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Review: The Crystallization of Cordierite Glass

Part 2 *The study of devitrification behaviour by differential thermal analysis and infra-red spectrophotometry*

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The analytical methods of differential thermal analysis and infra-red spectrophotometry and their applications to the study of glass crystallization are reviewed. The development of these methods for an investigation of the devitrification of a cordierite-type glass is described and the results of preliminary experiments are discussed.

1. Introduction

The crystallization of cordierite-type glasses has been studied in detail by several different analytical methods and the results of these studies were reviewed in Part 1 of this work [1]. In the present study [2] both differential thermal analysis and infra-red spectrophotometry were employed as the main analytical methods and complementary data were obtained from X-ray diffraction and optical microscope methods. This paper will describe and discuss the methods that were adopted and a later publication will deal with the results of an investigation of the crystallization of a cordierite-type glass in detail.

2. Differential thermal analysis

The technique of DTA has been extensively employed as a standard analytical method in chemical, mineralogical and ceramic applications and the literature dealing with the basic principles is extensive. Amongst the most useful works are those of Mackenzie [3], Smothers and Chiang [4], Mackenzie and Mitchell [5], Wendlandt [6], Garn [7], and Mackenzie [8]. Most of these authors first dealt with the theory of DTA and then discussed the practical requirements which are necessary for the production of accurate and reproducible data. The early theories of DTA [9-17] were well documented and described in detail and the problems involved in the development of quantitative methods have also received considerable attention [11, 18-24]. Although the literature is extensive and the method of quantitative DTA has been widely used it must be stressed that extreme care must be taken to ensure rigid standardization of the experimental procedure before any kind of quantitative assessment is attempted. In addition, the nature of the reaction being studied must be carefully considered.

Several DTA methods have been developed to study reaction kinetics and have been reviewed elsewhere [25-28]. One of the most useful papers on the measurement of reaction kinetics was published by Kissinger [29]. From the basic assumption that the temperature of maximum deflection in DTA is also the temperature at which the reaction rate is at a maximum, for decompositions of the type (solid → solid + gas), Kissinger concluded by detailed theoretical analysis that the activation energy for simple decomposition reactions could be evaluated from DTA at different heating rates. He defined a shape index by which the order of the reaction could be estimated and found that the dominant factor which determined the shape and position of the peak was the nature of the reaction itself. More recent work has used the same basic equation [30] and the technique of analogue computing to study DTA reaction kinetics in terms of a mathematical model. Garn [31] investigated the suitability of certain test materials for the calibration of DTA apparatus and found that it is quite improbable that any single expression will provide an accurate representation of $\text{solid}_1 \rightleftharpoons \text{solid}_2$ phase transformations. All of these publications are useful background for prospective users of DTA but there have been several works more directly concerned with the applications of the method in glass technology which are discussed below.

2.1. Applications of DTA in glass technology

Robredo [32, 33] published a comprehensive review of the application of DTA to glass research and technology which contained numerous references. The subject matter was divided into sections dealing with the applications in the study of (a) reactions between the components of the glass batch, (b) structure and thermal treatments and (c) phase changes – including phase separation, crystallization and polymorphism. The latter part was of particular interest and was divided under headings related to the compositions of the glass-forming systems that have been studied by the method. The work of Krasilnikova *et al* [34, 35] on the determination of the proportion of glassy to crystalline products in the Na_2O-SiO_2 system was described. The systems Li_2O-SiO_2 and Li_2O-Al_2O_3-SiO_2 have been extensively studied by DTA and several works were referenced [36-42], and the results of Kalinina *et al* [39] and Kalinina and Filipovich [43] were presented as examples. Thakur and Thiagarajan [44] studied crystallization of CaO-Al_2O_3-SiO_2 glasses with additions of TiO_2 and Na_2O to determine the influence of these additives on crystallization temperature and Pavlushkin *et al* [45] used DTA to study the influence of MgO and FeO on the crystallization of similar glasses.

More important for the purposes of the present work was the section on the studies of crystallization of MgO-Al_2O_3-SiO_2 glasses. The work of Toropov and Sirazhiddinov [46] was described and some of their thermal analysis curves were presented. Robredo also cited several other studies of the cordierite system [47-50] which had employed DTA. The DTA method for this type of study has been widely used in the Soviet Union and other work dealing with the system included the papers of Kitaigorodskii and Khodakovskaya [51], Kitaigorodskii and Usvitskii [52], Pavlushkin and Ellern [53] and Blinov [54]. There are numerous references in the Soviet literature to other uses for DTA in glass technology research, particularly in the determination of crystallization behaviour, and the review by Robredo gave an excellent summary of such applications. It is worth noting that Karkhanavala and Hummel [55] and Tyrrell, Gibbs and Shell [56] used DTA in their important investigations of cordierite polymorphism which were described earlier [1].

Thus it can be seen that DTA has been widely used in glass technology for many years and has become particularly important in the study of crystallization processes. The possibilities of the technique can be increased even more with improvement in instrumentation and more rigorous standardization; for example, a recent publication [57] has described a micro-DTA/hot-stage microscope apparatus which has been successfully used for studies of the crystallization of Li_2O-Al_2O_3-SiO_2-TiO_2 glasses. In the present study DTA was used to determine the crystallization behaviour of the base glass and to evaluate nucleation catalyst efficiency and a full discussion of the method is presented later.

3. Infra-red spectrophotometry

The predominant use of the infra-red spectrophotometer for many years has been for the structural analysis of organic materials. With advanced instrumentation and the introduction of new techniques over the past decade the importance of infra-red analysis of inorganic materials such as rocks, minerals, ceramics and glasses has become apparent. The character of each spectrum is determined by the vibrational modes of the atomic or molecular structure and is a complex function of the interatomic distances, bond angles, bond forces and relative masses of the constituent atoms. Consequently the infra-red analytical technique is very sensitive to short-range ordering and can provide useful complementary information to X-ray analysis. The advantages for the study of glasses are obvious and it is found that glass will give as strong a spectrum as crystalline material and that many more specific absorptions appear as secondany peaks when the structure becomes more ordered during the devitrification process.

