JOURNAL OF MATERIALS SCIENCE 8 (1973) 333–339

The crystallization of cordierite glass

Part 4 *Experimental studies of the crystallization of a cordierite-type glass and the effects of oxide additions on the devitrification characteristics*

A. G. GREGORY, T. J. VEASEY
Department of Minerals Engineering, University of Birmingham, UK

The results of a study of the devitrification of a cordierite-type glass, investigated by MATR infra-red spectrophotometry and X-ray analysis, are described and discussed in relation to earlier analysis by DTA. The effects of additions of vanadium pentoxide and tungstic oxide on the behaviour of the base glass, as determined by these analytical methods, are also discussed.

1. Introduction

The previous paper in this series [1] dealt with DTA of a cordierite-type glass of composition 15% MgO, 30% Al_2O_3, 55% SiO_2 by weight, and the effects of additions of V_2O_5 and WO_3 on devitrification behaviour. The base glass was also studied by MATR infra-red spectrophotometry and the method employed was described in an earlier publication [2]. This final part will describe and discuss the results of the complementary analytical techniques of MATR infra-red and X-ray diffraction analysis and summarize the conclusions of the study.

2. Infra-red analysis of the base glass

The spectrum obtained for the base glass is shown in Fig. 1 and can be seen to consist of three broad bands centred at 1065, 935, and 440 cm^{-1}. From the considerations presented earlier in the literature review [2] these bands may be considered as characteristic of a silicate structure all of which have strong bands in the region of 1000 and 500 cm^{-1} whether vitreous or crystalline in form. These main silicate absorptions were found to persist throughout the spectra of the various samples but in modified form according to the different heat-treatments applied to the samples.

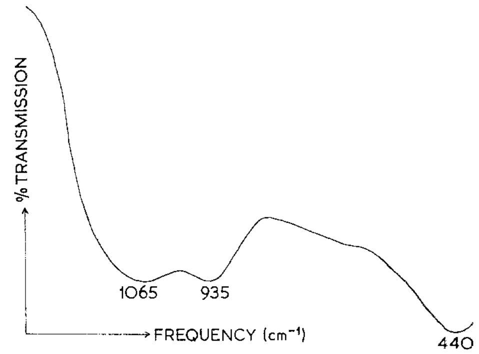

Figure 1 Infra-red spectrum of base glass.

DTA of the base glass had indicated that structural changes would occur with heat-treatments in the region of 935 and 1020°C, these temperatures being fixed by the positions of the exothermal peaks on the thermal analysis curves of the fine glass. There was also evidence of some change in the region of 825°C as indicated by the endothermal effect during DTA. Consequently these changes were studied by determination of the infra-red spectra of samples of the glass heat-treated at 800, 830, 935, 950, 1000, and 1100°C. The samples were heated to temperature at approximately 10°C min^{-1} and held for different lengths of time prior to infra-red analysis. For most of the samples the duration of heat treatment was 1, 3, and 24 h at each temperature. Intermediate times were used for some of the heat-treatments where more detailed examination of the crystallization path was required.

Heat-treatment at 800°C produced very little change in the spectrum. There was a slight shift of the broad silicate absorption bands towards higher frequencies and the longer heat treatments at this temperature tended to sharpen the bands although they were still broad and diffuse.

By contrast, heat-treatment at 830°C modified the infra-red spectrum quite considerably, particularly as the duration of the treatment was increased. Heat-treatment for 1 h produced a spectrum with broad weak bands at 1150, 940, and 750 cm^{-1}. There were also small but distinct bands at 500 and 455 cm^{-1}. As the duration of the heat-treatment was increased these bands became slightly sharper and in particular the band at 750 cm^{-1} developed into a well-defined trough.

DTA had indicated that heat-treatment at this temperature would encourage the development of the phase corresponding to the first exothermal of the crystallization doublet. This phase had been identified in earlier work as the metastable quartz-like phase or "μ-cordierite". The whole process of formation and conversion of this phase to the equilibrium cordierite phase had been traced by DTA of heat-treated glasses and was monitored by infra-red analysis in a similar manner. The spectra obtained are given in Fig. 2 and the changing nature of these correspond to the changes in the thermal analysis curves presented earlier [1] and represent the development of cordierite through the intermediate stage. The spectra were not well defined as they represented the continual rearrangement of structure that occurred throughout the devitrification process.

