view to studying their crystallization behaviour.

Previous work. Cordierite is an incongruently melting compound having a stable primary phase field in the MgO–Al₂O₃–SiO₂ system (see Osborn and Muan, 1960). Its mineralogy and polymorphism have been extensively studied (Deer, Howie, and Zussman, 1962). The form stable at all temperatures and called low-cordierite is orthorhombic. High- (or α-) cordierite is hexagonal and is considered to be metastable at all temperatures. Cordierite crystal structures provide typical examples of order–disorder in aluminosilicates.

Crystallization of cordierite from glasses of widely different compositions in the system MgO–Al₂O₃–SiO₂ has been recently studied in great detail by Schreyer and Schairer (1961 *a* and *b*). One important discovery in these studies was the observation that quartz solid solutions previously described as μ-cordierite by Karkhanavala and Hummel (1953) and silica O by Roy (1959) form metastably on devitrification of these glasses at relatively low sub-solidus temperatures and are usually the first crystalline

phases to appear. According to these authors, incorporation of foreign ions such as Al^{3+}, Mg^{2+}, Fe^{2+}, or Li^+ in the silica framework permits the metastable formation of these quartz-type structures. A summary of the present knowledge of the effect of heat treatment on cordierite glasses can be found in the work of Fleischner (1966) who has also provided much useful data on the physical properties of cordierite.

Experimental. Glasses were prepared in platinum vessels in electronically controlled muffle furnaces. The purities of the starting materials were as follows: $CaCO_3$ 99·9 %, SiO_2 99·5 %, Al_2O_3 99·58 %, and $MgCO_3$ 99·9 %. The homogeneity of the glasses was checked by optical examination. Nucleating agents of reagent grade quality were added, when necessary, to the starting mixes before the first melting.

The optimum nucleation temperatures were shown, by electron microscopy, to lie in the range between the strain relief temperature (T_a) and the softening temperature (T_s) of the glass. These characteristic points were determined by thermal expansion dilatometry. The nucleation range was found to correspond also to the regime defined by the onset and the peak temperature of the first endotherm observed in the differential thermal analysis (DTA) runs on blocks of glass.

Most of the DTA work was carried out using a 'Standata' apparatus having a twin-cup alumina head and a platinum resistance furnace. In order to study metastable processes within the body of the glass blocks of glass rather than powders were used in DTA runs, as it has been shown by Thakur and Thiagarajan (1966) and confirmed in the present study that with powdered glass surface nucleation and crystallization processes tend to obscure the internal structure changes. To use glass blocks relatively tall crucibles were fabricated from alumina slip to replace the normal platinum cups. Corundum was used as the reference material and a small quantity of α-quartz was generally added to serve as an internal standard. In the present study a DTA apparatus with a demountable head has been developed, which allows rapid quenching of samples from temperatures corresponding to any given DTA peak. This helps to characterize the reactions responsible for the thermal effects by examining the relevant DTA samples with a suitable method such as X-ray diffraction. The apparatus is similar to the 'Standata' unit but it uses a horizontal furnace and accommodates slightly larger samples. Nearly all DTA runs were made with a heating rate of 10 °C per minute.

The thermal expansion coefficients of glass-ceramic materials and the glass transition and softening temperatures of the parent glasses were measured with a 'Linseis' dilatometer using samples measuring $30 \times 4 \times 4$ mm at the minimum loading pressure. A heating rate of 10 °C per minute was used throughout.

The heat treatments of samples necessary for development of nuclei and crystal growth were carried out in muffle furnaces at set temperatures, in gradient furnaces, or in a programme-controlled furnace that can give heating schedules similar to industrial tunnel kilns.

The development of nuclei as a function of time or temperature of heat treatments was followed by scanning and transmission electron microscopy. The preparation of specimens was similar in both cases, a lightly etched fresh fracture surface having been

used. For work with the scanning electron microscope, the surface of the specimen was coated with carbon. For transmission work platinum-preshadowed carbon replicas were used.

The progressive development of crystalline phases in heat-treated glasses was examined by light and electron microscopy and by X-ray diffraction. For the latter technique, a Guinier–Nonius type of focusing camera was used.

The mechanical properties of glass-ceramic specimens were determined by using an Instron universal testing machine. The modulus of rupture was measured using square prisms of material $5 \times 5 \times 30$ mm, which were tested over a span of 19 mm. The tension and compression faces of the specimens were ground to a standard finish on a vertical spindle diamond grinder. Compression specimens, 5 mm cubes, were then cut from the bending test specimens and tested with ground faces held between mild steel blocks.