A useful introduction to the technique was published by Lyon [58] and the theoretical aspects were discussed by Harrick [59] and an earlier publication by Lyon [60] contained an impressive number of specimen spectra of natural materials. Most of these results were obtained using the absorption method which depends upon dispersing and mounting of a powdered specimen, at a very low level of concentration, in a transparent potassium bromide disc. The disc can be prepared by pressing in a heated vacuum die at pressures up to 65 tons per square inch, thus producing an homogeneous, transparent mounting medium.

The method has been described in detail by several authors [61-64] and the difficulties of sample preparation have been discussed. Other preparation techniques have also been used which included deposited films [65, 66], mulling samples with mineral oils [67] and deposition of sample pastes on other rigid substrates for transmission measurements [68, 69].

A relatively new technique, attenuated total reflection (ATR) was described by Fahrenfort [70] and was originally developed as a method for obtaining spectra of materials not amenable to transmission measurements. The method basically employs the phenomenon of total internal reflection. When radiation is totally internally reflected from a suitable face of a dielectric prism surrounded by a medium of lower index of refraction there is a penetration of the radiant energy into the rarer medium beyond the toally reflecting face for a short distance. If there is no absorption in the second medium the radiation is totally reflected. However, an analysis of the situation when the rarer medium contains material that absorbs shows that part of the incident radiation on the internally reflecting prism face is absorbed into those spectral regions which are characteristic for the absorbing material. Thus, spectra quite similar to transmission spectra can be obtained. Harrick [59] discussed this absorption into the rarer medium and derived an expression for the depth of penetration of the radiation which was used as a guide to the effective sample thickness for a spectrum as if it had been obtained by a transmission method. It was shown that spectra characteristic of samples up to several microns thick could be obtained. From the depth of penetration relationship it can be seen that the appearance of an infra-red absorption band will depend on the relative difference in refractive index between the totally reflecting prism and the rarer medium containing the absorber, as well as the internal angle of incidence. Thus, prism material is of prime importance and must possess the property of having a significantly higher refractive index than the absorbing material throughout the infra-red region. Materials such as KRS-5, silver chloride, germanium, silicon and Kodak "Irtran" products have all been successfully used (for a full description and discussion of the relative merits of these materials see [2]).

There are two types of reflectance units available for use with standard double-beam infra-red spectrophotometers:

(i) the single reflection unit, which consists of a mirror system and variable angle holder for a hemicylindrical prism, e.g. the Beckman-RIIC micro-ATR unit TR-5.

(ii) the multiple reflection unit consisting of a specially-shaped reflector prism which, by the process of multiple internal total reflection, effectively increases the path length of the radiation and an associated optical focusing module, e.g. the Beckman-RIIC MATR unit TRS-25.

The former type of unit produces relatively weak and sometimes distorted spectra in certain frequency regions. The multiple unit, on the other hand, can produce undistorted spectra provided there are enough reflections.

There is relatively little literature available on the applications of these methods although some qualitative and quantitative determinations have been made on organic polymeric materials and liquids [71, 72] and improvements in design of multiple-ATR units for different applications have been reported [73, 74]. As far as the present authors are aware there are no published data concerning the use of ATR and MATR methods for the analysis of silicate materials and the method that was adopted in the present study will be described in detail later.

3.1. Applications of infra-red spectrophotometry to the study of silicate structures and in glass technology

There have been several useful review articles which gave the characteristic infra-red spectra of minerals [75, 76] particularly the bibliography compiled by Lyon [60]. Although the infra-red method promises to be a useful tool for silicate analysis the problems of the interpretation of the spectra are considerable and Kolesova [77, 78] has discussed this aspect in detail. The most important recent publications from the point of view of the present work were those of Tarte [79] and Dutz [80]. The former gave a general discussion of the applicability of infra-red analysis to crystallochemical problems and served as a general introduction to the scope and limitations of available infra-red methods. The paper by Dutz [80] contained numerous references to the application of the methods to silicate analyses and is a most valuable reference source. Early work was described and the pioneer structural investigations of quartz were given in some detail and included the frequency assignations given to the isolated silica tetrahedron by Siebert [81]. The characteristic absorption frequencies of the different types of silicate structures were tabulated in the following way:

(i) All silicates – at least one major band in the region of 1000 cm^{-1}.

(ii) Nesosilicates – several strong bands between 800 and 1030 cm^{-1}, with some bands in the lower frequency regions less than 650 cm^{-1}.

(iii) Sorosilicates and inosilicates – generally less bands than the nesosilicates but addition of Al, Ti or Be increases the number.

(iv) Phyllosilicates – characteristic bands in different regions depending on the number of layers in the structure. Double layer silicates all have strong bands at 1025 cm^{-1} and a characteristic one at 913 cm^{-1}. The bands of the three layer minerals overlap between 900 and 1100 cm^{-1}, with the exception of the clay minerals.

(v) Tektosilicates – many strong bands that extend to 1160 cm^{-1}. The author stated that within these groups the different types are easily distinguishable. With increasing combination of the neso- and tektosilicates the vibration frequencies are raised. Reference was made to further aspects of this work using reflection spectra. In a similar context Lyon [69] pointed out that the covalent portions of the Si-O and Al-O bonds prove very sensitive to infra-red detection and that this method offers the greatest hope for solving some of the problems of the ordering of Al-O and Si-O tetrahedra and the amount of mutual substitution of Al^{3+} and Si^{4+}. Dutz also discussed substitution, co-ordination number, polymorphism and degrees of ordering and quoted the work of Tarte and reproduced his diagrams. In conclusion Dutz indicated that the possibilities of systematic analysis of the different silicate systems by infra-red techniques could yield much useful information, as had been demonstrated by the extensive analysis of the silica polymorphs by this method.

