

Glass-ceramics with random and oriented microstructures

Part 2 *The physical properties of a randomly oriented glass-ceramic*

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The variation of a number of physical properties of a glass-ceramic composition as a function of the crystallization heat-treatment temperature are reported. The properties studied include mechanical strength, modulus of elasticity, electrical properties and linear coefficient of thermal expansion. It is shown that several of the properties are dependent on microstructural effects. This dependence is especially marked for modulus of rupture and is also apparent for electrical properties such as conductivity and loss tangent. For the latter, however, compositional changes in the residual glass phase also exert a significant influence. For other properties, such as indentation hardness, the microstructural dependence is less well defined.

1. Introduction

The variation of the microstructure with heat-treatment of a glass-ceramic based on the $\text{Li}_2\text{O}-\text{SiO}_2$ system has been previously reported by the authors [1]. In the present paper, the physical properties of this glass-ceramic are described and compared with the statistical description of the microstructure. The physical properties measured include the coefficient of thermal expansion, the Young's modulus and rupture modulus and the electrical resistivity.

2. Apparatus and methods

2.1. Mechanical properties

The modulus of rupture and Young's modulus in bending of the glass-ceramic specimens were determined by a three-point bending technique. Initially a three-point bending jig with a 3.8 cm span between the outer knife edges was used; an Instron Universal Testing Machine operating at a cross-head speed of 0.02 cm min^{-1} was used to load the specimen. On average ten specimens were used for each strength determination, all of which were made at room temperature. All the samples were abraded in a rotary mill for 60 min with silicon carbide (≤ 100 mesh).

A second miniature bending jig with a span of 0.41 cm was also used; the dimensions of the specimen were typically $0.1 \text{ cm} \times 0.1 \text{ cm} \times 0.6 \text{ cm}$ and the sample was loaded at a cross-head speed of $0.002 \text{ cm min}^{-1}$. Small beams prepared from glass-ceramic beams broken on the large span jig were found to give results which were in excellent agreement.

Measurements of Vickers and Knoop hardness numbers (200 g load for 10 sec) were also made on specimens heat-treated according to the various conditions.

2.2. Electrical measurements

Impedance measurements in the range 100 Hz to 10 kHz were made with a Marconi TF2700 Universal Bridge; from 100 kHz to 1 MHz a Wayne-Kerr bridge type B602 was used. A specimen holder similar to one described by Owen [2] was constructed from stainless steel and refractory tubing; the samples being clamped between plane electrodes in the holder. The holder was electrically shielded in a stainless steel tube which fitted into a furnace. Electrical measurements were made with the sample in a dry nitrogen atmosphere.

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Specimens were prepared by cutting parallel sided slices (~ 0.1 cm thick) of the glass-ceramic and polishing both sides to a $6\ \mu\text{m}$ diamond paste finish. Silver electrodes of unequal size were evaporated onto the specimen. One side of the specimen was completely coated with silver to form one electrode and to the other side a smaller circular electrode of diameter 0.31 cm was applied. The electrodes were painted with a silver "Dag" suspension for strength. The specimens were dried at 120°C for 30 min before taking measurements to eliminate the possibility of surface conduction by water through small cracks which the heat-treatment might have produced. A guard ring was found to be unnecessary and a series of different electrode materials (Au, Ag, Pt, Au/Pd) were found to give equivalent results.

The electrical measurements were interpreted in terms of the volume resistivity the dielectric constant and the loss tangent ($\tan \delta$) of the specimen.

2.3. Thermal expansion measurements

The coefficient of thermal expansion of the glass-ceramics studied was measured with a silica dilatometer. Samples approximately 0.3 cm long were used and the expansion-temperature curves were corrected for the characteristic expansion of the specimen holder. Experiments with larger samples gave equivalent results.

The expansion curve of each glass-ceramic specimen was measured as a function of increasing and decreasing temperature; the temperature cycle was repeated five times. If no systematic variation in the expansion with temperature cycling was noted, the mean thermal coefficient of expansion was evaluated from the corrected curves.

3. Results

The glass-ceramic referred to in the following sections was devitrified from the glass whose composition is given in [1]; unless otherwise stated specimens of the glass were heat-treated for a period of 2 h.

