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The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic

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The transition from a glass to a glass-ceramic is usually accompanied by marked changes in physical properties. For some materials, this process may be studied by measurement of properties as crystallisation proceeds and can be related to the changing mineralogical structure of the glass-ceramic. Starting with a modified lithium-zinc-silicate glass, the uses of viscosity, differential thermal analysis, and electrical resistivity as means of detecting the onset of crystallisation are discussed. Changes in elastic modulus, mechanical strength, and thermal expansion coefficient illustrate the effect on these properties of crystallisation of different crystal types. The structures and composition of the material with increasing crystallinity are shown by electron microscopy and X-ray diffraction.

1. Introduction

Many important materials are composed of more than one crystalline, amorphous or vitreous phase. The properties of such polyphase materials and the relationship between the constitution and properties of the materials are of great interest. Most ceramics are polyphase materials, since they often contain one or more crystal phases together with a vitreous phase.

Glass-ceramics, which are made by the controlled crystallisation of special glasses, constitute a particularly valuable medium for investigating the relationship between properties and crystal content of ceramics. This arises because, by proper regulation of the crystallisation heat-treatment cycle, it is possible to produce, from a single composition, materials varying in constitution from the amorphous glass at one extreme to an almost completely crystalline ceramic at the other. Between these extremes, materials having intermediate glass and crystal contents can be produced.

To achieve controlled crystallisation of a glass, it is usually necessary to include in the composition a substance which will promote a high nucleation rate, to ensure that crystallisation takes place at many points distributed throughout the bulk of the glass. Some of these "nucleating agents" are metals, which can be obtained in the form of colloidal dispersions, and these serve to heterogeneously nucleate crystallisation. Other nucleating agents promote two-phase glass-in-glass separation as a precursor to crystallisation. One of the phases takes the form of very small droplets distributed throughout the other phase. This type of emulsion structure appears in many cases to favour the development of a fine grained structure when the glass is subsequently crystallised. The present paper is concerned with the behaviour of a glass-ceramic composition which contains phosphorus pentoxide as a nucleating agent, and the beneficial effect of this constituent arises at least partly from its influence upon glass-in-glass phase separation.

The crystal content of a glass-ceramic is determined by the time-temperature cycle employed to achieve crystallisation. The crystallisation process can be arrested at any stage by cooling the material, since the rapid increase of viscosity, which occurs as the temperature falls, effectively terminates both nucleation and growth processes. The proportion and nature of the crystals present in the material after cooling can therefore be regulated by varying the maximum temperature to which the material is heat treated or by varying the duration of heat treatment at a given temperature. It was considered of interest to investigate the effect of such variations upon the constitution and properties of a glass-ceramic having the molecular percentage composition: SiO_2, 72.5; Li_2O, 22.3; K_2O, 1.5; ZnO, 3.0; P_2O_5, 0.7. This material was chosen because preliminary work had shown that as a glass it could easily be melted and shaped into suitable test specimens. Also, glass-ceramics could be produced from this glass using a wide variety of heat-treatment cycles.

2. Preparation and Heat Treatment of the Glass

The glass was prepared from pure raw materials in a platinum crucible at a melting temperature of 1400° C. Rod specimens were prepared by drawing from the molten glass, and disc specimens by casting.

Crystallisation heat treatments were carried out in small electrically-heated muffle furnaces provided with automatic temperature controllers. The heat-treatment temperatures were in the range 500 to 850° C; further details of the actual heat-treatment cycles are given in later sections in which particular properties are discussed.

3. Constitution of the Glass-Ceramics

In investigating the structure of a glass-ceramic, it is useful not only to study the final material but also to examine changes occurring during the actual crystallisation process. X-ray diffraction analysis is used to determine the nature of the crystalline phases present in the final material and in quenched specimens removed at intervals during the heat-treatment process. Because of the very small sizes of the crystals usually developed, electron microscopy is used to investigate the morphology of the materials. X-ray diffraction analysis and electron microscopy are not readily applicable during the actual heat-treatment process, however, and less direct methods of establishing structural changes have to be employed.

One such method is Differential Thermal Analysis (DTA), in which the heat of crystallisation of the various compounds formed is detected. Another method involves the measurement of viscosity of the glass during crystallisation. The viscosity of the glass normally decreases exponentially with increase of temperature, but an increase can occur when crystallisation takes place. A third method is based on the observation that, for glasses containing mobile ions such as Li^+, marked changes occur in the electrical resistivity during the crystallisation process.

3.1. Experimental

3.1.1. Electron Microscopy and X-ray Diffraction

The specimens were prepared by polishing small cube samples of the glass-ceramics, using conventional metallographic techniques, to a final 1 μm diamond finish. The specimens were then etched for 10 sec in a 2% hydrofluoric acid solution and direct platinum carbon replicas were prepared, self-shadowed at an angle of 2:1. The replicas were examined using a Siemens Elmiskop I electron microscope. X-ray diffraction data were obtained using the powder method.

Fig. 1 shows the structure of the glass after heat treatment at 500° C for 1 h. It will be seen that, although a distinct two-phase structure is present, there is no evidence of crystalline regularity in the structure. No X-ray diffraction pattern could be obtained from this material, and it is therefore believed that the two-phase structure arises as a result of glass-in-glass phase separation. Since the globules, which have a mean diameter of 500 Å, were etched less readily by the hydrofluoric acid than the matrix, it is thought that they are silica-rich as compared with the matrix.