From these and similar studies [82-85] it can be seen that infra-red analysis taken together with other methods can give the mineralogist and crystal chemist much useful data on the structural nature of a wide range of materials. The application of infra-red analysis can be equally useful to the glass technologist. Vargin [86] emphasized that even the general appearance of the infra-red spectra of glasses and the changes that take place in them during progressive devitrification can give indications of nucleation, of changes produced by the heat-treatment, of the amounts of the phases separating out and of the changes in phase composition. He added that although quantitative determination of the phases produced by devitrification is relatively straightforward one of the major difficulties lies in the preparation of standard spectra of the silicate materials for comparison. Native silicates and aluminosilicates contain impurities and their spectra vary quite considerably. Mixtures of different crystalline phases may separate out during the devitrification process and so confuse the analyst, hence standards cannot always be readily and reliably made by this method. There is often the added complication of overlapping bands in the spectra.

Nonetheless, with careful control and with complementary information from other analytical methods such as X-ray diffraction the infra-red method can be a very useful tool, e.g. the characteristic spectra of a series of glass compositions were investigated by Moore and McMillan [87], and Jellyman and Proctor [88] studied the reflection spectra of glasses. In the context of the controlled crystallization of glasses several Soviet authors reported extensive use of the method to study alkali-aluminosilicates, low-alkali and alkali-free aluminosilicate glasses [89-92] and some of the authors mentioned in Part 1 [1] used infra-red spectra to characterize their crystalline products from controlled crystallization.

More recently the papers by Kondratev [93] and Noshiro and Jisugiri [94] illustrated the use of infra-red analysis in glass crystallization studies. The former consisted of an investigation of the formation of metastable phases in the system Li_2O-Al_2O_3-SiO_2 for compositions nucleated by TiO_2 and the latter study determined the percentage crystallinity of lithium metasilicate and lithium disilicate devitrified from stoichiometric glasses, using the potassium bromide disc absorption method. These studies gave a semi-quantitative method of analysing the products which were reliable and relatively rapid. Only very small quantities of the materials under test were required, thus the principles of such analyses are of obvious interest to the glass technologist.

4. Experimental studies

4.1. Differential thermal analysis

Many studies have used DTA to produce thermal analysis curves from which heat-treatment schedules for glass-ceramic production were devised. Thakur and Thiagarajan [41] used a modified DTA method to estimate the nucleating efficiency of small additions of nucleating agent to various glasses. The principle of the method depends essentially upon the fact that the suitability and optimum concentration of nucleant can be determined by consideration of the activation energies involved in the processes of nucleation and crystal growth in glasses. If the changes in activation energy can be measured with varying amounts of nucleant, the efficiency and optimum concentration can thus be determined.

Since the free energy change associated with nucleation in the catalysed crystallization of glass is very small compared with the free energy change accompanying crystal growth there are considerable practical limitations involved in distinguishing these two stages. Also, because of the interaction of the two processes, for the two stages, it is more of a practical proposition to determine and follow the complex activation energy comprising all the activated steps in the process if this occurs as a measurable reaction. From theoretical considerations it can be seen that the surface free energy term for crystallization rates plays a dominant role in the process. Thus, if a glass is prepared, then crushed and sized into coarse and fine fractions and subjected to DTA, it is found that the fine glass produces an exothermic peak at a lower temperature than the coarse glass. If, however, a glass is prepared that contains additives to promote efficient catalysed crystallization, the bulk glass should crystallize simultaneously and the difference between the exothermic peak temperatures of the two size fractions should be very small or even zero for maximum nucleation efficiency. This is the basis of the method adopted by Thakur and Thiagarajan, i.e. the lowering of the exothermic peak temperature in DTA by both the increased surface and volume crystallization of nucleated glasses. If the same amount of sample is analysed for both size fractions, and the size ranges kept constant, then the difference between the exothermic peak temperatures of the two fractions should quantitatively represent the complex activation energy of crystallization. This measure can therefore be employed to determine the efficiency of additives to the glass as nucleating agents.

Thakur and Thiagarajan ran DTA of coarse and fine glass particles, using the coarse material as reference for the fine. Equal weights of the two fractions were used. The samples of -35 mesh $+65$ mesh and -200 mesh for coarse and fine fractions respectively were packed in the DTA cell and run so that the peaks due to crystallization were superimposed. The cell was connected so that exothermic reactions of the fine fraction were recorded as exothermic peaks and the reactions of the coarse fraction were recorded in opposition, i.e. as "endotherms" in the conventional sense. The authors claimed that the net result of running the DTA in this way was the same as though the two samples had been analysed individually against alumina as reference and presented the diagram given as Fig. 1a to illustrate this. Fig. 1b shows a typical result of one of their determinations for a lithium disilicate glass. They went on to determine the effect of additions of nucleating agents upon the value of ΔT (the peak temperature difference) for this glass. In some of the compositions studied the value decreased to a minimum for certain concentrations of the nucleating agents, thus indicating efficient nucleation. This analysis method seemed to offer a rapid and accuate means of investigating the crystallization of cordierite-type glass and was adopted in the

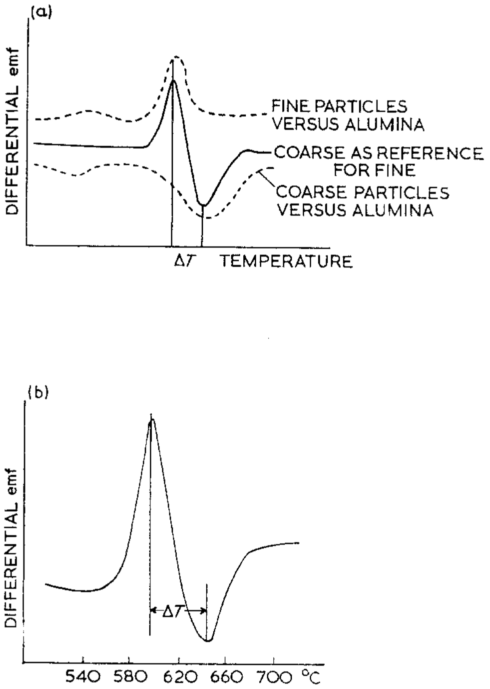
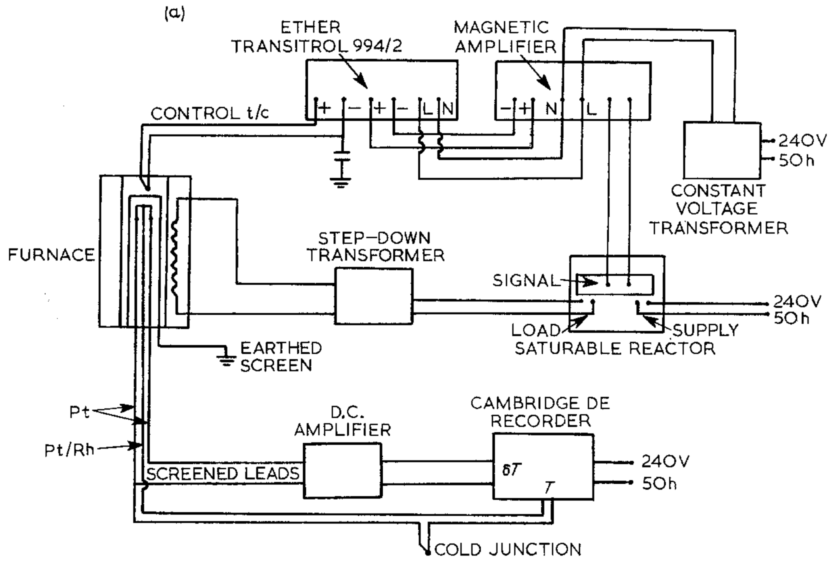