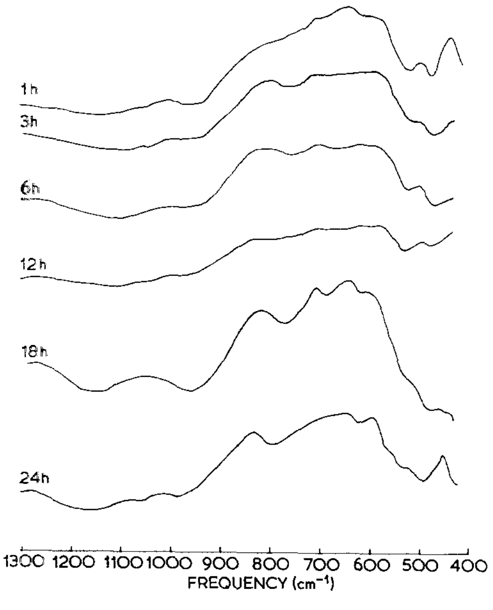

Figure 2 Infra-red spectra of base glass heated at 830°C.

Spectra were also obtained that corresponded to the distinct structural changes in the crystallization process by analysis of samples heat-treated at temperatures corresponding to the major effects on the thermal analysis curves. Thus, a sample was heat treated at 935°C for 1 h to develop the metastable phase and a long heat-treatment (120 h) at 1100°C was employed to develop the equilibrium cordierite phase.

The former produced relatively weak spectral features which consisted of broad bands at 1120, 950, 750, 650, 580, and 430 cm^{-1}. The high frequency bands were shifted to higher values and two minor bands developed at 750 and 580 cm^{-1}. A weak, broad inflection also appeared at 650 cm^{-1} and the low frequency band at 430 cm^{-1} was better defined.

The spectrum obtained for the product of heat-treatment at 1100°C for 120 h was found to be in good agreement with earlier data [3] for the infra-red spectrum of cordierite. The spectrum is compared with the low-temperature heat-treatment spectrum in Fig. 3.

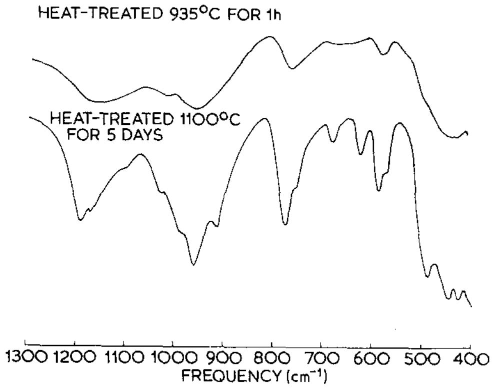

Figure 3 Infra-red spectra of base glass (a) heat-treated 1 h at 935°C, (b) heat-treated 5 days at 1100°C.

In order to obtain an overall picture of the spectral shifts associated with devitrification of the base glass, samples were heat-treated at 950, 1000, and 1100°C for periods of 1, 3, and 24 h. These schedules were selected as representative of the key stages in the process and the spectra were compared with those obtained for glasses containing V_2O_5 and WO_3 subjected to similar treatments.

3. Infra-red studies of glasses with other oxide additions

The glasses designated CG/V1 - CG/V5 and CG/W1 - CG/W5 [1] were heat-treated and the general trends observed for the spectral shifts in the base glass were determined. The transition from relatively ill-defined spectra after 1 h heat-treatment to well-defined spectra after 24 h was consistent through the series of schedules, and details are given in the following sections.

3.1. Heat-treatment of glass with V_2O_5 at 950°C

The four glasses showed similar spectra after heat-treatment for 1 h except that the spectrum of sample CG/V2 was better resolved. Samples CG/V1, CG/V3, and CG/V5 all had indications of an inflection or weak band in the region of 660 cm^{-1} which was absent in the spectrum of glass CG/V2.

After 3 h heat-treatment all the glasses had well-defined spectra showing the same general features. Only slight differences were apparent, these being the development of a well-defined shoulder at 750 cm^{-1} in the spectrum for glass CG/V2 which was absent in spectra of samples CG/V1 and CG/V5 and only very weak in the spectrum of sample CG/V3. A weak shoulder was also apparent at 990 cm^{-1} in the spectrum for CG/V2 which was absent from the others, Fig. 4.