3.1. Young's modulus, rupture modulus and indentation hardness

The value of the Young's modulus, E_b , for the as cast glass was found to be:

$$E_b = (5.4 \pm 0.6) 10^{10} \text{ N m}^{-2}$$

and the rupture modulus, σ_f :

$$\sigma_f = (9.7 \pm 0.6) 10^7 \text{ N m}^{-2}.$$

Fig. 1 shows the variation of the Young's modulus of the glass-ceramic with various heat-treatment temperatures. The dependence of the rupture modulus on different heat-treatment temperatures is shown in Fig. 2.

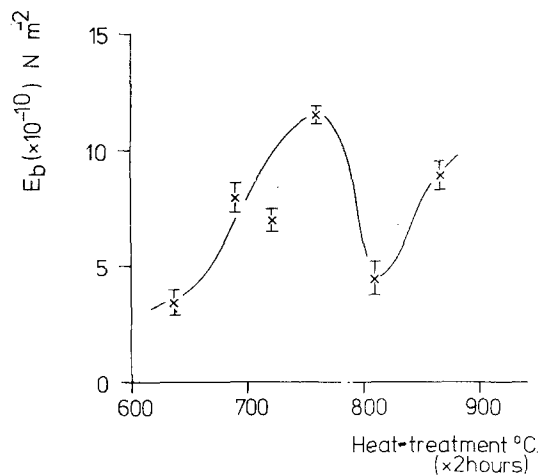


Figure 1 The variation of the Young's modulus, E_b , of the glass-ceramic with various 2 h heat-treatment temperatures.

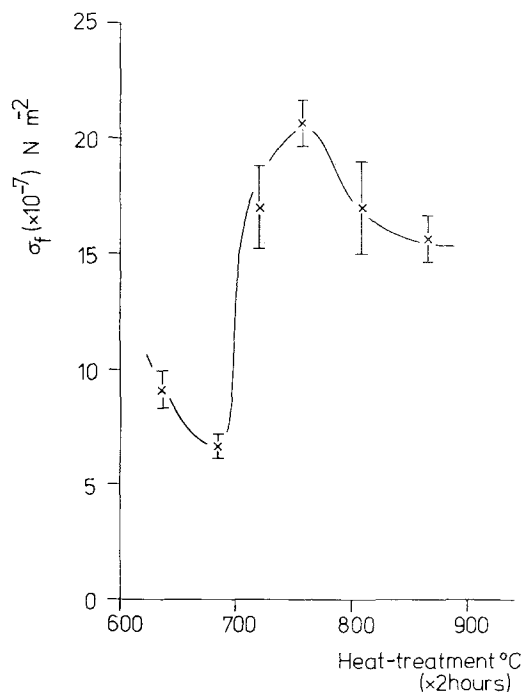


Figure 2 The variation of the modulus of rupture, σ_f , of the glass-ceramic with various 2 h heat-treatment temperatures.

It has been suggested that the mechanical strength of a polycrystalline aggregate σ , is related to the mean grain diameter d , by the relationship [3, 4]:

$$\sigma = K_1 d^{-1/2} \quad (1)$$

where K_1 , is a constant.

The implication in this equation is that the crack length, c , in the Griffith equation

$$\sigma = \left(\frac{2E\gamma}{\pi c} \right)^{1/2}$$

is proportional to the grain diameter, d . In the Griffith equation, E is the Young's modulus of the material and γ is the effective surface energy for crack initiation. Tashiro and Sakka [5] have shown that Equation 1 holds for a glass-ceramic based on a $\text{Li}_2\text{O}-\text{SiO}_2$ composition. This suggests that the critical flaws are present within the crystal grains and do not extend into the glass phase or that they exist at the glass-crystal interface and are, therefore, proportional to the circumference of the grains.

In the present work the variation of σ_f with the square root of the mean crystal size is shown in Fig. 3. It can be seen from this graph that this dependence of the strength on the grain size does not explain the difference in the values of the rupture modulus observed.

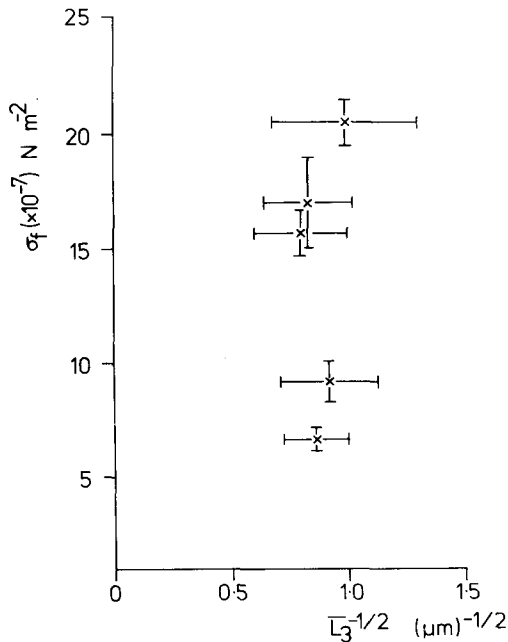


Figure 3 The variation of the rupture modulus, σ_f , with the square root of the mean crystal size of the glass-ceramic.