Figure 1 DTA curves from Thakur and Thiagarajan [41]: (a) devitrification of fine glass with coarse glass as reference; (b) data for lithium disilicate glass.



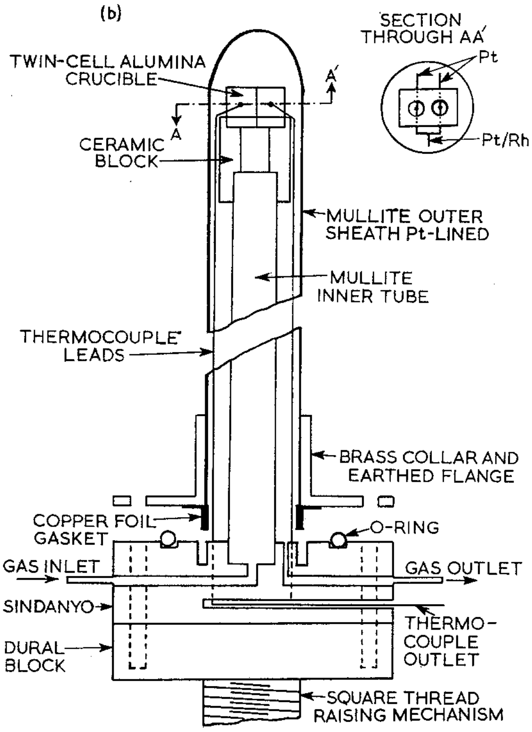


Figure 2 DTA apparatus: (a) circuit diagram; (b) details of furnace arrangement.

present study, although in slightly modified form as will be described in detail later.

A comprehensive programme of testing of the DTA apparatus was undertaken prior to the main investigation. The equipment was essentially the same as described in detail by Reeve [95] and the circuit diagram and sample holder arrangement are shown in Figs. 2a and b. It was found that the "differential temperature" scale could be read with a precision of ± 1.0 μV on the recorder print-out with the maximum amplification setting. The differential scale sensitivity could be reduced by factors of 10, 100 and 1000 by alteration of the range selector and the most sensitive scale, which gave a full-scale deflection equivalent to ± 50 μV on the chart recorder, will be referred to as the "× 1000" scale.

Test runs were conducted on samples of potassium sulphate and Brazilian quartz. With low amplification (× 100, × 10) stable thermograms were obtained but these yielded only limited information due to the small recorded differential signals. For the DTA of potassium

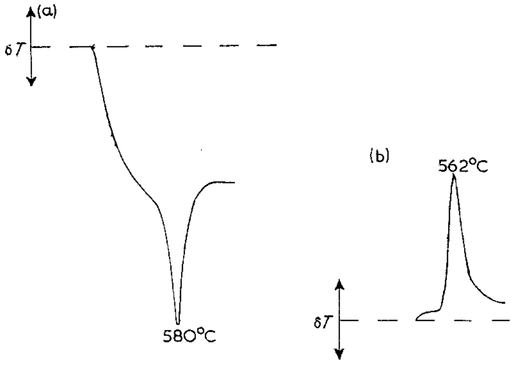


Figure 3 Portions of DTA curves for potassium sulphate.

sulphate, Analar grade material was crushed and sized in the range − 100 mesh B.S. + 200 mesh B.S. and initially a sample weighing 136 mg was intimately mixed (by careful stirring) with 142 mg of dried calcined alumina sized within the same limits. The sample was subjected to DTA at a heating rate of 10°C/minute against calcined alumina as reference.

The thermogram obtained using maximum amplification (× 1000) is given as Fig. 3a and illustrates the large endothermic centred at 580°C corresponding to the inversion of the material. The system was allowed to cool and the thermogram given as Fig. 3b was obtained. The peak corresponding to the inversion of potassium sulphate was easily recognized, although under these conditions was centred at 562°C. The difference in results may have been due to undercooling of the material or to the difference in the heating and cooling rates that were used. The cooling cycle was not controlled, the furnace was allowed to cool at its natural rate which was about 14°C min^{-1} in the region of the peak temperature.

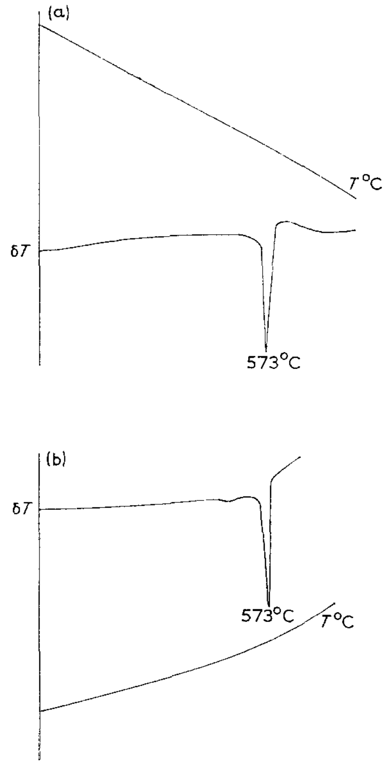


Figure 4 DTA curves for Brazilian quartz: (a) heating; (b) cooling.