TABLE I. *Properties of glasses*

No.	Composition (wt %)					Dilatometric properties				Endotherm peak temp.
	SiO_2	Al_2O_3	CaO	MgO	TiO_2	T_a	T_g	T_s	$\alpha 20-720$ °C	
42	51·4	34·9	—	13·7	—	704 °C	810 °C	847 °C	$4·76 \times 10^{-6}$	860 °C
42A	45·7	31·1	—	12·2	11·0		744	786	4·45	800
40	55	25	5	15	—		764	806	4·98	810
40A	48·9	22·2	4·5	13·3	11·0	684	738	777	4·27	780
39	60	25	5	10	—					
39A	53·4	22·2	4·5	8·9	11·0	668	758	800	3·99	790
46	50	30	5	15	—					
46A	44·5	26·7	4·5	13·3	11·0	670	739	783	5·11	790

Results and discussion. About two dozen glasses have been studied so far in respect of their nucleation and crystallization. The quaternary compositions were so chosen as to lie inside or very near the cordierite primary phase field on the 5 wt % CaO plane of the $CaO–MgO–Al_2O_3–SiO_2$ system. Work on the delineation of phase boundaries of this field at the liquidus surface is not complete yet but presently available results suggest that cordierite has a primary phase field on the 5 % CaO plane of the quaternary with an area comparable in size to that in the $MgO–Al_2O_3–SiO_2$ system. On this plane invariant phase relationships involving the cordierite phase are also similar to those in the ternary system; an exception may be the absence of the sapphirine phase field adjoining that of cordierite. This phase has not been detected in any of the quench runs so far.

A few of the ternary and quaternary compositions studied so far are listed in table I. The annealing (T_a), transition (T_g), and softening (T_s) temperatures of some of the glasses are also listed together with their endotherm peak temperatures in DTA runs. The lowering of T_g and T_s by the addition of CaO suggests that quaternary compositions would have lower viscosities than the ternary mixes at the same melting temperatures. Nucleating agents such as TiO_2 have a similar effect.

The nucleating agents tried in the present study were TiO_2, ZrO_2, V_2O_5, MoO_3, WO_3, CeO_2, and ThO_2 in amounts ranging from 5 to 12 wt %. All these oxides cause some nucleation but sufficient nucleation density for glass-ceramics of good quality is bestowed only by TiO_2 and by a mixture of TiO_2 and ZrO_2. In cases where there is an insufficient nucleation density, large crystals grow within a glassy matrix, which flows during the heat-treatment, resulting in a weak, distorted product. When the density of nuclei is right, there are sufficient crystallites present to hold the structure rigidly while they grow so that the material keeps its shape. By trial and error it has
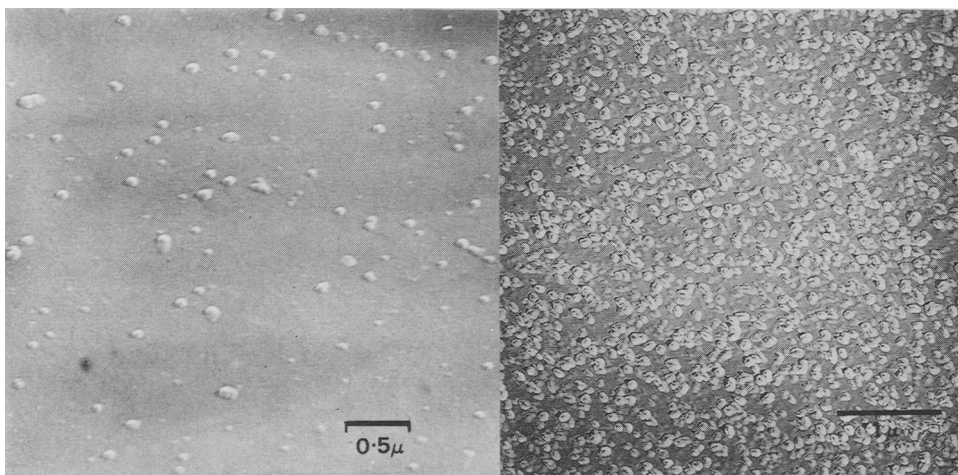
FIGS. 1 and 2: Fig. 1. Electron micrograph of phase-separated glass. Glass no. 42A was held at 705 °C for 16 h. Fig. 2. Electron micrograph showing angular nuclei after heat-treatment of glass no. 40A for 4 h at 770 °C.

been established that 10–12 wt % of TiO_2 provides satisfactory nucleation densities. The effectiveness of nucleus formation can be enhanced by adding 1–2 wt % of diffusion accelerators such as Na_2O or Li_2O.