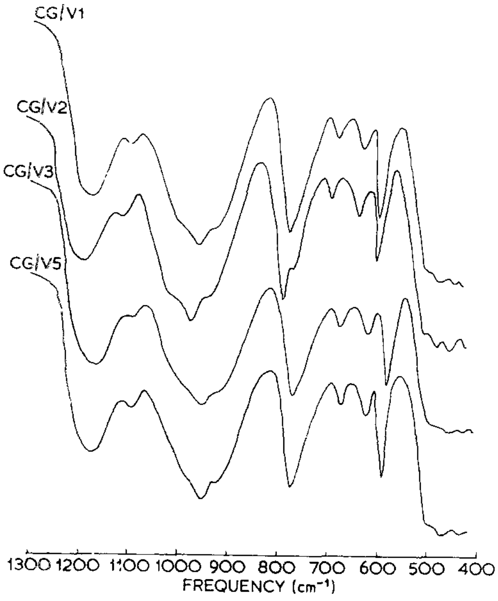

Figure 4 Infra-red spectra of glasses with V_2O_5 heat-treated for 3 h at 950°C.

Protracted heat-treatment at 950°C resulted in the appearance of more detailed subsidiary bands in all the spectra and in general the bands were "sharpened" towards higher frequency values and the weak shoulders were more easily resolved. There were no highly significant differences between samples except that CG/V2, CG/V3, and CG/V5 gave distinct shoulders at 750 cm^{-1} and also developed a subsidiary band at 910 cm^{-1}. These features were only very weakly apparent in the spectrum of sample CG/V1.

3.2. Heat-treatment of glass with V_2O_5 at 1000°C

Spectra obtained after 1 h heat-treatment at 1000°C were similar to those obtained after heat-treatment at 950°C for 24 h. However, the subsidiary bands associated with the major absorptions at the highest frequencies were absent from the former. The shoulder in the region of 775 cm^{-1} had not developed in sample CG/V1 but was fairly strong in the other spectra, and the main high frequency band for sample CG/V1 was located at a lower frequency value to the others. The trend described earlier was repeated in the other spectra in this series, i.e. all samples exhibited stronger spectral definition with longer heat-treatment but the development was reduced in comparative terms for glass CG/V1.

3.3. Heat-treatment of glass with V_2O_5 at 1100°C

At all stages of heat-treatment at 1100°C the samples gave spectra characteristic of cordierite. Many of the small subsidiary bands that had occurred in the other spectra had developed into distinct bands after heat-treatment at this temperature. The same general trends were apparent in that the spectra obtained for sample CG/V1 showed fewer details than the other vanadium-doped glasses. The best defined spectrum in terms of narrowing and intensification of bands was given by sample CG/V5 in this case.

Similar determinations were made of the spectra of the glasses containing WO_3 and these are described below.

3.4. Heat-treatment of glass with WO_3 at 950°C

The spectra obtained for glasses heated at 950°C for 1 h exhibited gradually increasing definition with increased tungsten content. This effect was particularly clear in the range between

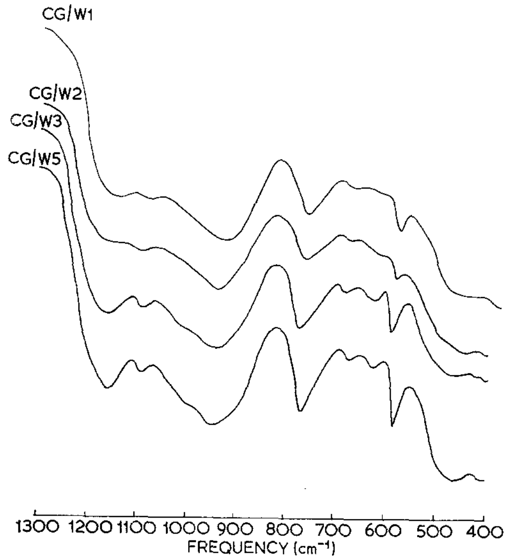

Figure 5 Infra-red spectra of glasses with WO_3 heat-treated for 1 h at 950° C.

a medium-broad band at 770 cm^{-1} and a small band at 580 cm^{-1} in all the spectra. These bands became better defined with increased tungsten content and two small bands at 670 and 620 cm^{-1} gradually developed in the interval between the two. The high frequency ends of the spectra were characterized by large, broad bands (Fig. 5).

Heat-treatment at 950°C for 3 h improved definition considerably and all four samples gave similar spectra with no significant differences between them. The longest heat-treatment at this temperature gave results similar to those obtained for 3 h treatments. The band centred in the region of 950 cm^{-1} developed distinct shoulders but other features remained fairly constant in form. Unlike the vanadium-containing glasses no significant development of bands at 670 and 620 cm^{-1} occurred and there was no apparent development of subsidiary bands associated with the highest frequency broad absorption.

