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The crystallization of cordierite glass

Part 3 *Experimental studies of the crystallization of a cordierite-type glass and the effects of oxide additions on the devitrification characteristics*

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The results of a study of the crystallization characteristics of a glass near the cordierite composition are discussed. The devitrification of the base glass was studied by the method of DTA and the development of this technique is described. The effects of additions of vanadium pentoxide and tungstic oxide on the behaviour of the base glass were also determined and are discussed.

1. Introduction

The crystallization of cordierite glass was reviewed in a previous publication [1] and the experimental methods used in the present study were described in Part 2 [2]. This paper will deal with the results of crystallization studies of a cordierite-type glass, as determined by DTA, and discuss the effectiveness of small amounts of vanadium and tungsten oxides as nucleating agents for the production of cordierite glass-ceramics.

2. Glass preparation

Pure oxide components were used for the preparation of the glasses, BDH Analar magnesia and alumina and Thermal Syndicate pure crushed Brazilian quartz. Stock batches were accurately weighed out in the proportion 47.4% SiO_2, 44% Al_2O_3, 8.6% MgO (mol) after drying at 110°C for at least 24 h and cooling in a desiccator. The stock batches were mixed in 250 g lots in a Y-cone blender operated at 60 rev/min for 30 min. All sample preparation was carried out with extreme care, e.g., glazed paper was used to transfer quartz to minimize loss by creeping on glassware and precautions were taken to exclude dust etc., thus the chance of introducing unwanted impurities into the mixture was minimized.

The mixed oxides were then coned and quartered into melting batches of approximately 50 g and transferred to platinum crucibles. Melting was carried out initially using a Hirsch carbon granule furnace but later an Amalgams CH5 chamber furnace was used. In both cases the glasses were formed by melting the mixture at temperatures in the range 1580 to 1600°C and soaking at top temperature for at least 2 h. The melts were readily quenched to an homogeneous glass by dropping the crucible into cold water. The quenching fragmented the glass which facilitated removal from the crucibles. The glasses were quenched, crushed and remelted at least three times to ensure homogeneity. Intermediate crushing was achieved using an agate pestle and mortar and the fragments were crushed under acetone to act as coolant and to minimize loss through splintering. Microscopic examination of the products after the final refining soak and quench indicated that the preparation method yielded a bubble-free glass with no undissolved inclusions. Examination of the grains in refractive index liquid also indicated homogeneity of the glasses. This preparation technique was employed to produce glass samples for DTA, MATR infra-red analysis and X-ray diffraction analysis. Several size fractions were required and the coarser ones were obtained directly by sieving, finer fractions being produced by crushing as described later.

Bulk specimens of the glasses in the form of cast buttons were also required. These were cast into a graphite mould 25 mm diameter by 10 mm deep and were not subjected to annealing heat treatment since one of the objects of the programme was to determine the effect of all subsequent heat-treatments on the glasses. Consequently, although the bulk samples were bubble-free and contained no undissolved material, they were characteristically strained and flow-lines were visible.

Several different size fractions of the glasses were required for the different analyses. Coarse fractions were produced by hand grinding in an agate mortar and pestle under acetone and the fine fractions were produced by milling in a Tema disc mill utilizing a tungsten carbide grinding barrel. The grinding surfaces of the barrel were "run-in" by grinding batches of quartz until no colouration of the silica flour was visible. It was noted that dry grinding of the silica produced some compaction which reduced the grinding efficiency. The addition of a small amount of carbon tetrachloride to the charge prevented this effect and was easily removed by evaporation in a drying oven prior to sieving of the product.

Sizing was carried out using nylon mesh screen cloth in preference to wire mesh to minimize contamination of the abrasive glass powder by metal. The nylon mesh was uniformly tensioned across the mouth of glass jars using a threaded screw cap in the form of a ring around the perimeter of the necks of the jars. Using this system, contact of the glass with metal surfaces was minimized. The undersize was shaken out "pepperpot" fashion into a glass beaker which could be held tightly against the sieve and thus excluded dust and other possible contaminants. The oversize was retained in the jar.