Heat treatment at 500° C for 1 h followed by 600° C for 1 h gives rise to the structure shown in fig. 2. Acicular crystals are present interspersed with large relatively structureless areas. X-ray diffraction analysis showed that the only crystal phase present was lithium disilicate, and the crystals revealed by the electron microscope were therefore of this compound. It will be noted–the globular particles are still present and the number of these appears to have increased. An interesting feature is that the lithium disilicate crystals enclose large numbers of the globules.

After heat treatment at 500° C for 1 h followed by 700° C for 1 h, the needle-like crystals are very well developed (fig. 3), and these again contain many globular particles. X-ray diffraction showed that lithium disilicate was the major phase present but that a moderate amount of quartz was also present. In the electron micrograph however, it is difficult to distinguish features which might correspond with the quartz crystals.

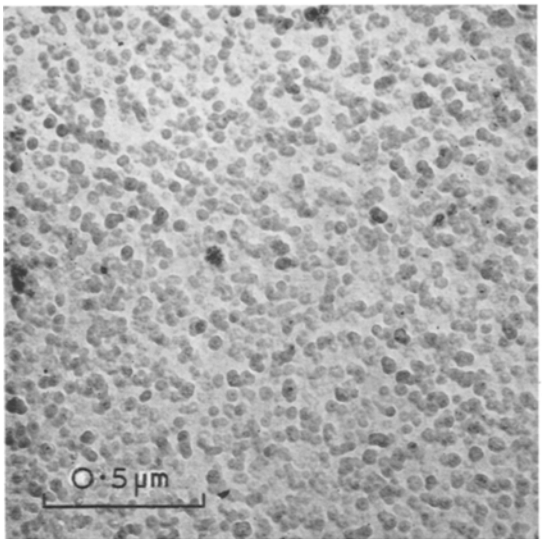

Figure 1 Structure of glass-ceramic after heat treatment of 500° C for 1 h.

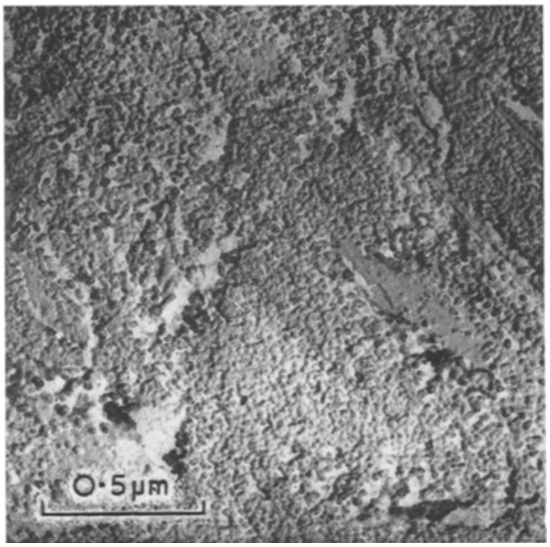

Figure 2 Structure of glass-ceramic after heat treatment of 500° C for 1 h, 600° C for 1 h.

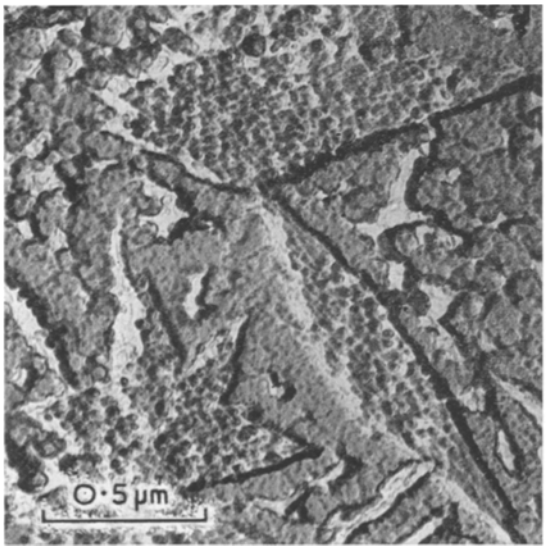

Figure 3 Structure of glass-ceramic after heat treatment of 500° C for 1 h, 700° C for 1 h.

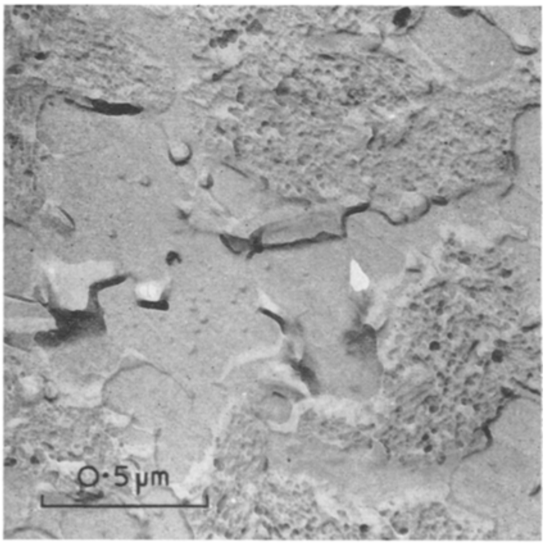

Figure 4 Structure of glass-ceramic after heat treatment of 500° C for 1 h, 800° C for 1 h.