When heat-treated in the nucleation regime both ternary and quaternary glasses containing TiO_2, such as those listed in table I, show phase separation. In the absence of nucleation catalysts phase separation does occur in these glasses but its extent is much too small to promote sufficient internal crystal nucleation, and growth and surface crystallization is always predominant. When TiO_2 is added, phase-separated glasses produced at, say, 750 °C after 16 h heating may appear almost unchanged from the original yellow glass or may have developed a slightly brown or blue opalescence. The nuclei are readily visible in the electron microscope (fig. 1). Within the optimum nucleation range for the quaternary glasses (700–800 °C in presence of 11 wt % TiO_2), progressive heat-treatment produces the following results: there is an increase in the number of nuclei with time at any temperature, at least up to a limiting density; there is a decrease in the number of nuclei as the temperature is raised; there is an increase in the size of the nuclei as the temperature is raised; and above 800 °C

there is an apparent increase in the nucleation rate, possibly due to additional ions in the glass becoming mobile, and all the nuclei develop an angular form indicative of increasing crystallinity (fig. 2).

It has been reported recently (de Vekey and Majumdar, 1970) that some of these processes are accelerated if an external electric field is applied to the glass during its heat treatment.

Typical DTA traces corresponding to the nucleation and crystallization of these glasses are shown in figs. 3 and 4. Curve A in fig. 3 is due to glass no. 42, which is of stoichiometric cordierite composition. For the DTA run illustrated in curve B, this glass was first heat-treated at 800 °C for 2 hours. Curve C represents the DTA trace of glass no. 42A, which is the cordierite composition modified by the addition of TiO_2. Curves D and E were taken with the same glass heat-treated at suitable nucleation temperatures prior to the thermal analysis.

All the DTA traces show an endotherm in the range 750–900 °C, which becomes more pronounced if the glasses are previously heat-treated above their annealing temperatures. This increase is probably due to the fact that stress release is an exothermic process that, in unannealed glasses, tends to reduce the magnitude of the heat absorption corresponding to the endotherm. The endotherm corresponds approximately to the range defined by T_g and T_s. Apart from the endotherm there is very little difference in the DTA curves of cordierite glass as cast and after prior heat treatment.
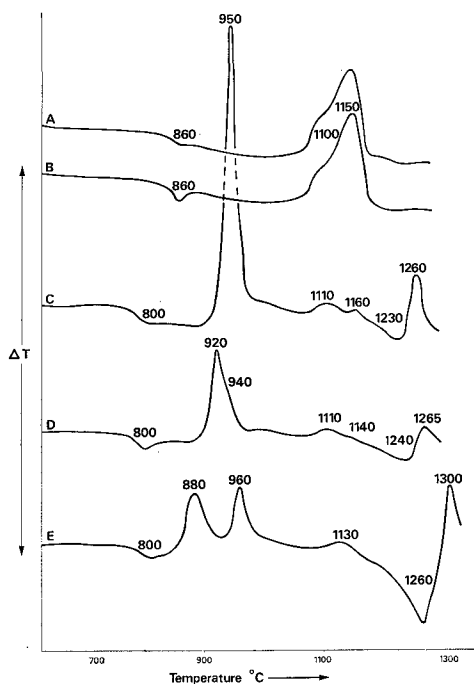

FIG. 3. Typical DTA traces obtained with glasses: A—no. 42 as cast, B—no. 42 annealed, C—no. 42A as cast, D—no. 42A held at 670 °C for 4 h, E—no. 42A held at 740 °C for 16 h.

X-ray examination of suitable samples indicates that crystalline solutions based on the quartz structure (Schreyer and Schairer, 1961a) are present in very small quantities at the temperatures of the endotherm. The relative proportion of this phase increases progressively till the exothermic reaction at 1100 °C. Above this temperature the quartz crystalline solutions are absent. Hexagonal cordierite makes its appearance at 1100 °C and is the sole product of the completed reaction. In the absence of nucleating agents crystallization is by surface nucleation and growth mechanism only and this is easily revealed in optical examination.