The samples of the base glass prepared by these methods were characterized by examination of physical properties. The following tests and methods were used.

(a) Visual appearance: the glass was transparent and had a bright vitreous lustre. Fracture was conchoidal and the base glass was colourless. Hardness was determined as 7+ on the Mohr scale (scratched quartz).

(b) Microscopic examination: grain samples were examined with a petrological microscope. The grains were isotropic and appeared homogeneous. Refractive index determinations were made in white light using the immersion technique and the Becke and Schroeder van der Kalk tests were employed. Refractive index liquid values were checked using an Abbe refractometer and the estimated accuracy was ±0.002 using a medium power (×40) objective for the Becke test. The value obtained for the refractive index of the glass was 1.549 ± 0.002 which was in agreement with earlier data for glasses from the system [3].

(c) Density: the standard pyknometric method was used to determine the specific gravity of the glass. A 25 ml capacity glass pyknometer was used. To minimize error the pyknometer was filled to at least a quarter of its capacity with solid material and care was taken to exclude air bubbles. The mean value of ten determinations gave a specific gravity of 2.52 ± 0.01 for the base glass.

The base glass devitrification characteristics were determined by DTA and X-ray diffraction analysis and as a result of these tests heat-treatment schedules were devised to study the crystallization processes in detail. Crushed and sized samples of the glass were heat-treated in a small muffle furnace according to the schedules outlined in the following sections. The samples were placed in shallow trays made from platinum foil and supported on a refractory block in the furnace. The temperature control and monitoring thermocouples were positioned above and below the trays in the muffle and the heat-treatments were carefully controlled by the outputs from these thermocouples.

3. Differential thermal analysis of the base glass

The general devitrification characteristics of the base glass were investigated under a variety of experimental conditions. The preliminary tests had indicated that certain of the instrument and sample variables could have significant effects upon the thermal analysis curves [2]. The literature review had shown that these variables had not been discussed in any detail by previous workers [1], and it was therefore decided to study them thoroughly before proceeding to the investigation of the effects of additives on the devitrification of the glass.

The effects of thermocouple location, dilution and particle size of the sample were investigated and an evaluation of the "comparative" method [4] for studying nucleation efficiency by DTA was made. The results are given below.

3.1. Studies of undiluted samples of coarse glass

The devitrification of samples of coarse glass (−25 mesh BS +72 mesh BS) was determined by DTA using temperature monitoring in both reference and reacting sample. Sample weights of 320 mg of glass were used for both series of tests and calcined alumina was used as reference material. The amplifier sensitivity was set to give a full-scale deflection of ±500 μV on the chart recorder for the differential scale. A standardized procedure was adopted for sample packing and care was taken to ensure that the sample cell was centred in a reproducible position for each determination. The results are given in Table I:

TABLE I DTA results for samples of coarse base glass

Sample no.	Thermal effects and peak temps. (°C)			Thermocouple location
	Endotherm	Exotherm 1	Exotherm 2	
CG/C1	825 (vs)	1011 (ml)	—	Reference
CG/C2	825 (vs)	1018 (ml)	—	Reference
CG/C3	—	1026 (ml)	—	Reference
CG/C4	—	1018 (ml)	—	Reference
CG/C5	825 (vs)	1011 (ml)	—	Reference
CG/C6	825 (vs)	1037 (ml)	—	Sample
CG/C7	825 (vs)	1037 (ml)	—	Sample
CG/C8	825 (vs)	1037 (ml)	—	Sample

The expression following the peak maxima values gives an indication of the relative sizes of the peaks. The system adopted is similar to that used in the Scifax DTA data index [5], in which the symbols correspond to the following descriptions: vl – very large; l – large; ml – medium large; m – medium; ms – medium small; s – small; vs – very small. This system is adopted throughout.