Fig. 4 shows the appearance of the glass-ceramic after heat treatment at 500° C for 1 h followed by 800° C for 1 h. In addition to the lithium disilicate crystals, other irregularly shaped and relatively featureless structures are present. It is likely that these are quartz crystals, since X-ray diffraction showed that this phase was present in a fairly high proportion as well as lithium disilicate. From the electron micrograph, it appears that the two crystal phases were present in roughly equal proportions and that only a small proportion of residual glass phase was present.

Additional X-ray diffraction data obtained for specimens subjected to other maximum heat-treatment temperatures confirmed and extended the foregoing results. The general conclusions are that, at heat-treatment temperatures below 600° C, the extent of crystallisation is very small. For example, specimens heat treated at 550° C show only a very weak diffraction pattern which cannot be positively identified. Heat treatment at temperatures of 600° C and upwards leads to the formation of lithium disilicate. Quartz appears in significant amounts after heat treatment of the glass-ceramic at 700° C although a small trace is possibly formed during heat treatment at 650° C.

3.1.2. Differential Thermal Analysis

A powdered sample of the glass was used, together with powdered alumina as the inert reference material. The platinum cups containing the powdered materials were heated at 5° C/min and the furnace temperature and the differential emf were recorded.

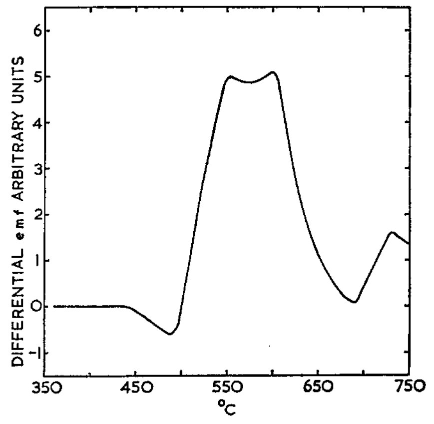

Figure 5 Differential thermal analysis of the glass during crystallisation.

A DTA record for the glass during heating from 350 to 750° C is given in fig. 5. The direction of the differential thermo-emf was such that exothermic effects are recorded as peaks, and endothermic reactions as dips. A shallow dip occurs over the temperature range 450 to 490° C and this is associated with annealing of the uncrystallised glass. A marked exothermic peak is observed which appears to be made up of two peaks, one centred at 550° C and the other at 600° C. A smaller but significant exothermic peak is observed at 730° C. It seems likely that this peak is due to the crystallisation of quartz, and that at 600° C to the crystallisation of lithium disilicate. Discussion of the reason for the exothermic effect at 550° C will be deferred until the results of viscosity and electrical resistivity measurements have been described.

3.1.3. Viscosity Measurements

The fibre extension method was used for the measurement of viscosity. For this, thin rods (1.0 mm diameter and 10 cm long) were prepared by drawing from the molten glass. The specimen was suspended in a vertical tube furnace having a uniform central temperature zone 10 cm long. The lower end of the glass rod was loaded and the extension was measured by an optical lever. The upper limit of viscosity measurable with this apparatus is about $10^{12.5}$ poise and this corresponded with a temperature of 440° C for the glass being studied.

In one experiment, measurements of viscosity were made at temperatures in the range 440 to 600° C, with the temperature increasing at 1° C/min. In a second experiment, the temperature was increased from 440 to 500° C, held constant at the latter for 1 h, and then increased at 1° C/min to 600° C. The $\log_{10}$ viscosity versus reciprocal absolute temperature curves are given in fig. 6.

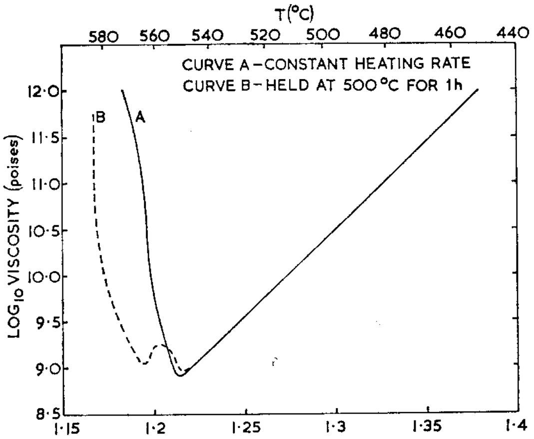

Figure 6 Change of $\log_{10}$ viscosity with reciprocal absolute temperature during crystallisation of the glass.

In the first experiment (curve A), the viscosity-temperature characteristics initially follow the behaviour normally expected for a glass, and a straight line relationship is observed. A sudden increase of viscosity occurs at 500° C, however, and this is thought to be due to the onset of crystallisation. Above this temperature, the viscosity continues to increase owing to the rapid formation of an interpenetrating crystal network. When a holding stage at 500° C is introduced (curve B), two minima appear in the curve: one at 550° C and one at 565° C.