In a glass-crystal composite such as a glass-ceramic containing a relatively strong crystalline dispersion, fracture could be initiated within the glass matrix. Hasselman and Fulrath [6] have suggested that for such composites at a sufficiently high volume fraction of the crystalline phase the maximum flaw size in the glass is restricted by the presence of the dispersion. This implies that the flaws present in the glass are terminated at the crystal-glass boundaries and the spacing between the crystals or the mean free path in the glass phase will, therefore, be a critical parameter in determining the mechanical strength of the composite.

Equation 1 can, therefore, be modified to:

$$\sigma = K_2 \lambda^{-1/2} \quad (2)$$

where K_2 is a constant and λ is the mean free path in the glass phase. Freiman and Hench [7] have reported a similar dependence of strength on the mean free path, in a partially crystallized glass of molecular composition $70 \text{SiO}_2 \cdot 30 \text{Li}_2\text{O}$. The result as expressed in Equation 2 is also consistent with the work of Hing and McMillan [8].

Fig. 4 shows the dependence of the rupture modulus with the mean free path λ , for the glass-

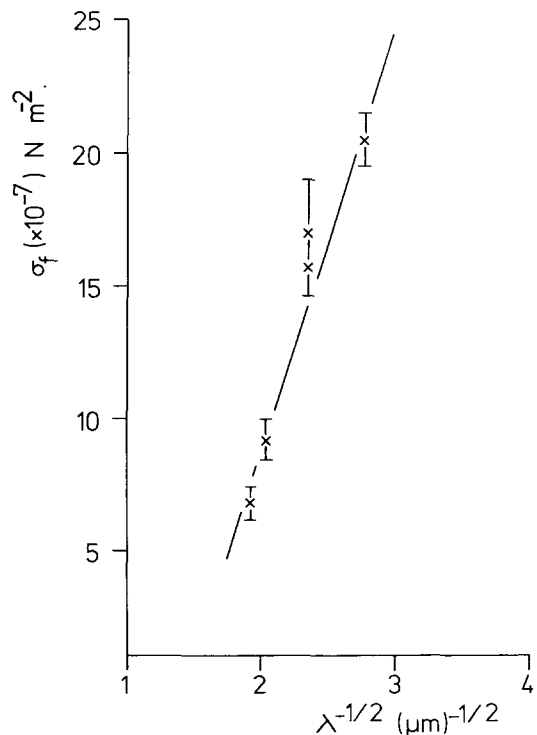


Figure 4 The dependence of the rupture modulus upon the mean free path, λ , for the glass-ceramic.

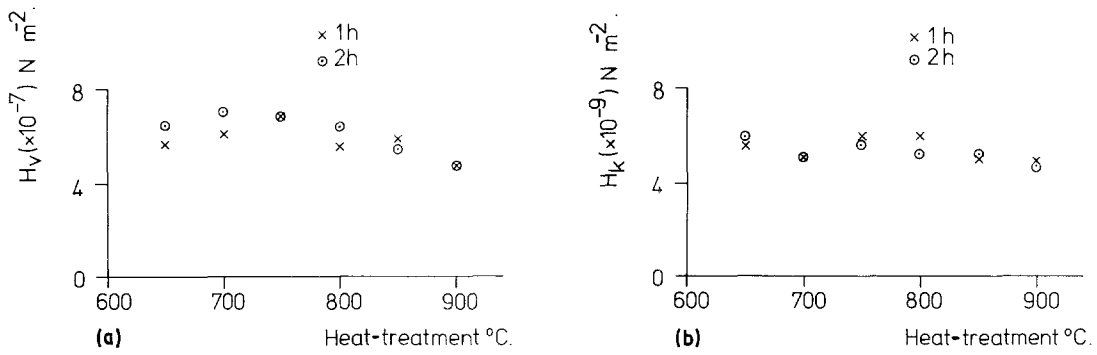


Figure 5 The variation of indentation hardness with the heat-treatment temperature: (a) Vickers hardness; (b) Knoop Hardness.

ceramic. Examination of the Griffith equation reveals that the surface energy for crack initiation, γ , can be calculated from the slope K_2 of the graph shown in Fig. 4 by means of:

$$\gamma \approx \frac{K_2^2}{E}$$

If the maximum value of E_b ($\approx 11.5 \cdot 10^{10} \text{ N m}^{-2}$) is substituted in this equation then:

$$\gamma \approx 0.2 \text{ J m}^{-2}$$

This low value for γ is consistent with fracture initiation occurring in the glass phase.