The general features of the thermal analysis curves from this series were similar. Fairly steady base-lines were obtained up to temperatures in the region of 800° C. In this region a slight endothermic dip appeared, and in all cases was centred at about 825° C. The dip persisted until the main crystallization exotherm occurred. This was characteristically symmetrical and well defined for the second series of analyses, although slightly skewed for the first series. The important differences between the results were the apparent lowering of the peak temperatures and the increased scatter of results in the first series. Thus, the effect of thermocouple location was demonstrated to be significant and it appeared that system temperature measurement in the reacting sample would provide reproducible results.

3.2. Studies of undiluted samples of fine glass

Similar determinations were made on samples of fine glass sized to −200 mesh BS. The operating conditions for these analyses were the same as for coarse glass and the same sample weight (320 mg) was analysed against alumina at 10° C min^{-1}. The results are summarized in Table II and it can be seen that the general features of the thermal analysis curves were similar.

TABLE II DTA results for samples of fine base glass

Sample no.	Thermal effects and peak temps. (°C)			Thermocouple location
	Endotherm	Exotherm 1	Exotherm 2	
CG/F1	856 (s)	943 (ms)	989 (m)	Reference
CG/F2	830 (vs)	950 (ms)	988 (m)	Reference
CG/F3	856 (vs)	927 (ms)	984 (m)	Reference
CG/F4	825 (s)	935 (ms)	973 (m)	Reference
CG/F5	825 (s)	954 (ms)	999 (m)	Sample
CG/F6	825 (s)	954 (ms)	999 (m)	Sample
CG/F7	825 (s)	954 (ms)	999 (m)	Sample

The thermal effects comprised a slight endothermic dip in the region of 800 to 850° C, followed by an exothermic doublet. In most cases these exotherms overlapped, although the peaks were clearly resolved. In all cases the first exothermic was smaller than the second. The low-temperature exotherms also tended to be more rounded than the high-temperature ones. The effect of thermocouple location on the form of the curves was similar to that noted for coarse glass fractions.

The effect of particle size on the devitrification characteristics was most significant and was in agreement with other workers' observations on similar glasses [6]. In the earlier studies the first exotherm was attributed to the formation of "μ-cordierite" and the second to the conversion to "α-cordierite", and in the present study further analyses were carried out to determine the nature of these changes indicated by DTA.

3.3. Studies using the "comparative method" of DTA

The method of Thakur and Thiagarajan [4] was tested to determine the accuracy compared with conventional DTA. Five replicate analyses were made with coarse glass acting as reference for fine. The samples were undiluted and equal sample weights, 320 mg, of each fraction were used. Standard analysis conditions were used, i.e., heated at 10°C min^{-1} with × 100 amplification of the differential signal.

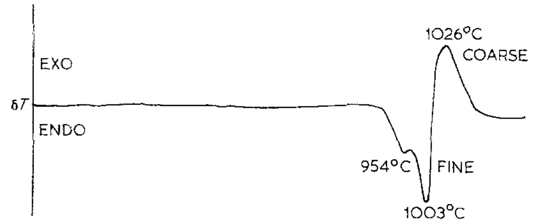

Figure 1 Thermal analysis curve of undiluted glass with coarse acting as reference for fine.

A representative thermogram is given as Fig. 1 in which the crystallization of the fine fraction is shown as an "endothermic" doublet and the crystallization of the coarse glass as an exothermic effect in the conventional direction. According to the theory described in an earlier paper [2] any reduction of the difference between the coarse glass crystallization exotherm temperature and the first fine glass crystallization exotherm temperature, brought about by the addition of other components to the base glass, would quantitatively indicate nucleation efficiency. This difference, designated by ΔT, was found to be 72°C for all five analyses. It was noted that the ΔT value obtained using this method was lower than the value obtained by taking the differences in peak temperatures that are given in Tables I and II. These indicated that the true value of ΔT under the stated conditions should be 83°C. Further analyses were made using different glasses and these results and their significance is discussed later.