In order to investigate more closely the behaviour of the glass in the temperature region in which minimum viscosities were observed, the effects of time on viscosity of specimens held at 520, 540, 560, and 575° C were studied. During heating to these temperatures, the glass specimens were subjected to a holding stage of 500° C for 1 h. Fig. 7 gives the $\log_{10}$ viscosity versus time curves. It will be noted that marked changes of viscosity occur under isothermal conditions for specimens heated at temperatures of 540° C and upwards.

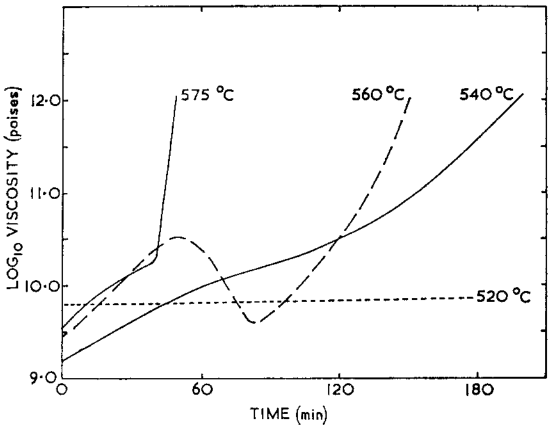

Figure 7 Change of $\log_{10}$ viscosity with time at temperatures in the crystallisation range.

3.1.4. *Electrical Resistivity*

The measurements were made in the temperature range 300 to 800° C, using 2.5 cm diameter discs having parallel ground faces and an alternating current bridge. In a first experiment, the temperature was increased continuously at 2° C/min, and, in a second experiment, a holding stage of 1 h at 500° C was introduced.

With a continuous increase of temperature (curve A, fig. 8), the resistivity-temperature behaviour was that of a normal glass until a temperature of 585° C was attained. At this point, a marked increase of electrical resistivity occurred. When a holding stage at 500° C was introduced (curve B), two minima were observed in the curve at 525 and 590° C.

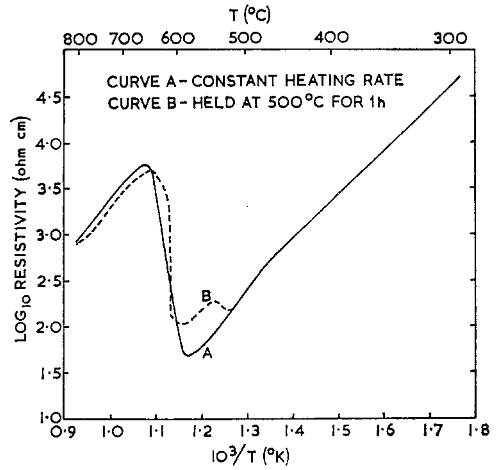

Figure 8 Log_{10} resistivity versus reciprocal absolute temperature.

The increases of resistivity which occur during heating of the glass are undoubtedly due to crystallisation. The charge carriers in the glass under investigation are mainly lithium ions, with a small contribution from potassium ions. The lithium ions have a high mobility in the glass phase, but the incorporation of the ions in the lattice of a lithium silicate crystal considerably lowers their mobility and of course reduces the number remaining in the glass phase.

An interesting point with regard to the electrical resistivity results is that they closely parallel the effects observed with the viscosity measurements, in that continuous heating gives rise to one minimum in the resistivity-temperature curve and the use of a holding stage at 500° C gives rise to two minima.

3.2. Discussion of Results

From the DTA, viscosity, and electrical resistivity results, it appears that structural changes associated with crystallisation take place in the glass at temperatures below 600° C. This may appear surprising, because X-ray diffraction analysis did not reveal any significant degree of crystallisation for specimens heat treated at temperatures less than 600° C. A possible explanation is that, for the lower heat-treatment temperatures, the crystals formed are very small (less than 100 Å in size) and do not yield a sharp X-ray diffraction pattern. One might expect such crystals in bulk specimens to be visible under the electron microscope at high magnifications, but so far no real evidence of this nature has emerged. It appears both from the present work and from parallel investigations that measurement of certain physical properties, in particular of electrical resistivity, may be a more sensitive way of detecting the onset of crystallisation than X-ray diffraction analysis.

The presence of two exothermic peaks in the DTA curves in the temperature range 550 to 600° C suggests that two crystalline compounds are formed. The peak at 600° C can fairly certainly be ascribed to the formation of lithium disilicate, in view of the X-ray diffraction data. The peak at 550° C cannot be attributed with certainty to any particular crystal, since specimens heat treated to this temperature do not give a sharp X-ray pattern. It is believed, however, that this peak may be associated with the formation of lithium metasilicate, since this compound can be formed in glass-ceramics of generally similar composition to that investigated in the present study. For example, in a binary $Li_2O.SiO_2$ glass, lithium metasilicate ($Li_2O.SiO_2$) was observed to form when a thin film of the glass was heated in the electron microscope [1]. Identification was by electron diffraction analysis. On further heating, the $Li_2O.SiO_2$ appeared to redissolve in the glass. Although the large surface-to-volume ratio of thin glass films may influence crystallisation, this observation suggests that $Li_2O.SiO_2$ may also be formed in small amounts in the present glass. The reasons for the failure to detect this phase by X-ray diffraction may be that the volume of lithium metasilicate developed is small, and also that the crystals have small dimensions. The failure to develop detectable amounts of the lithium metasilicate could also arise if this crystal acts as a "transient" phase, i.e. if the effects of further heat treatment are to convert lithium metasilicate into another phase. In fact, the conversion of lithium metasilicate to lithium disilicate is known to occur and has been reported by Stookey [2] for glass-ceramics having compositions fairly similar to that of the present investigation. If the transient formation of lithium metasilicate is accepted, it is possible to interpret the results of the electrical resistivity and viscosity measurements in a meaningful way.