The results of indentation hardness measurements are summarized in Fig. 5.

3.2. Electrical results

The electrical volume resistivity, ρ , the dielectric constant, K , and the loss tangent, $\tan \delta$, were measured over a range of temperatures for the glass-ceramic devitrified at different temperatures. Each of these electrical properties was measured at 100 Hz and frequencies increasing by a factor of 10 to 1 MHz.

The dependence of the resistivity, ρ , on the absolute temperature, T , can be expressed by the Rasch-Hinrichsen equation [9]:

$$\rho = A \exp \frac{E}{RT}$$

where E is the activation energy for conduction for the particular glass or crystal and A is a constant. In the present work no dependence on the measurement frequency was observed for the

values of the constants A and E evaluated from data taken above 300°C . The activation energy for a specimen of the glass, E_{glass} was found to be:

$$E_{\text{glass}} = 15.5 \text{ kcal mol}^{-1}$$

and $\ln A = -5.6$.

For this glass specimen a sharp increase in the resistivity was observed at a temperature of approximately 600°C ; this increase was associated with the initial devitrification of the sample. The resistivity at 300°C , ρ_{300} , was calculated from the experimentally determined values of A and E for specimens of the glass-ceramic and is shown in Fig. 6.

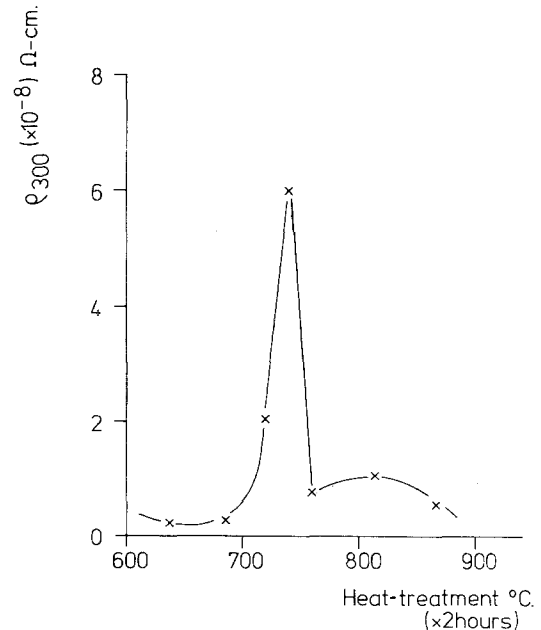


Figure 6 The variation of the resistivity at 300°C , ρ_{300} , with the heat-treatment temperature for the glass-ceramic.