3.4. Studies of diluted samples of the base glass fractions

Dilution of the samples was considered desirable in order to increase the sensitivity of recording so that better resolution of the small endothermic effects could be obtained. As a result of a comprehensive testing scheme involving the use of different ratios of alumina diluent to glass samples and different mixing techniques the following conclusions were reached. (a) The sensitivity of recording could be increased by dilution, (b) the resolution of the small endothermic effect could be improved, and (c) the effect of sample particle size became more apparent under the more sensitive conditions.

In view of these conclusions the following operating parameters were adopted as standard for the determinative investigations employing DTA. 1. Sample weights of 70 mg were used. 2. Calcined alumina was intimately mixed by careful stirring to give a total diluted weight of 250 mg. 3. Maximum amplifier gain was used. 4. System temperature was monitored in the reacting sample.

3.5. The effect of particle size on devitrification thermal analysis curves

Closely-sized fractions of the base glass were prepared by sieving and subjected to DTA under the standard conditions that have been described. The results of these analyses are given in Table III.

TABLE III DTA results for different size fractions of base glass

Sample	Size range (BS mesh)	Exothermic peaks (°C)	
A	−25 + 30	1064	
B	−30 + 44	1060	
C	−44 + 52	1049	
D	−52 + 60	1046	
E	−60 + 72	1041	
F	−72 + 85	1033	
G	−85 + 100	1026	
H	−100 + 150	1018	
I	−150 + 200	1011	
J	−200 + 240	1003	*
K	−240 + 300	996	1037
L	−300 + 350	980	1033

The thermal analysis curves all showed the same general features, the characteristic endothermic dip occurred in the temperature region 800 to 850°C with peak maximum at about 825°C. This was followed by a single crystallization exotherm for the coarse glasses and by an exothermic doublet for the fine glasses. There was only slight evidence of the second exotherm for sample J, which showed a well defined exotherm followed by a diffuse hump whose maximum value was difficult to locate precisely. With the finer fractions, samples K and L, small but relatively distinct exotherms were obtained. The resolution of the doublets was not as distinct as had been observed in earlier tests with undiluted fine glass which had been sized as −200 mesh BS. However, considering the results above it appeared that the "−200 mesh" glass must have been finer than 350 mesh and this assumption was confirmed by the observations of Tyrrell *et al* [6] whose results had shown that complete resolution of the crystallization doublet could be obtained for glass "... considerably finer than 350 mesh". Grinding tests were therefore carried out to determine the optimum grinding times, using the Tema mill, to produce a "fine-glass fraction" whose DTA devitrification characteristics would produce distinct and well resolved peaks. A grinding time of 5 min was adopted and although the resultant sample was only characterized as "−350 mesh", this procedure was considered justified in terms of the resolution of the peaks and from the consideration that longer grinding time might have influenced subsequent crystallization behaviour. Fig. 2 represents the thermal analysis curve for a diluted sample of the fine base glass obtained under the standard analysis conditions. The coarse glass size range for further determinations was defined as −25 mesh +72 mesh BS and the crystallization behaviour of this fraction was assumed to be approximately equivalent to bulk glass crystallization behaviour.

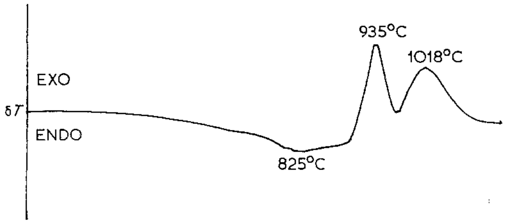

Figure 2 Thermal analysis curve of diluted fine fraction.