When TiO_2 is added to a glass of cordierite composition, the endotherms in DTA runs occur at lower temperatures, as would be expected from T_g and T_s values listed

in table I. In this case, however, crystallization is almost exclusively a bulk process and the sequence of occurrence of phases during devitrification is rather difficult to follow. This is due to the fact that independent crystallization of two or more phase-separated glasses is possible here and the reactions taking place are largely metastable. The glass (no. 42A) as cast gave definite exotherms at 950, 1110, 1160, and 1260 °C. In addition a possible endotherm at 1230 °C is also indicated. X-ray examination of the material quenched from suitable temperatures during the course of the DTA runs has given some idea of the chemical processes involved in the devitrification of these glasses. After the first endotherm at 800 °C, only three X-ray powder lines appear with d-spacings of 3·42, 3·20, and 2·075 Å respectively. These lines are probably due to a quartz crystalline solution although the possible appearance of a magnesium titanate phase having an appreciable amount of Al^{3+} ion in the crystal structure cannot be ruled out. During the exothermic reaction corresponding to the DTA peak at 950 °C large quantities of the quartz phase form and the phase persists up to 1140 °C. Another phase, at present uncharacterized, with X-ray powder lines at 4·79, 3·33, 2·58, 1·92, and 1·71 Å also makes its appearance around 950 °C. It has not yet been possible to relate the 1110 and 1160 °C exotherms with the appearance of definite crystalline phases.

Traces of hexagonal cordierite begin to appear at 1090 °C and its amount increases progressively till 1180 °C. In this temperature range at least two other phases are also present. One has an X-ray powder pattern very similar to synthetic sapphirine (Foster, 1950) and the other phase is probably a crystalline quartz solution that is different from the quartz phase encountered at lower temperatures. The new X-ray powder lines appearing at this stage occur at 4·3, 3·38, 2·70, 2·01, and 1·82 Å. The crystallization of a phase with high SiO_2 content may be reasonably expected since precipitation of sapphirine with its high alumina content would leave the residual matrix rich in silica. In the endothermic region around 1230 °C sapphirine and quartz crystalline solutions react together to produce more hexagonal cordierite. Much of the TiO_2 in the glass crystallizes out as rutile, but this reaction does not take place until 1260 °C, the temperature of the final exotherm.

If the TiO_2-containing glass (no. 42A) is given a prior heat-treatment in the temperature range between the annealing and glass transition temperatures, there is a marked change in the corresponding DTA traces. As can be seen from curves C, D, and E in fig. 3, the first endotherm has increased in size and its peak temperature is lower for both the heat-treated glasses. There are, as before, only three weak lines on the X-ray pattern at this temperature, but their positions and intensities are slightly different from the unheated glass. The most interesting features in this case, however, are the appearance of a new exotherm between the endotherm and 950 °C, the modification of the peaks at 1110 and 1160 °C, and the increase in the size of the endotherm at ~1230 °C. When the glass is pre-heat-treated at 740 °C for 16 hours the new exotherm is fairly large with the peak maximum at 880 °C (curve E) whereas if the heat treatment is more moderate, e.g. 4 hours at 670 °C two peaks appear with maxima at 920 and 940 °C respectively (curve D). The X-ray pattern of the sample quenched from 900 °C in curve E shows powder lines at 4·77, 3·35, 2·69, 2·08, 1·92, and 1·79 Å and the phase

(or phases) giving these lines persists up to the next exotherm and is possibly present also at 1250 °C.

Crystalline solutions based on quartz first appear at 950 °C but they disappear beyond 1130 °C. The DTA peak at 1130 °C occupies approximately the same position as in the samples not subjected to prior heat treatment, but the double peak has changed into a single one. As before, X-ray examination indicates the presence of sapphirine and a type of quartz crystalline solution but no hexagonal cordierite can be detected at this stage. The cordierite phase does not appear to form in substantial quantities until the final exotherm at 1300 °C is well under way. The samples quenched from temperatures slightly higher than that of the final exotherm did not contain rutile.

Any interpretation of the sequence of reactions described above must take into account the extremely rapid nucleation rate induced in silicate glasses by the addition of TiO_2. It is doubtful if phase separation in these glasses can be completely prevented by conventional quenching. When these glasses are heat-treated near the softening point a small number of phase-separated spherical particles are present and these provide sites for growth of seed crystals during the first exotherm; quartz crystalline solutions develop from these seeds. If prior heat treatment is given at the nucleation temperature, phase separation is extensive and the seed crystals now develop into a phase different from quartz crystalline solutions, probably as a result of a significant change in the composition of the phase-separated glasses. Quartz crystalline solutions grow during the next stage in the heating cycle. The reactions at and above 1100 °C are very complex and do not admit of a simple interpretation.

When a glass (such as no. 42A) nucleated with TiO_2 but not previously heat-treated is analysed by DTA, the composition of the bulk glass is still close to that of cordierite so that crystallization of this phase is possible. When phase separation is extensive due to prior heat treatment, the compositions of both of the amorphous phases are probably so different from that of cordierite that formation of this phase is only possible at higher temperatures where diffusion reactions between phase-separated glasses or crystalline products derived from them are possible.