3.5. Heat-treatment of glass with WO_3 at 1000°C

There were no significant differences between samples in the spectra obtained for glasses heat-treated at 1000°C. All the spectra exhibited the general trend of increasing definition with increased duration of heat-treatment, and this effect was best demonstrated by the bands at 670 and 620 cm^{-1}. The development of a shoulder at 750 cm^{-1} that had been noted for the vanadium-containing glasses was absent in the case of the tungsten-containing glasses except after 24 h heat-treatment at 1000° C when the effect was very weak.

3.6. Heat-treatment of glass with WO_3 at 1100°C

The spectra obtained after heat-treatment at 1100°C were very similar and showed the familiar trend of increased definition with increased duration of treatment. The development of bands at 670 and 620 cm^{-1} was retarded in this series compared with the results for the vanadium-containing glasses. The subsidiary bands that had occurred in association with the high frequency absorption in the vanadium-doped glasses were also absent from this series.

The results summarized in the preceding sections indicated the major changes and differences between the spectra of glasses subjected to different heat-treatment schedules. The results will be discussed in detail later in conjunction with the reported results from other analytical methods.

4. X-ray diffraction analysis of the heat-treated glasses

X-ray diffraction analysis was used to identify the products of devitrification. Initially the base glass was analysed using a Philips PW 1030 recording diffractometer employing nickel filtered copper radiation (40 kV, 20 mA). There were no lines apart from the broad band with a maximum value corresponding to a *d*-spacing of approximately 3.20 Å, characteristic of a vitreous material.

The crystallization of the glass subjected to low-temperature heat-treatment at 830°C was monitored by X-ray analysis and the results are summarized below.

(i) Heat-treatment for 1 h; typical X-ray pattern characteristic of glass structure.

(ii) Heat-treatment for 3 h; predominant glass structure pattern with appearance of small peak corresponding to a *d*-spacing of 3.40 Å. From considerations presented earlier this could be taken as indicative of the formation of the metastable quartz-like phase, and confirmed the results from DTA and infra-red analysis.

(iii) Heat-treatment for 6 h; very similar pattern to previous one with additional small peaks corresponding to *d*-spacings of 1.87, 2.25, and 4.50 Å. The intensity of the peak at 3.40 Å had increased considerably but there was still evidence of the diffuse band characteristic of residual glass.

(iv) Heat-treatment for 12 h; very similar trace to previous one except that the broad "glass" band was considerably reduced.

(v) Heat-treatment for 18 h; no evidence of residual glass in this sample and distinct lines had developed which corresponded to *d*-spacings of 1.63, 1.88, and 3.50 Å.

(vi) Heat-treatment for 21 h; fairly intense trace with well defined lines at 1.63, 1.87, 2.28, and 3.49 Å which could be indexed against the standard data for the principle *d*-spacings of the quartz-like phase.

(vii) Heat-treatment for 24 h; trace had many well defined peaks which were indexed and found to be characteristic of the simultaneous occurrence of the quartz-like phase and the equilibrium cordierite phase.

X-ray analysis was also used to identify the products of crystallization of the glass subjected to higher temperature heat-treatments and the resultant patterns could be satisfactorily matched with the ASTM data for cordierite. Similarly the heat-treated glasses containing V_2O_5 and WO_3 were analysed and the results were found to be in agreement with data obtained from the infra-red analysis.

5. Discussion

The devitrification of the base glass was shown to proceed through an intermediate crystallization stage to form cordierite. DTA indicated that the first part of the two-stage crystallization began at 910°C and reached maximum rate at 935°C. The exothermic effect in this range was shown to correspond to the crystallization of the quartz-like phase. Further heating caused the conversion of this metastable phase to the equilibrium cordierite phase and the maximum rate of conversion corresponded to an exothermic effect centred at 1018°C. These two distinct stages of devitrification could only be resolved by analysis of very fine glass powder. Coarse glass particles (+200 mesh BS) gave results that showed a single exothermic peak whose maximum position was dependent upon the particle size of the glass. These observations were in general agreement with the earlier work of Tyrrell, Gibbs, and Shell [4] in which a study had been made of the devitrification characteristics of glass with the cordierite stoichiometry. Toropov and Sirazhiddinov [5] had also made DTA studies of cordierite glasses and had resolved the crystallization doublet but had observed that only a relatively small amount of the metastable phase was formed from the compositions that were employed. The dependence of the amount of the quartz-like phase on the bulk composition of the parent glass was then demonstrated by the DTA results of Toropov *et al* [6].