3.6. Studies of heat-treated samples of the base glass

The importance of low-temperature heat-treatments of cordierite-type glasses was discussed in an earlier paper [1], and it was decided to investigate the influence of heat-treatment in the precrystallization range of the base glass by DTA. Samples of the glass were milled for 5 min in the Tema mill and placed in platinum boats in a heat-treatment muffle furnace. The temperature was taken up to 830°C at 10°C min^{-1} and samples were withdrawn and air-quenched after 1, 3, 6, 12, 18, 21 and 24 h. It was noted that some of the samples had sintered slightly after the longer heat-treatments, so all samples were disc milled for $\frac{1}{2}$ min prior to DTA to ensure that the whole sample was −350 mesh BS.

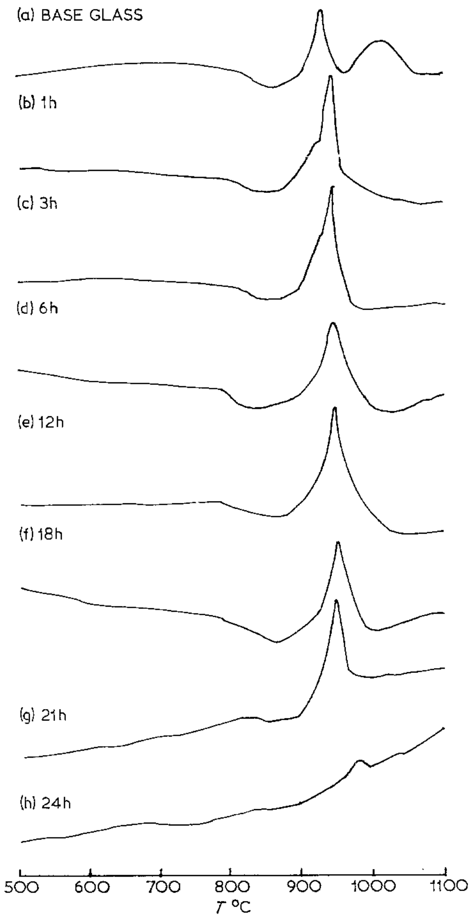

Figure 3 Thermal analysis curves for samples heat-treated at 830° C for the times given.

The series of thermal analysis curves given as Fig. 3 illustrate the results and clearly demonstrate that low-temperature heat-treatment effectively alters the crystallization of the glass. The curves show that the primary crystalline phase had started to form and as a result the magnitude of the low-temperature exotherm was reduced progressively with increased duration of heat-treatment. The doublet was not resolved after fairly short heat-treatment and was barely detectable after 21 h treatment. The curve obtained after 24 h treatment was subject to excessive base-line drift and showed no distinctive features, apart from a very ill-defined exothermic reaction in the region 980 to 1020°C. The results indicated that DTA could be used to determine the degree of crystallization of the glass although it is doubtful whether precise quantitative estimation of the percentage crystallinity could be made owing to the long periods of time required for the equilibrium phase to be formed by devitrification at low temperatures.

4. Differential thermal analysis of other glasses

From the results that were obtained for the base glass it was observed that there was some discrepancy between the ΔT values obtained using the "comparative method" and those from conventional analyses. A further series of tests were carried out to investigate this difference using a different series of glasses. Three more glasses were prepared which had the same base composition as the original glass but also contained small additions of vanadium pentoxide. The compositions were altered by the addition of 1, 2 and 3% V_2O_5 by weight and were prepared by the standard method described earlier. These glasses were designated CG/V1, CG/V2 and CG/V3 respectively.

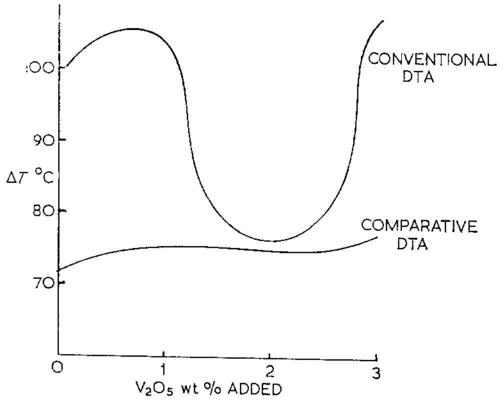

Figure 4 Variation of ΔT with V_2O_5 added (up to 3%).