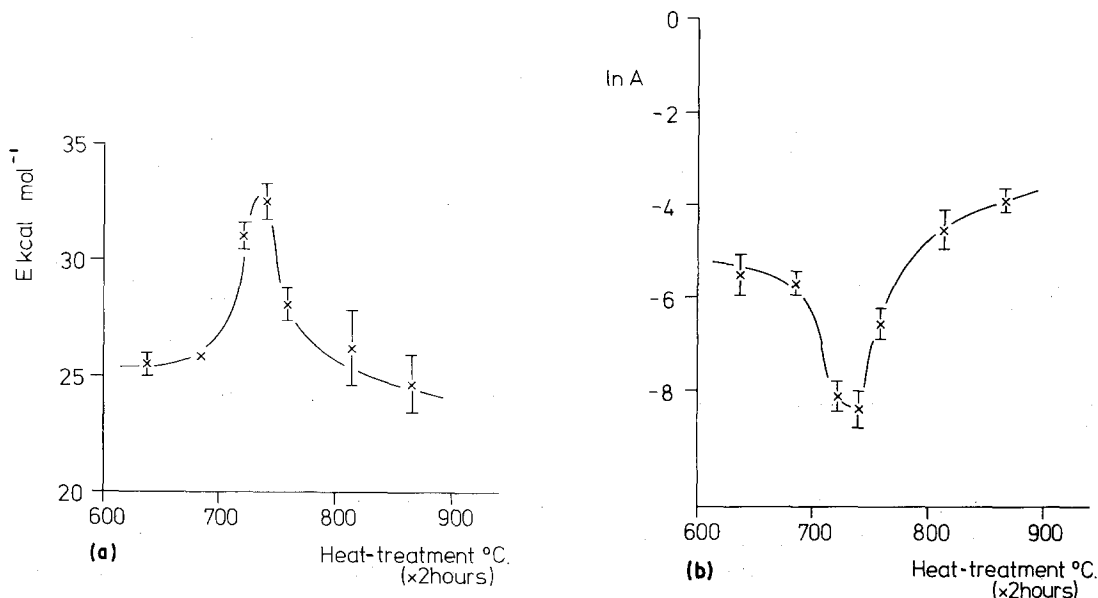


Figure 7 (a) The variation of the activation energy, E , with heat-treatment temperature (b) The variation of the pre-exponential constant, $\ln A$, with the heat-treatment temperature.

Fig. 7a shows the variation of the activation energy E , with the heat-treatment temperature; the variation of the pre-exponential constant in A is shown in Fig. 7b.

The resistivity of the glass-ceramic shows a sharp peak, for a glass heat-treated at approximately 740°C for 2 h (Fig. 6); at this temperature the second crystalline phase of tridymite was first observed.

Fig. 8 shows the variation of the dielectric constant, K , with temperature, T , for the five measuring frequencies between 100 Hz and 1 MHz. This is a typical graph and the following comments are valid for all the dielectric constants measured on different glass-ceramic specimens.

(1) The dielectric constant decreases as the measuring frequency is increased; at low frequencies (< 10 kHz) the dielectric constant increases rapidly with the increasing temperature of the specimen.

(2) At frequencies of 100 kHz and 1 MHz the dielectric constant varies slowly with increasing temperature. The dielectric constant measured at 300°C, K_{300} , is shown as a function of heat-treatment temperature in Fig. 9a and b for measurement frequencies of 100 kHz and 1 MHz respectively.

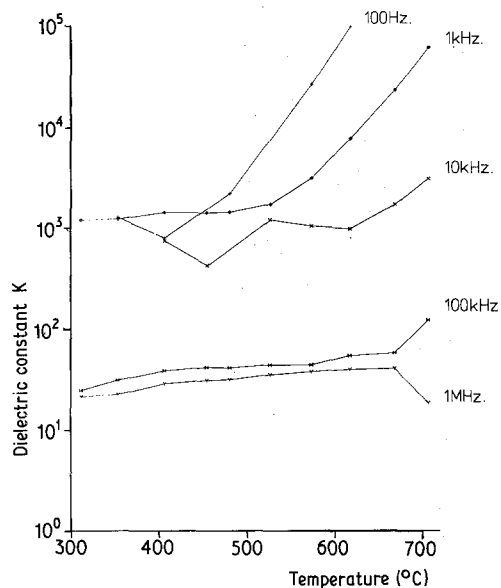


Figure 8 The variation of the dielectric constant, K , with the measuring temperature.

Fig. 10a and b show the variation of the loss tangent at 300°C, $\tan \delta_{300}$, with the heat-treatment of the glass-ceramic for frequencies of 100 kHz and 1 MHz respectively. Both curves show minima at a heat-treatment temperature of approximately 750°C.