It was concluded that general devitrification characteristics of cordierite-type glasses could be accurately determined by DTA, but that quantitative assessment of the relative amounts of the crystalline products could only be made if strict control of the sample variables was maintained. It was found that very fine grinding of the glass gave data related to the surface nucleation and crystallization of the glass and could be regarded as indicative of the optimum physical condition for the devitrification process. The variations in resolution of the two crystallization stages introduced by conducting analyses of relatively coarse glass could give misleading results. In a recent paper [7] glass blocks rather than glass powders were used to study metastable processes occurring within the body of cordierite glasses during DTA. The use of powder samples was justified in the present work which was essentially concerned with the differentiation between surface and volume nucleation and growth, the latter being the result of efficient catalysation of the process.

DTA of samples heat-treated at 830°C for 1 h had indicated the formation of the preliminary crystallization product and this was confirmed by the shifts observed in the infra-red spectra and the small change in refractive index. X-ray analysis was relatively insensitive to this small change. Increased duration of heat-treatment at this low temperature produced significant changes in the thermal analysis curves, infra-red spectra and X-ray diffraction traces. It was established that the crystalline phase developed by up to 21 h heat-treatment was the quartz-like material. The principle lines on the diffraction pattern could be accurately indexed against the data presented in the literature as diagnostic of this phase. The thermal analysis curves also clearly indicated the development of this phase by the disappearance of the exotherm characteristic of its formation from the glass. There were also changes in the infra-red spectra although these were not well defined. Comparison with data presented by Langer and Schreyer [8], however, indicated that the ill-defined band at 650 cm^{-1}, together with the general effect of the shift of the higher frequency bands to even higher frequencies, could be taken as characteristic of the formation of the metastable phase. Heat-treatment for 24 h encouraged the conversion of the metastable phase to cordierite and this was clearly shown by the thermal analysis curves and confirmed by X-ray analysis. The infra-red spectrum was not as well defined due to the co-existence of the quartz-like phase and cordierite and the resultant overlapping of their characteristic absorption bands.

DTA had indicated that the crystallization of the fine base glass to the metastable phase was at a maximum at 935°C and the infra-red spectrum of a sample heat-treated for 1 h at this temperature was determined. The spectrum had several features which distinguished it from the glass and the cordierite spectra. Most distinctive were the shifts of the board absorption bands to higher frequencies and the development of two small bands at 750 and 578 cm^{-1} together with a broad band centred at about 650 cm^{-1}.

Although no rigorous interpretation of the infra-red spectra was attempted the following observations were made. The glass spectrum showed characteristics typical of a silicate structure, namely the bands in the region of 1000 and 500 cm^{-1}. The subdivision of the band at 1000 cm^{-1} has been attributed to the difference between the vibrational energies of SiO_4 and AlO_4 [8] and the stretching mode of SiO_4 has been calculated as 1085 cm^{-1} and that of AlO_4 as 960 cm^{-1}. The present data showed close agreement with these values. It has also been pointed out [8] that the band in the region of 750 to 770 cm^{-1}, previously defined as characteristic of cyclosilicates with six-membered rings [9, 10], is in fact characteristic of the metastable quartz-like phase, and there was limited evidence of such a band at 750 cm^{-1} for glass heat-treated for 1 h at 830°C. This band steadily developed into a broad absorption as the duration of the heat-treatment was increased. The spectrum of the glass heat-treated for 1 h at 935°C had a distinct band centred at 750 cm^{-1} and a fairly well defined band at 578 cm^{-1} which can be associated with the formation of cordierite. The latter was absent from the spectra of samples heat-treated at 830°C for up to 12 h and only weakly apparent after 21 h at this temperature. It was well resolved after 24 h heat-treatment and the X-ray diffraction results indicated the formation of cordierite. Thus it was concluded that the infra-red and X-ray analyses had confirmed the DTA results concerning the formation of the metastable phase and its conversion to the equilibrium phase. The infra-red method seemed particularly sensitive to the continual structural rearrangements that had occurred throughout the heat-treatment schedules.