Further preliminary tests were carried out using samples of Brazilian quartz. The behaviour of quartz during DTA is well documented in the literature and the rapid $\alpha \rightarrow \beta$ inversion at 573°C can be used to calibrate the system. In this test 304 mg of undiluted Brazilian quartz, sized in the range − 100 mesh B.S. + 200 mesh B.S., were analysed against calcined alumina. A heating rate of 10°C min^{-1} was used together with maximum amplification. The sample and reference materials were tightly packed into the DTA cell using a shaped tamping tool. The system temperature was measured by the thermocouple located in the quartz sample. The thermogram given as Fig. 4a was obtained, showing the sharp endothermic at 573°C due to the $\alpha \rightarrow \beta$ inversion. The base-line drift was considered acceptable for an undiluted sample.

The sample was then subjected to the same procedure adopted for the potassium sulphate sample, i.e. allowed to cool to room temperature and monitored under similar conditions. The thermogram showing both the reheating and cooling cycles is given as Fig. 4b, and in this case the temperatures of the effects were found to be repeated in the heating and the cooling modes. The base-lines were stable and the tests were taken to confirm the reproducibility of results using this apparatus.

Centring of the sample holder in the hot zone of the furnace is also an important consideration for the production of consistent results in DTA. In the apparatus the work tube was rigidly located in position in the vertical tube furnace by means of three screws at the base of the assembly. Accurate repositioning of the sample cell and support in the vertical plane was achieved by fixing a retaining collar on the movable stem of the screw-jack assembly incorporated in the system. Once the furnace had been set in its centred position it was unnnecessary to readjust it and the whole assembly could be accurately and reproducibly positioned.

To test the centring of the apparatus the following procedure was adopted. Both sides of the DTA cell were packed with − 100 mesh B.S. + 200 mesh B.S. Brazilian quartz. The sample weights were approximately equal, i.e. "sample" weight 306 mg, "reference" weight 308 mg. The analysis was run at 10°C min^{-1} at maximum sensitivity, and the system temperature was monitored in the "sample" side of the cell. The thermogram given as Fig. 5 was obtained.

In a perfectly balanced and symmetrical

system the two thermal effects, due to the simultaneous inversion of the two samples of material, would be expected to interfere destructively. The resultant thermogram would therefore be expected to show only an uninterrupted straight line.

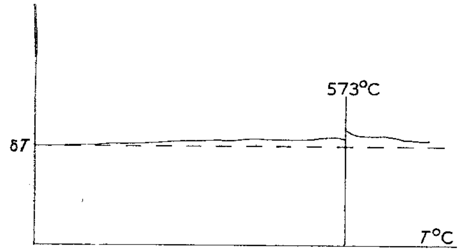


Figure 5 DTA curve from centring test.

The base-line obtained was fairly steady and the differential trace only showed a small discontinuity in the region of the inversion temperature. The test was therefore considered to have demonstrated that the cell was satisfactorily centred and that there was no drastic imbalance in the system.

The shape and position of curves obtained by DTA are also dependent upon the source of the reference temperature. The differential temperature may be plotted against the system temperature measured at one of several possible locations (a) at the centre of the reference sample, (b) at the surface of the sample material or (c) at the centre of the sample material. From consideration of these variables most authors have reported that accurate and reproducible results are best obtained by measurement of the system temperature at the centre of the reacting sample. The following test was therefore carried out to check the effect of system temperature measurement in the sample and reference materials and correlation of the results with the true inversion temperature.

Two analyses were performed on the same sample of Brazilian quartz. The sample of 304 mg of − 100 mesh B.S. + 200 mesh B.S. quartz was carefully packed into the cell with 236 mg of calcined alumina (− 100 mesh B.S. + 200 mesh B.S.) as reference. The temperature measuring thermocouple was first connected across the sample side of the cell. A Rikadenki X-Y potentiometric recorder was substituted for the Cambridge DE chart recorder for these determinations so that direct comparison of the results could be made. Using maximum sensitivity the thermogram given as Fig. 6a was obtained. The system was then allowed to cool to room temperature and the circuit was modified so that the temperature measuring thermocouple was connected across the reference side of the cell. The analysis was then repeated under the same conditions and the thermogram given as Fig. 6b was obtained.

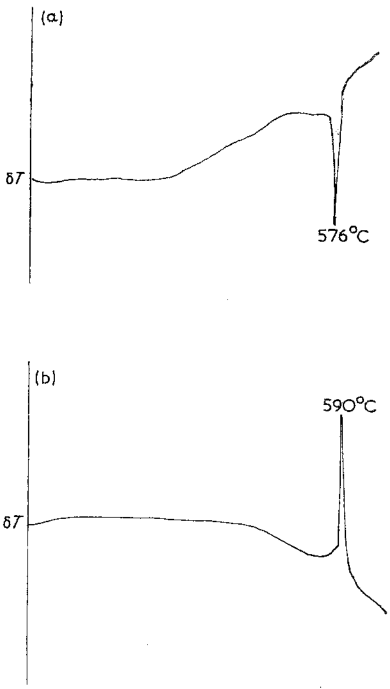


Figure 6 DTA of Brazilian quartz: (a) temperature measured in reacting sample; (b) temperature measured in reference.

These two thermograms indicate that the effect of thermocouple location is very marked. Under the conditions of the first run the characteristic endotherm was centred at 576 ± 2° C. Both thermograms showed considerable base-line drift prior to the inversion, but this appeared to be consistent between the two determinations. In the second thermogram i.e. thermocouple to reference side of the cell, the effect was centred at 590 ± 2° C. Location of the exact position of the first deviation of the curve from the base-line under the conditions of the second part of the test was difficult due to the base-line drift, although extrapolation of this distorted base-line did indicate that the deviation occurred at a temperature below the true inversion temperature. These observations were in agreement with other workers results concerning thermocouple location [6] and from the tests it was decided that system temperature would be monitored in the sample side of the cell.