During continuous heating, a marked increase of resistivity occurs at 585° C, and this is attributed to the formation of lithium disilicate. The introduction of a holding stage at 500° C leads to a first increase of resistivity at 525° C, and this would be ascribed to the formation of lithium metasilicate; further increase of the temperature leads to a fall of resistivity, and this might be partly due to the normal tendency of the resistivity to decrease as the temperature is raised. Possibly, an important contribution to the lowering of resistivity would result from the conversion of lithium metasilicate to the disilicate, however. In a reaction of the type:

$$2\ Li_2O.SiO_2 \rightarrow Li_2O.2\ SiO_2 + Li_2O$$

lithia would be released from the crystalline phase, and the number of lithium ions in the glass phase would therefore increase, leading to an overall decrease in electrical resistivity. Further increase of temperature leads to the production of increased amounts of lithium disilicate by direct crystallisation from the glass, and it is probable that the lithium disilicate crystals formed by breakdown of the metasilicate serve to catalyse this process. The growth of lithium disilicate crystals then accounts for the increase in resistivity occurring at temperatures above 590° C.

An implication of the electrical resistivity studies is that the formation of a significant amount of lithium metasilicate requires a holding stage in the region of 500° C. From the DTA results, it appears that the metasilicate is formed as a transient phase even though no holding stage at 500° C is used during the DTA run. For this test, however, the specimen is in the form of a very fine powder. The very large surface area and consequently the large numbers of possible surface defects (microcracks) may catalyse the nucleation of the metasilicate crystals. This possibility is consistent with the knowledge that reduction to a fine powder has a catalysing effect on nucleation and growth processes.

The viscosity results show a generally similar behaviour to that observed in the resistivity measurements. With continuous heating, a single minimum is observed in the viscosity curve at about 550° C. This is attributed to the formation of lithium disilicate, although the temperature of the minimum is lower than that normally associated with the crystallisation of the disilicate (c. 600° C)

The introduction of the 500° C holding stage leads to a first minimum in the viscosity curve at 550° C, and it is proposed that this is due to the growth of lithium metasilicate crystals, these having been nucleated at 500° C. Increase of the temperature above 558° C leads to a reduction of viscosity, and it is suggested that in the temperature range 558 to 565° C (the temperature of the second minimum) lithium metasilicate is being converted into the disilicate. The lithia released during this reaction will enter the glass phase and will lead to a reduction of viscosity. At temperatures of 565° C and upwards, formation of lithium disilicate by direct crystallisation from the glass phase would account for the increased viscosity.

The viscosity measurements carried out under isothermal conditions (fig. 7) are useful in confirming and extending the foregoing deductions. Holding at 520° C leads to virtually no change of viscosity after 180 min, or even after much longer times, and it can be concluded that crystallisation does not occur to a significant extent. At 540° C, which is close to the temperature of the first minimum in the viscosity-temperature curve, the viscosity increases continually during the time of measurement. This increase can be attributed at least partly to the formation of lithium metasilicate crystals, since nucleation of this phase would occur during the holding stage at 500° C to which the fibres were subjected. The results for the fibre held at 560° C, a temperature approximately midway between the two minima in the viscosity-temperature curve, are particularly interesting. The initial increase of viscosity is likely to be due to the growth of lithium metasilicate crystals. At this temperature, however, the conversion of the metasilicate to the disilicate will also occur, and the release of lithia into the glass phase as a result of this reaction will lead to reduced viscosity of the glass phase. Eventually, this effect will predominate, giving rise to the reduction of overall viscosity from about 50 min after the start of the holding period. The lithium disilicate crystals produced in this reaction would catalyse the growth of further lithium disilicate, and the rapid increase of viscosity which begins about 100 min after the start of the holding period is attributed to this. Similar but less marked processes may occur at 540° C, since comparison of the viscosity-time curve for this temperature with that for 560° C shows that the inflection in the former curve corresponds roughly with the minimum in the latter curve. One would not expect exact correspondence, since the rates of the various reactions will obviously be temperature-dependent. At 575° C, the initial rate of viscosity increase is replaced by a much higher rate, after about 40 min from commencement of the holding period. In the initial region, it seems likely that formation of lithium metasilicate occurs and this tends to increase the viscosity. At this temperature, however, conversion of the metasilicate to disilicate with consequent reduction of the viscosity of the glass phase will be quite rapid. The actual slope of the viscosity-time curve will be determined by the combined effects of these two processes. Eventually, the nucleation of lithium disilicate by the crystals derived from the metasilicate/disilicate transformation will predominate, and a higher rate of viscosity increase would occur. This condition is apparently achieved about 40 min after the commencement of the holding period.