Replicate determinations of the ΔT index for this series of glasses were made under the standard conditions outlined previously. One set of replicate determinations was made using the conventional scheme of DTA and the other set was made using the comparative technique. The results are presented graphically in Fig. 4. It can be seen from these curves that although the general trends of the two types of determination are similar, the comparative method indicated that the addition of V_2O_5 did not catalyse the crystallization whereas the conventional analysis indicated that the addition of 2% V_2O_5 could be beneficial for promoting crystallization of the glass.

The apparent discrepancy in the results can be explained in terms of the effect of thermocouple location on the position of the peaks obtained during DTA. The importance of this variable had been demonstrated in the preliminary tests which had indicated that temperature monitoring in the reference material gave consistently lower peak values and increased the scatter of the results. Thus, the coarse glass fraction acting as reference material for the fine in the comparative analysis is registered on the DTA curve in a similar way to the analysis where temperature is monitored in the reference cell. The overall effect of this arrangement would be a peak shift to lower temperatures for the coarse glass exotherm and a reduced ΔT value. Although the comparative method has the advantage of requiring fewer determinations compared with conventional DTA the results can be misleading. If a very efficient nucleating agent were incorporated in the glass, the value of ΔT would be reduced to zero by the simultaneous volume crystallization of the two size fractions. With less efficient nucleation the reduction would be less due to peak shift dependent upon thermocouple location effects, and the less efficient nucleation would thus be masked. The method that was adopted for the present study was the analysis of fine and coarse fractions of the different glasses individually by DTA using calcined alumina as reference material. The analysis conditions were standardized with temperature measurement in the reacting glass sample, diluted samples, standardized packing and positioning of the cell and heating at 10° C $\min^{-1}$.

Nine glasses were investigated in this way, all based on the original glass composition given earlier. Additions of vanadium pentoxide and tungstic oxide were made at the 1, 2, 3 and 5% (weight added) levels, and the glasses were designated (i) CG: base glass (ii) CG/V1 – CG/V5 refer to the glasses with V_2O_5 and (iii) CG/W1 – CG/W5 refer to the glasses with WO_3. All glasses were prepared by the standard method described earlier and in each case 70 mg samples of the different size fractions were diluted by intimate mixing with 180 mg calcined alumina for DTA. The graph given as Fig. 5 illustrates the variation of the quantity ΔT with addition of other oxides.

The thermal analysis curves for the coarse base glass and the coarse vanadium-containing glasses were similar in that all showed characteristic crystallization peaks which were fairly broad at the base and rounded at the top. The

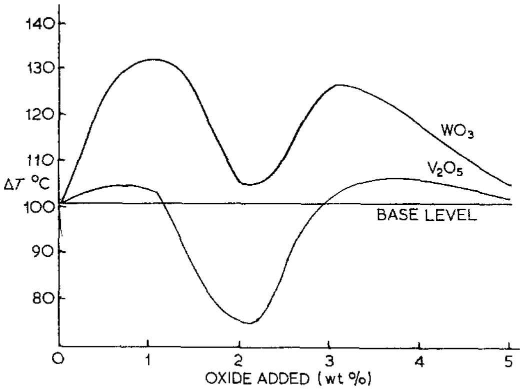

Figure 5 Variation of ΔT with V_2O_5 and WO_3 added to base glass.

curves for the tungsten-containing coarse glasses were much sharper and higher, although the areas under the peaks were approximately equal for equal sample weights for all glasses.