The tests indicated that the DTA apparatus could be used to produce accurate and reliable results. The importance of instrument and sample variables had been demonstrated and further discussion of these in respect to the devitrification characteristics of the glasses will be made in a later publication.

4.2. Infra-red analysis

The applicability and usefulness of infra-red techniques for silicate and glass analysis has already been indicated and this section is concerned with the method and results of preliminary tests obtained in the present study for the evaluation of reflectance methods.

Initial studies were made to determine the applicability of Attenuated Total Reflectance (ATR) to the problem of devitrification studies. The method was compared with the more conventional techniques such as mulling and pressing in potassium bromide discs which were briefly described earlier. The results of this investigation were quite encouraging, and led to further comparative studies of the Multiple Attenuated Total Reflectance (MATR) method. The latter was shown to be superior to the ATR method and was the one adopted for the study.

The feasibility studies were conducted on mineral specimens which have all been well documented in the research literature and whose infra-red characteristics are well established by the conventional analytical techniques.

A Perkin-Elmer 457 Grating Infrared Spectrophotometer was used in the study and the auxiliary equipment was supplied by Beckman-RIIC, parts coded micro-ATR unit TR-5 and Multiple ATR unit TR-25. Both of these were fitted with thallium bromide-iodide (KRS-5) prisms. Sample preparation for both these units was very simple. Powder samples, all − 350 mesh B.S., were produced by dry grinding in a Tema disc mill fitted with tungsten carbide grinding barrels. For the single reflectance unit the powder was mounted in the sample well and optical contact with the prism was achieved by tightening a stainless steel backplate with a grub screw. A reference beam attenuator was used to compensate for the loss of energy through the system. Using this method there was a slight imbalance due to the different path lengths of the sample and reference beams which resulted in "noise" at frequencies which were characteristic for atmospheric carbon dioxide, roughly in the region 1900 to 1400 cm^{-1}. Compensation for this effect could have been achieved by duplication of the mirror focusing system and a prism without sample in the reference beam of the instrument. However, the effect was small and as the useful range for silicate analysis lies beyond this, 1400 to 250 cm^{-1}, no such measures were considered necessary.

The MATR unit was similar, except that the prism was larger and the sample was mounted against both sides of the prism. Powdered sample, similarly produced by milling, was dispersed on to the sample holder from a micro-screen of the "pepperpot" type. This was constructed by tensioning 350 mesh nylon screen cloth across the neck of a small glass vial. The cloth was held in place by a small rubber band. A continuous and coherent layer of the powder was applied and the unit clamped up with four stainless steel screws. Excess powder was gently brushed from the ends of the prism, and the unit placed on locating pins fitted to the base plate. The holder was only clamped finger tight to minimize the damage to the polished prism faces.

A series of spectra of minerals that have been quite extensively studied by other infra-red methods was first obtained to determine the accuracy and reproducibilty of the ATR method. In some cases the spectra were also compared with data obtained using the potassium bromide disc method. The results of these preliminary tests are as follows:

(i) Quartz: The infra-red spectrum of quartz is probably the most widely documented of the silicates and has been the subject of many investigations. Its importance arises as a result of the frequency with which the mineral occurs as an important constituent of silicate rocks. The distinctive spectrum allows quantitative determination of the mineral to be made, working from the characteristic adsorptions. The spectrum given by Lyon [69], which has been reproduced by many authors, as reference, is given in Fig. 7a together with the spectra obtained for Brazilian quartz using the ATR and MATR techniques. For these latter determinations milled quartz samples were used. For ATR a small sample was placed in the sample well of the unit and the back plate clamped to give uniform contact across the polished prism face. Determinations were made using the slow scan mode of the spectrophotometer between 1200 and 250 cm^{-1}. The incident angle was varied, determinations being made at 25, 30, 45 and 60° in the initial trials. The least distorted and best defined spectrum was obtained at an angle of 30°.

For the MATR determination the sample was dispersed on the holder to ensure good contact with both sides of the prism and the slow scan mode was employed to obtain the spectrum at a fixed angle of 30°.

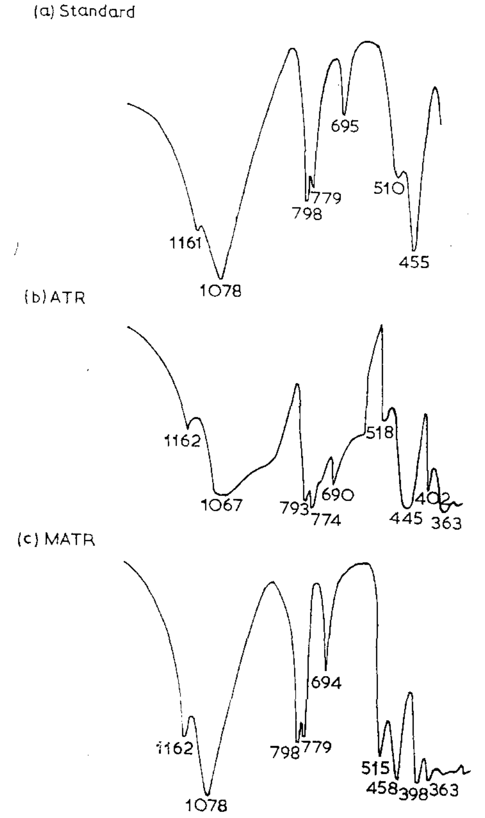


Figure 7 Infra-red spectra of quartz.

The results of these determinations are shown in Figs. 7b and c. Comparison with the data of Lyon [69] shows that although the ATR method gave adsorption bands which could be used to characterize quartz, these tended to be distorted on the low frequency side. The relative intensities of the bands were not consistent with the standard data and in particular the diagnostic doublet in the region 798 to 779 cm^{-1} exhibited a reversal of relative intensities. The vertical displacement at 600 cm^{-1} was due to a grating change and could have been eliminated by readjustment of the reference beam attenuator at this point in the scan.