Fig. 9 summarises the various rate processes which are believed to occur during heat treatment of the glass in the range 450 to 600° C. This figure is schematic, of course, but enables the various nucleation and crystallisation phenomena to be interrelated. At temperatures above 600° C, growth of lithium disilicate continues and, at temperatures in the region of 700° C, crystallisation of silica (quartz) occurs, as evidenced by the DTA results and by X-ray diffraction data. Little is known about the nucleation of this crystal in the present glass and further work on this aspect is needed.

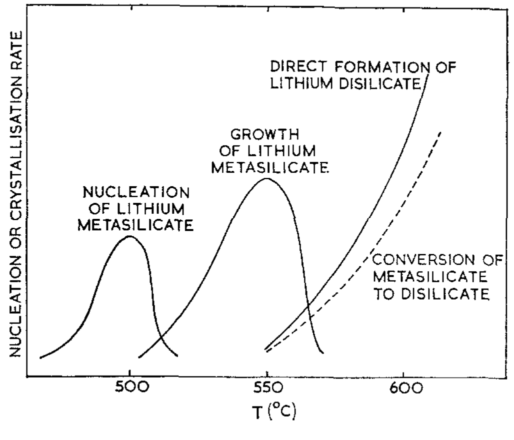

Figure 9 Schematic representation of possible rate processes occurring during crystallisation.

4. Change in Properties during Crystallisation

The changes in heat content, viscosity, and resistivity of the glass during crystallisation show that there are two temperature regions in which crystallisation is rapid. The first is about 600° C, where the main phase formed is lithium disilicate. At 700° C and upwards, crystallisa-

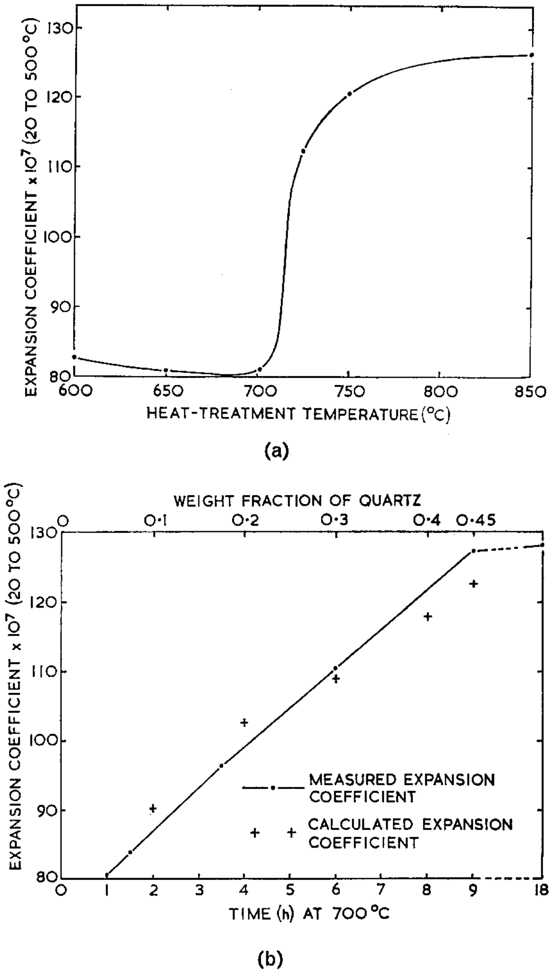

Figure 10(a) Change in thermal expansion coefficient with heat-treatment temperature. (b) Change in thermal expansion coefficient with time of heat treatment at 700° C.

tion of silica occurs, giving quartz in the final material. Thermal expansion characteristics, mechanical strength, and elastic modulus are three of the properties which are affected by the amount and type of crystals present.

4.1. Experimental

4.1.1. Thermal Expansion

Rod specimens of the glass were heat treated in an electric furnace at 500° C for 1 h with second holding stages of 1 h at 600, 700, 725, 750, and 800° C. The thermal expansion characteristics of each crystallised specimen were measured, using an automatic recording dilatometer. From these measurements, the average thermal expansion coefficient over the temperature range 20 to 500° C was calculated; it is plotted against second holding-stage temperature in fig. 10a. The thermal expansion coefficient decreased slightly from 82.5×10^{-7} cm/cm° C for the 600° C heat treatment to 80.5×10^{-7} at 700° C, then increased to 120.5×10^{-7} for the specimen heat treated at 750° C for 1 h. The effect of increasing time of heat treatment at a constant temperature of 700° C is shown as the continuous curve in fig. 10b. Here, the time at 700° C was increased from 1 to 18 h, and the resulting expansion coefficients 20 to 500° C were measured. The expansion coefficient increased from 80.5×10^{-7} for a 1 h heat treatment at 700° C, to 126×10^{-7} for 9 h at 700° C, with little further increase for heat treatments up to 18 h.

The appearance of the materials gradually changed with heat treatment, from translucent grey for the specimens heat treated at 600° C, to white for those treated at 750° C, and finally to opaque white for the material crystallised at 800° C. At all stages, the crystal sizes were very small and the mechanical strength was high.

4.1.2. Mechanical Strength

For determination of mechanical strength variations with heat-treatment conditions, groups of rod specimens with 10 rods per group were heat treated at 500° C for 1 h, followed by 1 h at temperatures in the range 600 to 850° C. After crystallisation, the rods were broken in three-point loading, using a Hounsfield tensometer; the rupture modulus of each rod was calculated as the maximum stress at fracture. The mean rupture moduli of the groups with 95% confidence limits are shown in fig. 11 as a function of heat-treatment temperature. It is seen that the rupture modulus of the glass-ceramic heat treated at 600° C is twice that of the annealed glass, and the rupture moduli decreases with increase of heat-treatment temperature to 850° C to a value about 50% greater than the annealed glass.