The thermal analysis curves for the fine glass fractions were slightly different as outlined following:

TABLE IV DTA peak features for fine glass fractions

Sample	Peak features	Separation (°C)
CG	Completely resolved doublet, first peak large	83
CG/V1	Resolved doublet, first peak small	31
CG/V2	Badly resolved, first peak large	12
CG/V3	Badly resolved, first peak small	15
CG/V5	Resolved doublet, first peak small	87
CG/W1	Large peak with very small second peak	76
CG/W2	Large peak with very small second peak	53
CG/W3	Overlapping doublet, large first peak	23
CG/W5	Overlapping doublet, large first peak	35

The crystallization temperatures for both fractions for the complete series of tests are summarized in Table V:

Thus, the results of this series of tests can be seen to have given the following indications.

(i) The addition of vanadium pentoxide to the base glass resulted in a reduction of the crystallization temperatures of both coarse and fine fractions up to the 3% level.

TABLE V DTA results for coarse and fine fractions

Glass	Exothermic peak temperatures (°C)			Difference ΔT°C
	Fine	Fine	Coarse	
CG	935	1018	1037	102
CG/V1	927	958	1033	106
CG/V2	935	947	1011	76
CG/V3	920	935	1026	106
CG/V5	939	1026	1041	102
CG/W1	950	1026	1085	135
CG/W2	988	1041	1093	105
CG/W3	965	988	1093	128
CG/W5	976	1011	1085	109

(ii) The addition of 2% V_2O_5 to the base glass gave a slight reduction in the quantity ΔT.

(iii) For the fine fraction alone, the addition of V_2O_5 reduced the temperature interval of transition from the first crystallization product to the second. This interval was at a minimum for addition of 2% V_2O_5.

(iv) The addition of tungstic oxide resulted in a general increase in crystallization temperature of the fine and coarse glass.

(v) The addition of WO_3 to the base glass did not reduce the quantity ΔT.

(vi) For the fine fraction alone, the addition of WO_3 also resulted in a reduction of the temperature interval of transition from the first crystallization product to the second, although the amount of conversion estimated in terms of the relative areas of the peaks on the curves was considerably reduced.

5. Optical analysis

Optical microscopy was used to check homogeneity of the glasses, as described earlier, and for examination of the devitrification products. The technique was not extensively employed because of the limitations imposed by the nature of the crystalline products, i.e. small crystal size and intimate and complex crystal intergrowth.

Initially a study was made of devitrified grains of the coarse glass which had been subjected to low-temperature heat-treatment at 830°C. The grains were prepared as temporary mounts and examined by polarized light. Refractive index determinations were made using the immersion technique in sodium light and the results are given in Table VI.

In general, completely crystalline grains exhibited a mosaic-like appearance in polarized light with crossed polars. The results of these

TABLE VI Optical examination of grains heat-treated at 830°C

Duration (h)	Appearance	Refractive index
0	Non-crystalline homogeneous glass	1.546 ± 0.001
1	No visible crystals, isotropic	1.548 ± 0.001
3	No visible crystals, isotropic	1.548 ± 0.001
6	Very slight visible crystallinity	1.549 ± 0.001
12	Very slight visible crystallinity	1.548 ± 0.001
18	Some grains completely crystalline	1.548 ± 0.001
24	Whole sample completely crystalline	1.533 ± 0.001

optical analyses showed good agreement with the indications from DTA (see Fig. 3) concerning the formation of the metastable phase during low-temperature heat-treatment.

Bulk samples of the glasses were also subjected to heat-treatments corresponding to the optimum conditions for crystallization as determined from the results of DTA and the results are summarized in the sections below.

5.1. Bulk sample heat-treated at 935°C for 30 h (base glass)

Examination in thin section showed that the sample was completely crystalline and consisted of a mass of fine acicular crystals. The general appearance of the sample was milky-white and semi-opaque and this opacity was predominantly associated with surfaces. It also appeared that internal crystallization had originated from the boundaries of flow lines formed when the glass was cast into the graphite mould.

5.2. Bulk sample heat-treated at 1000°C for 2 h (base glass)

The general appearance of this sample was characterized by a milky-white surface opacity and translucent interior. In thin section the surface crust consisted of a well-developed layer of relatively coarse intergrown crystals, oriented perpendicular to the surface. The interior was completely crystalline and consisted of a mosaic-like pattern of radial aggregates. The crystals were very closely intergrown and there was no indication of any residual glassy phase.