The MATR spectrum was in most respects identical with the standard, and this indicated that direct comparison of spectra obtained by this method with conventional absorption data was valid. The multiple reflection technique had eliminated the distortion, and at the higher frequencies, 1200 to 600 cm^{-1}, correspondence was within the manufacturers' limits of accuracy for the instrument ($\pm$ 2 cm^{-1}). The spectrum was not so well defined below 600 cm^{-1}, and this may have been due to the loss in energy associated with the grating change. The spectrum was extended in the present study and the appearance of weak bands at 398 and 363 cm^{-1} were noted.

(ii) Cristobalite: Very similar results were noted for samples of cristobalite. The spectra are given in Fig. 8. The standard reference spectrum in this case was taken from Lippincott *et al* [96]. The ATR spectrum was very weak and highly distorted, but the MATR spectrum exhibited excellent agreement with the standard.

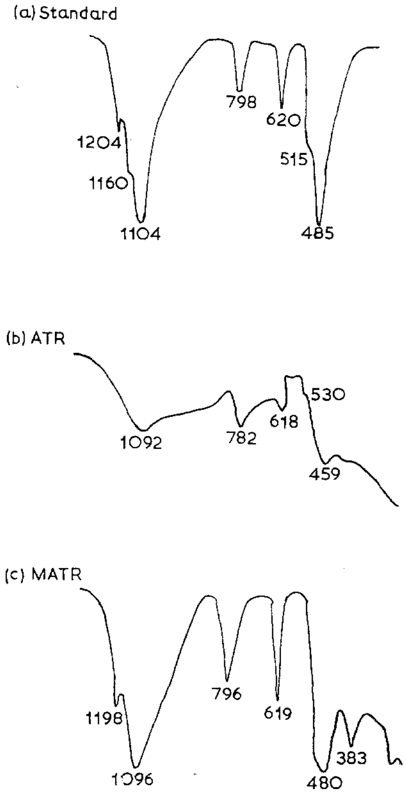


Figure 8 Infra-red spectra of cristobalite.

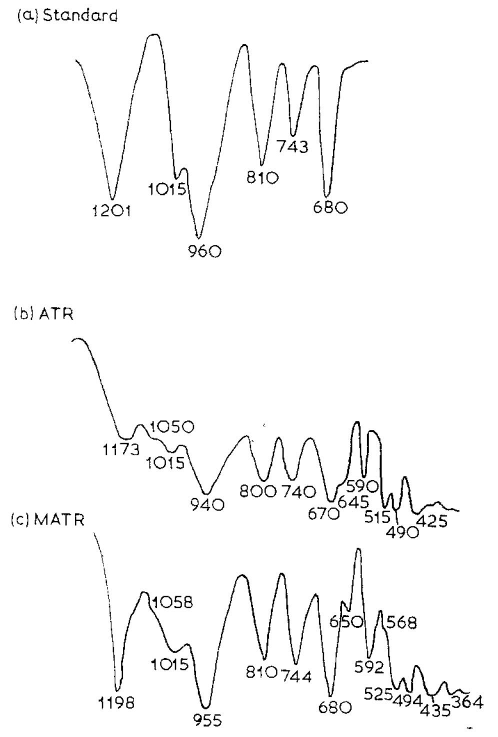


Figure 9 Infra-red spectra of beryl.

(iii) Beryl: Samples of beryl were also investigated because this mineral has a similar structure to cordierite, both being cyclosilicates. Beryl spectra have been well documented in the literature, and the results of the present studies are given in Fig. 9. In common with the previous observations, the ATR spectrum was relatively weak and distorted – particularly on the short frequency sides of the bands. The MATR spectrum again showed good agreement with the data of Lyon [69].

Minerals such as beryl contain impurities which may affect the form of the spectrum to some extent and variation would be expected in the fine details of some of the bands. It was therefore considered necessary to prepare and determine the spectrum of the sample of beryl in this investigation using the KBr disc method. Spectrophotometric grade potassium bromide (100 mg) was vibromilled with approximately 2 mg of the beryl powder in an agate mill for 15 min. The mixture was pressed in a Wilks Scientific "Mini-press" unit to produce a clear homogeneous disc. This was mounted in the Perkin-Elmer 457 and the infra-red spectrum determined. A detailed comparison of the spectrum obtained by this method and the MATR spectrum is given in Fig. 10. The close agreement of the two is obvious, and although the MATR spectrum lacks the fine resolution in the range beyond 600 cm^{-1}, the low-frequency absorption bands are still easily distinguished.

(iv) Devitrified Glass: As a final test, spectra were obtained of a glass from the MgO-Al_2O_3-SiO_2 system that had been heat-treated for 5 days at 1100°C. The crystalline product after this treatment was identified as cordierite by X-ray diffraction. The ATR and MATR spectra are given as Figs. 11 and 12. The standard spectrum from Lyon [69] is also given for reference (Fig. 13) and a specimen absorption spectrum is

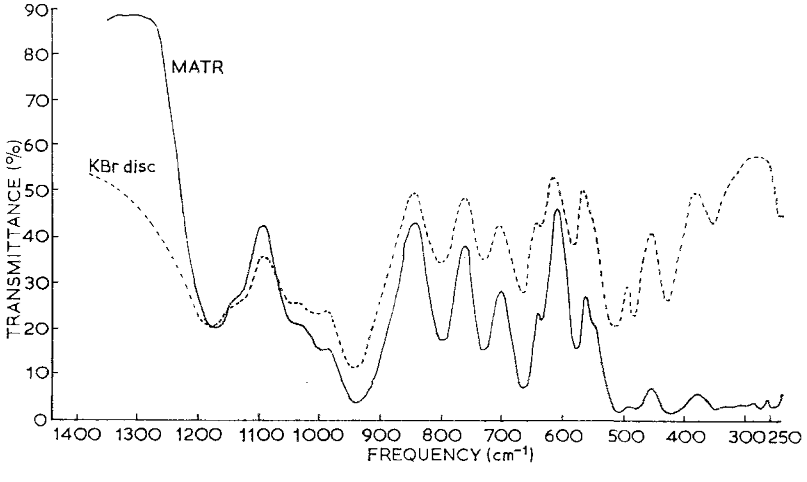


Figure 10 Comparison of infra-red spectra of beryl.