Crystallization at higher temperatures was also monitored by the infra-red method. Heat-treatment at 950°C produced a spectrum with the characteristics of both the quartz-like phase and cordierite. Increased duration of heat-treatment at this temperature enhanced the conversion to the equilibrium phase and after 24 h a spectrum characteristic of cordierite was obtained. However, heat-treatments at higher temperatures (1000 and 1100°C) produced further modification of the infra-red spectrum. The results of the other analyses had indicated that the glass would be completely converted to cordierite at these temperatures and it is proposed that the further modifications in the spectra were due to the gradual ordering of the cordierite structure.

Optical examination of the devitrified products after high-temperature heat-treatments had shown that the interior of bulk specimens contained coarse dendritic crystals which had developed from a matrix of acicular crystals. The development of these clusters may have corresponded to the more detailed cordierite spectra and these observations were in agreement with the earlier work of Sirazhiddinov [11]. The latter author had used X-ray diffraction analysis to determine the degree of order of cordierite formed by devitrification of glass with the cordierite stoichiometry. He also used infra-red analysis to characterize devitrification products but this analysis was restricted to determination down to a frequency of 800 cm^{-1} at the lower end of the range. It has been shown in the present study that the diagnostic changes in the spectra corresponding to the quartz-like phase and transition to cordierite occur at lower frequencies beyond the limit of this range.

The additions of vanadium pentoxide and tungstic oxide to the base glass did not promote fine-grained volume crystallization. Optical examination of the devitrified samples showed the characteristic surface crystallized crust with relatively coarse crystallization in the interior of the samples. The general trends determined from the results of DTA indicated that the addition of 2% V_2O_5 could be beneficial for the promotion of more rapid crystallization, and this was confirmed by the infra-red analysis. This result also shows close similarity with data presented by Williamson [12] concerning the effects of additions of V_2O_5 on the kinetics of crystal growth in glasses of the CaO-MgO-Al_2O_3-SiO_2 system. This author and his colleagues had previously reported the results of a study of the effects of reduced and oxidized vanadium ions on the crystallization of glasses in this system [13], and concluded that V_2O_5 was more effective than V_2O_3 at enhancing the rate of crystal growth. The proportion of reduced to oxidized vanadium was not investigated in the present study and the percentages quoted all refer to vanadium pentoxide wt % added to the glass batch.

The infra-red analyses of the vanadium-containing glasses also indicated that addition of 2% V_2O_5 was beneficial for promoting crystallization. The spectrum obtained after heat-treatment for 1 h at 950°C was better defined than the others in the series and did not show the broad band at 650 cm^{-1}. The absence of this band and the development of a medium sized band at 765 cm^{-1} were both indicative of the formation of cordierite from the metastable phase. The spectra became progressively more detailed with increased length of heat-treatment, e.g., the spectrum for the glass with 2% V_2O_5 heated for 3 h at 950°C developed a band in the form of a shoulder at 750 cm^{-1} which was absent in the samples containing 1 and 5% V_2O_5 and only very weak in the spectrum for the glass with 3% V_2O_5. With increased duration of heat-treatment the spectra all showed the general trends that had been observed for the base glass.

The spectra obtained for the tungsten-containing glasses confirmed the results of DTA. There was no evidence of catalysed crystallization of the glasses and the infra-red spectra were much less well-defined than the corresponding spectra for the vanadium-containing glasses.

6. Summary and conclusions

In conclusion, the results of the study of the devitrification of the base glass showed that the process proceeded through an intermediate crystallization stage to form cordierite. This process was initiated by surface nucleation and crystal growth and the product showed coarse crystallization. The volume crystallization of the base glass appeared to depend upon the formation of the metastable quartz-like phase, which could be developed by low-temperature heat-treatment of finely ground glass. The whole process of crystallization was followed by the analytical techniques of DTA and infra-red spectrophotometry with complementary information from X-ray diffraction analysis and optical microscopy.

Similarly, the effect of additions of vanadium and tungsten oxides was determined and the results indicated that these oxides were not suitable for the production of glass-ceramics based on the glass studied. The combination of DTA and MATR infra-red analysis were shown to offer an accurate and rapid method for the determination of nucleation efficiency and it is suggested that the latter might be developed into a quantitative method for determination of crystallization products from glasses.

Acknowledgements

Grateful acknowledgement is made to Professor Stacey G. Ward, Head of the Department of Minerals Engineering, for his interest and encouragement and thanks are also due to the Science Research Council for the award of a studentship to one of us (T.J.V.).

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Received 14 June and accepted 8 September 1972.