5.3. Bulk sample heat-treated at 1020°C for 1 h (base glass)

Again, the sample showed surface crystallization which was composed of coarse intergrown acicular crystals and the interior had randomly oriented mosaic clusters of very small crystals in radial groups.

5.4. Bulk sample heat-treated at 1100°C for 1 h (base glass)

A sample was prepared as a small cube, approximately 8 × 8 × 8 mm, by grinding from a cast button using a diamond grinding wheel. The surfaces were fine ground through the grades of carborundum used for thin section production, down to 600 mesh. Finally the faces of the cube were polished with diamond paste on a polishing lap to give a clear, uniform transparent sample. This procedure was adopted to give a sample free from flow lines (the cube was selected from a portion of the original button that appeared completely homogeneous).

After heat-treatment, a thin section of the sample showed the characteristic crystalline crust, which penetrated to a depth of about 1.5 mm from each surface. The interior of the cube consisted of large spherulitic growths consisting of radially-oriented interlocking acicular crystals. These "rosettes" consistuted the whole of the interior of the sample and no residual glass was detected.

5.5. Bulk sample heat-treated at 1200°C for 24 h (base glass)

The general appearance of this sample was similar to others subjected to high temperature heat treatments. Opaque white areas occurred throughout the sample in apparently random orientation and the intermediate material was substantially transparent although of rather "waxy" appearance. Microscopic examination in thin section indicated complete crystallinity with the opaque sections corresponding to masses of radially-oriented fine crystals and the transparent portions consisting of relatively large acicular crystals. In general the "matrix" phase consisted of relatively large crystals compared with those produced by lower temperature heat-treatments.

This series of samples was taken to illustrate the typical devitrification morphology of the base glass and clearly indicated the formation of the metastable phase with low temperature heat-treatment followed by development of the equilibrium phase with higher temperature heat-treatments. The series was not extended to cover heat-treatment schedules for all of the experimental glasses as only limited information would have been gained. However, the overall visual appearance of all the samples after heat treatment corresponding to the optimum crystallization conditions as determined by DTA was noted. In all cases the samples exhibited typical devitrification features, namely predominantly surface crystallization consisting of a crust of coarse crystals oriented perpendicularly to the sample surfaces. The interiors of the samples all showed mosaic-like crystallization patterns and there was no evidence of catalysed volume crystallization in the form of evenly dispersed sub-microscopic crystals.

6. Conclusions

The DTA studies were used to investigate the normal devitrification behaviour of the base glass and the importance of sample variables was illustrated. The sequence of crystal growth and form was monitored by optical microscopic examination of heat-treated samples to confirm the DTA results and finally the nucleating efficiency of small additions of V_2O_5 and WO_3 was determined by DTA. Although no evidence of efficient catalysed crystallization was found using these additives (the term "efficient catalysed crystallization" meaning in this context the production of a uniform, fine-grained product of the glass-ceramic type), their effect was also studied by the methods of MATR infra-red spectrophotometry and X-ray diffraction analysis and the results of these studies will be reported in the final part of this series of papers.

References

1. A. G. GREGORY and T. J. VEASEY, *J. Mater. Sci.* **6** (1971) 1312.
2. *Idem, ibid* **7** (1972) 1327.
3. W. SCHREYER and J. F. SCHAIRER, *Z. Krist.* **116** (1961) 60.
4. R. L. THAKUR and S. THIAGARAJAN, *Bull. Cent. Glass Ceram. Res. Inst. (India)* **13** (1966) 33.
5. R. C. MACKENZIE, "Scifax Differential Thermal Analysis Data Index" (Macmillan, London, 1962).
6. M. E. TYRRELL, G. V. GIBBS, and H. R. SHELL, *US Bur. Min. Bull.* no. 594 (1961).

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