4.1.3. Modulus of Elasticity

The effect of increasing crystallinity on the elastic modulus of this material is shown in table I. The moduli were obtained by measuring the deflection of a centrally-loaded rod, and the limits of accuracy shown are ±5%. The elastic modulus increased from 7.6×10^5 kg/cm², for the annealed glass, to 9.2×10^5 kg/cm² on heat treatment at 600° C. A maximum in the

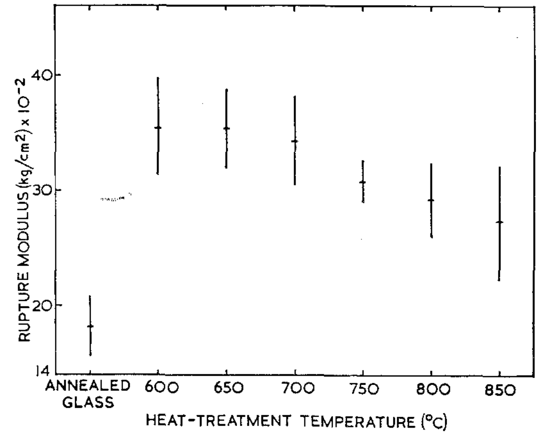

Figure 11 Variation of mean rupture modulus with heat-treatment conditions.

modulus of 9.7×10^5 kg/cm² was reached after treatment at 700° C for 2 h, and further treatment of 500° C for 1 h, 800° C for 1 h resulted in a decrease to 8.9×10^5 kg/cm².

TABLE I Change in elastic modulus with heat treatment.

Heat treatment	E (kg/cm²) $\times 10^{-5}$
Chilled glass "as drawn"	7.15 ± .36
Annealed at 450° C for 1 h	7.60 ± .38
500° C, 1 h; 600° C, 1 h	9.15 ± .46
500° C, 1 h; 700° C, 1 h	9.60 ± .48
500° C, 1 h; 700° C, 2 h	9.75 ± .49
500° C, 1 h; 800° C, 1 h	8.95 ± .45

4.2. Discussion

4.2.1. Change in Thermal Expansion Coefficient

With increasing temperature of heat treatment, the material is initially entirely vitreous, then contains lithium disilicate crystals and glass, and finally consists of lithium disilicate, crystalline silica, and some residual glass. These are the major phases present; lithium metasilicate probably occurs as a transient phase, and traces of ternary Li_2O-ZnO-SiO_2 compounds [3] have been identified in this material. These, however, are present in very small amounts and may be disregarded. From qualitative X-ray analysis and electron microscopy, the material after heat treatment at 600° C consists of approximately equal amounts of glass and lithium disilicate, although the latter crystals are not very well formed. With treatment at 700° C, the amounts of glass and lithium disilicate are still approximately equal, though now the characteristic dendrites of the disilicate appear clearly. The interesting feature is that although the glass-ceramic now contains large amounts of lithium disilicate, of higher expansion than the original glass, the thermal expansion coefficient of the composite actually decreases slightly from 82.5×10^{-7} to 80.5×10^{-7} with increasing crystal content. (The thermal expansion coefficient of lithium disilicate over the range 20 to 500° C was 101.6×10^{-7}, measured on a crystallised glass specimen containing more than 95% lithium disilicate.) The removal of lithia from the glass in forming lithium disilicate crystals changes the composition of the remaining glass to one of effectively higher silica content, and it is expected that this glass would have a low coefficient of expansion. The overall expansion of the material thus shows little change even though the expansion coefficients of the constituents are now different. With increase in heat-treatment temperature above 700° C, or by holding at 700° C for more than 1 h, the high-silica glass now crystallises to one of the crystalline modifications of silica, which have high expansion coefficients over the temperature range examined. With the conversion of the glass, the overall expansion now increases as more crystalline silica is developed. The material heat treated at 850° C for 1 h contains approximately equal amounts of crystalline silica and lithium disilicate, together with a small amount (5% or less) of residual glass, and has an expansion coefficient of 126.5×10^{-7}. Quartz is the usual form of crystalline silica found, though cristobalite and tridymite have been found by X-ray analysis for some heat-treated specimens.

The thermal behaviour of a composite material has been discussed by Kingery [4], who gives the following expression for the overall thermal expansion coefficient α of a composite:

$$\alpha = \frac{\dfrac{\alpha_1 K_1 F_1}{\rho_1} + \dfrac{\alpha_2 K_2 F_2}{\rho_2} + \dots\dots\dots}{\dfrac{K_1 F_1}{\rho_1} + \dfrac{K_2 F_2}{\rho_2} + \dots\dots\dots}$$