Fig. 4 shows DTA traces obtained with a quaternary glass (no. 40 in table I) having a composition in the primary phase field of cordierite on the 5 % CaO

FIG. 4. Typical DTA traces obtained with glasses containing CaO: A—no. 40 as cast, B—no. 40A as cast, C—no. 40A held at 725 °C for 16 h.

plane of the $CaO-MgO-Al_2O_3-SiO_2$ system. For DTA curves B and C 11 wt % TiO_2 was added to this glass as before. In the absence of the nucleating agent, only an endotherm and a broad exotherm were observed (curve A). The exotherm corresponds to the crystallization of hexagonal cordierite. In presence of TiO_2 the sequence of
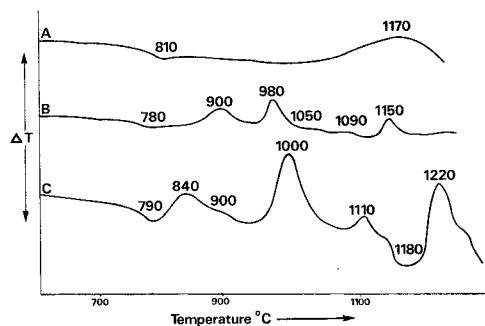
reactions is similar to that observed in the case of glasses without CaO but there are one or two important differences. In this case, after prior heat treatment, there is only an incomplete separation of the additional exotherm at 840 °C from the parent peak at 900 °C. The 900 °C peak is due to the appearance of a quartz-like phase but no sapphirine is produced from these glasses. Hexagonal cordierite makes its appearance around 1100 °C and persists through the final exotherm. Rutile is not formed during

TABLE II. *Properties of glass-ceramics*

No.	Batch	Crystallization		Average thermal expansion	Modulus of rupture	Compressive strength
		temp. (°C)	time (h)	α20–920 °C	(MN m⁻²)	(MN m⁻²)
39A	A	1100	5	3.16×10^{-6}	89·5	665
40A	D	1100	3	4·11	128·0	1001
46A	E	1100	3	3·23	77·4	696
40A	K	1050	4	4·0	155·0	1407
40A	L	1050	2	4·48	132·0	1270
46A	R	1050	4	6·77	161·0	—
42A	Q	1200	2	2·63	126·0	753

the course of the DTA run. Finally it may be noted that, compared with ternary glasses, quaternary compositions show substantial shifts in the DTA peak temperatures associated with the crystallization of particular phases. This is due to the differences in bulk compositions of these glasses and their degree of departure from the stoichiometric cordierite comp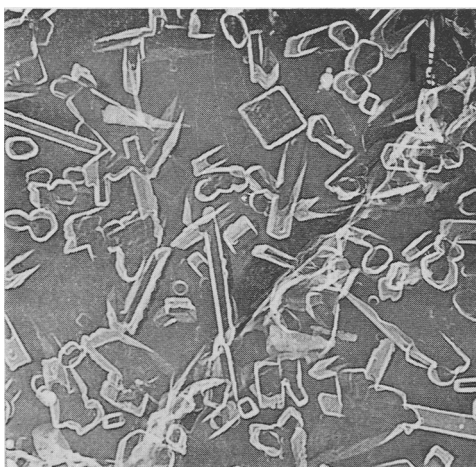osition. Some of the properties of glass-ceramics based on the glasses listed in table I are given in table II. As yet no attempt has been made to maximize the strength by choosing the most suitable heating and cooling schedules but moduli of rupture greater than 150 MN m⁻² and compressive strengths higher than 1000 MN m⁻² have been obtained with some specimens.[1] The coefficients of variation for strength values listed in table II were in the range 15–40 % for bending strength and 3–15 % for compressive strength.

As might be expected, the further the composition of the parent glass is away from that of cordierite the greater is the thermal expansion of the glass-ceramic. The effect of incomplete heat treatment on the thermal expansion is shown by the

FIG. 5. Electron micrograph of glass-ceramic (batch L of table II).

[1] One MN m⁻² (meganewton per square metre) = 1 N mm⁻² = 10 bars.

results obtained with different batches of the glass-ceramic materials derived from glasses of the same composition. Samples of batch nos. D, E, and K, which had crystallization heat treatments for longer times or at higher temperatures, gave lower expansion coefficients than samples from batch L or R. In fig. 5 an electron micrograph of a specimen of glass ceramic of batch L is shown. It can be easily seen that there is a considerable amount of residual glass, which may well control the effective thermal expansion coefficient of the material. Samples of batch R exhibit glassy fracture, whereas samples of other batches listed in table II give granular fracture, excepting samples from batches A and L, which show an intermediate fracture behaviour.

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