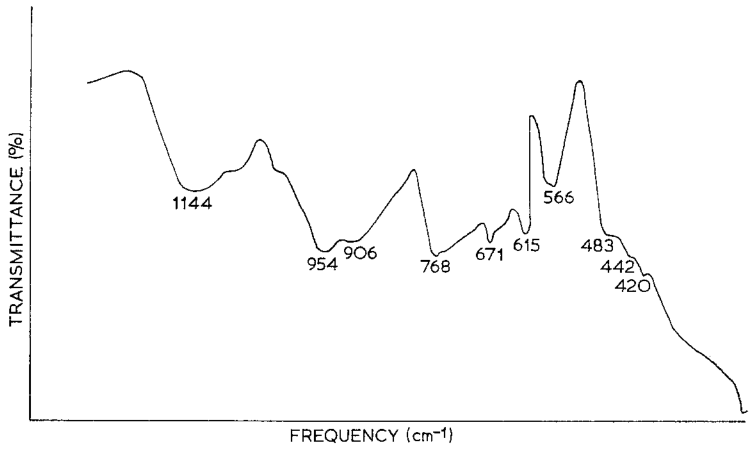


Figure 11 ATR spectrum of devitrified glass.

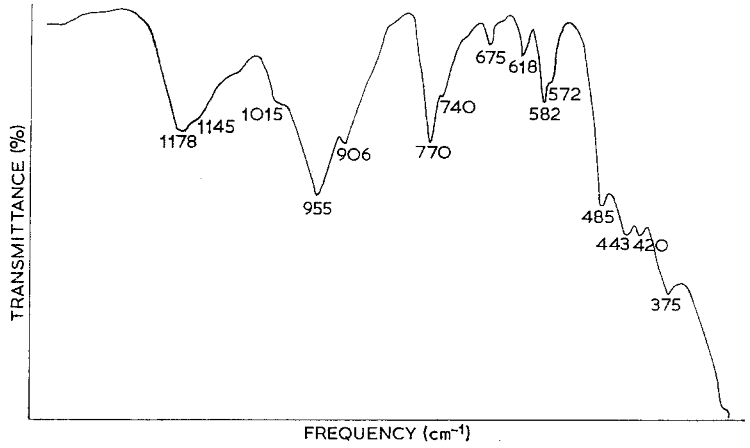


Figure 12 MATR spectrum of devitrified glass.

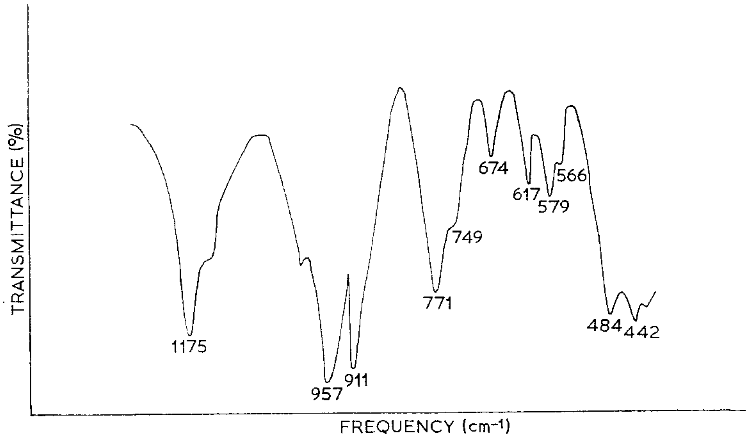


Figure 13 Infra-red spectrum of cordierite, after Lyon [69].

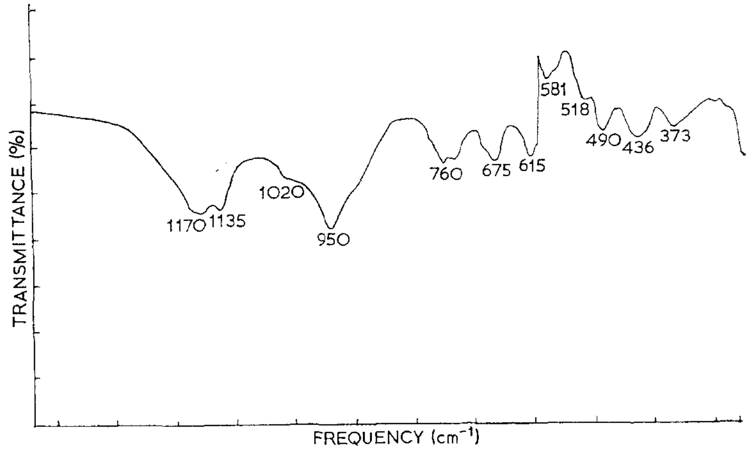


Figure 14 Infra-red spectrum of devitrified glass by KBr disc method.

illustrated which was obtained by the pressed disc method, Fig. 14.

The good agreement between the spectra is apparent. The standard spectrum did not have some of the frequencies marked for subsidiary bands, and these could not be estimated with any accuracy from the original publication. However, comparison of this data with the MATR spectrum shows a marked similarity in the general position and size of the bands.

5. Conclusions

The conclusions drawn from these feasibility tests were that the ATR method could be used to monitor devitrification and to identify the products, although the method was found to be relatively insensitive and liable to produce distorted spectra. The MATR method was shown to be as accurate and reproducible as the pressed disc method and had several advantages over the latter. The most obvious advantage was the ease of sample preparation, which merely involved grinding of the sample. There were no problems of mixing or dispersing of the sample in a supporting medium as can be experienced with the pressed disc method. There were also no handling problems, potassium bromide discs being very moisture sensitive and liable to become opaque if exposed to atmospheric moisture. The spectra obtained by the MATR method can be compared directly with existing data, making it unnecessary to compile a new set of standards for the technique.

The combination of DTA and MATR was therefore used to study the effect of nucleating agents on the crystallization of a cordierite glass. A thorough study was made of the characteristics of the base glass using these techniques and the experimental results will be reported and discussed in the final part of this series.

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