where α_1, α_2 are the expansion coefficients; K_1, K_2 are the bulk moduli; ρ_1, ρ_2 are the densities; and F_1, F_2 are the weight fractions of the components. If the Poisson's ratios of the components are similar, then the elastic moduli may be used in place of the bulk moduli. This expression for α assumes an ideal material, with the contraction of each component the same as the overall contraction, and all microstresses pure hydrostatic tension and compression. Using this expression, α was calculated for the material heat treated at 700° C for increasing periods and compared with the experimentally obtained values in fig. 10b. In calculating α, correction was made for the reduced expansion of the glass after lithium disilicate crystallisation, and it was assumed that all the crystalline silica appeared as quartz rather than as cristobalite. The crosses in fig. 10b show the calculated expansion coefficient of a material which changes in composition from 50% lithium disilicate, 50% glass, and no quartz, to 50% lithium disilicate, no glass, and 50% quartz, assuming the rate of production of quartz to be linear with time. The calculated expansion coefficients were fairly close to the experimental values up to 6 h at 700° C heat treatment; with longer times, the experimental values were higher. This may be due to the presence of relatively small amounts of cristobalite, since this has a higher expansion than quartz. Quantitative X-ray analysis would be necessary to establish more precisely the nature and amounts of crystal phases present as a function of heat-treatment conditions, and would allow a better comparison of calculated and experimental expansion coefficients to be made.

4.2.2. Mechanical Strength

Two interesting aspects of the effect of crystallisation of mechanical strength are the marked increase in strength on crystallisation in the temperature range 600 to 700° C compared with the annealed glass, and the falling-off in strength with crystallisation above these temperatures. The rupture modulus of bulk glass free from surface flaws is of the order of 250,000 kg/cm^2, whereas the rupture modulus of the annealed glass in this experiment was 1800 kg/cm^2, over 100 times smaller. Flaws of severity such as to give this level of fracture stress were present in specimens prior to heat treatment, since the specimens were prepared in the same way and randomly assigned to groups for heat treatment. The increase in rupture modulus from 1800 to 3500 kg/cm^2 on heat treatment to 600° C could have arisen from: (i) a reduction in surface flaw severity; and (ii) a change in internal structure which makes crack propagation more difficult. It is known that gross surface flaws on glassware produced by severe abrasion are effective nuclei for crystal growth from solution or for growth of gas bubbles. It seems likely, therefore, that surface microflaws represent suitable sites or nuclei for crystal growth in the glass when heated to the appropriate temperature. The "radius of curvature" of the flaw is modified by crystal growth to decrease its strength-reducing effect. Evidence for this effect has been obtained in these laboratories, using abraded glass-ceramic specimens of composition different from the one used here.

The change in internal structure to a network of interlocking crystals may increase the fracture stress by making crack propagation more difficult across the crystals. If the boundaries of the crystals are then assumed to be the sources of weakness, a relation would be expected between crystal size and fracture stress. The Griffith flaw theory relates the depth C of a flaw to the elastic modulus E and fracture stress σ:

$$\sigma \approx \left(\frac{Ea}{C}\right)^{\frac{1}{2}}$$

where a is the energy of formation of the fracture surface. Measurements on soda-lime-silica glass [5] have given the value $\sigma\ C^{\frac{1}{2}} \approx$ 33.8 kg/cm$^{3/2}$. Using the measured fracture stress of 3500 kg/cm^2 for the glass-ceramic, the flaw depth to be expected from this relation is approximately 1 μm. Examination of the electron micrographs of this material heat treated at 600 and 700° C for 1 h (figs. 2 and 3) shows that the crystals of lithium disilicate were about 1.5 by 1 μm, with patches of residual glass 0.5 μm across. There is thus an apparent agreement between crystal size as shown by electron microscopy and that given by the Griffith flaw theory, but it is thought that crystal size is not the only factor determining strength. The mechanical strength of glass-ceramics of very low thermal expansion coefficient (less than 10×10^{-7}) is generally relatively low (1000 to 1500 kg/cm^2), owing to the anisotropy of expansion of each crystal and to the stresses resulting as the crystal-glass composite cools from its crystallisation temperature. The crystal size in these low expansion materials can be small, 0.5 μm or less, which would imply a much higher strength than is found, if crystal dimensions were the only relevant factor. A similar situation may obtain in the present work, where crystalline forms of silica are developed at higher temperatures, and the rupture modulus decreases compared with the material heat treated to 600 to 700° C. Although some stress release probably occurs by viscous flow of residual glass, the stresses between adjacent dissimilar crystals could be sufficient to produce microcracks.

4.2.3. Elastic Modulus

Referring to table I, the growth of lithium disilicate crystals after treatment at 600° C results in a marked increase in elastic modulus to 9.15×10^5 kg/cm^2, compared with 7.6×10^5 kg/cm^2 for the annealed glass. With the growth of silica crystals at 700° C, the maximum value of 9.75×10^5 kg/cm^2 was obtained. However, increase in the amount of quartz on heat treatment at 800° C resulted in a decrease of modulus to 8.95×10^5 kg/cm^2. It is thought the most likely explanation of this, as with the decrease in mechanical strength, is that microcracks appear between the quartz crystals and surrounding crystals or glass, permitting locally non-elastic deformation with a consequent reduction in macroscopic elastic modulus.

5. Conclusions

Crystallisation of a lithium-zinc-silicate glass takes place in well-marked stages, definable by changes in some physical properties of the material. Changes in the glass viscosity and resistivity in the early stages of crystallisation are attributed to the growth and disappearance of lithium metasilicate as a transient phase.

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