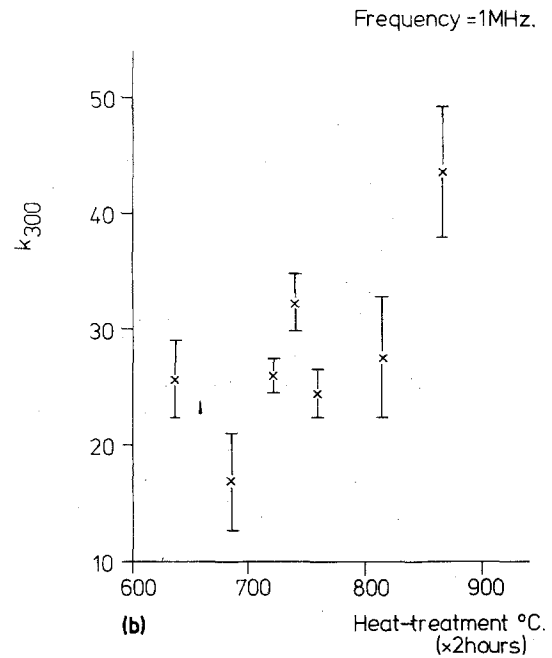
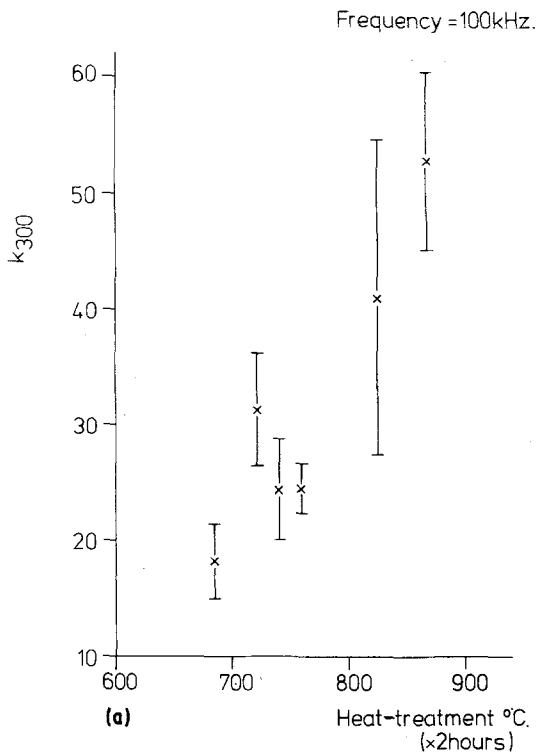


Figure 9 The variation of the dielectric constant, K_{300} , with heat-treatment temperature of the glass-ceramic for a frequency of (a) 100 kHz (b) 1 MHz.

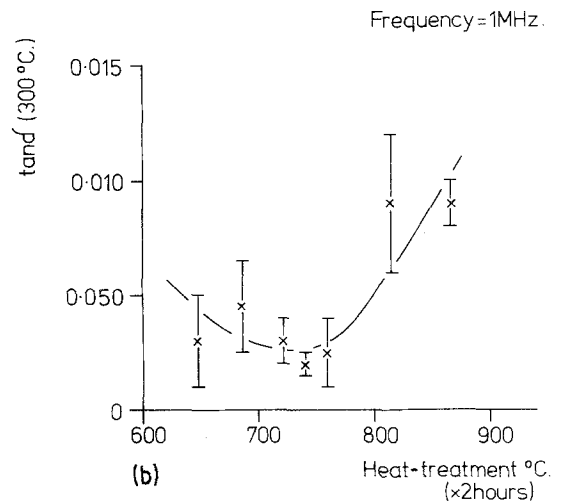
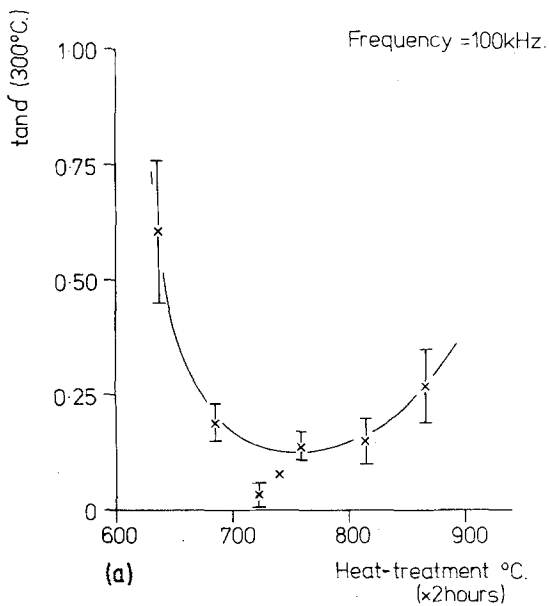


Figure 10 The variation of $\tan \delta_{300}$ with the heat-treatment of the glass-ceramic for frequencies of (a) 100 kHz and (b) 1 MHz.

3.3. Coefficient of thermal expansion

The coefficient of thermal expansion of the glass α glass, was found to be:

$$\alpha \text{ glass} = 12.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

measured over the temperature range 100 to 500°C, the glass had a dilatometric softening temperature M_g , of: $M_g \approx 500^\circ\text{C}$. The coefficient of thermal expansion was measured for specimens of the glass-ceramic heat-treated for 2h at temperatures between 600 and 900°C. A typical expansion curve of the glass-ceramic was found to be composed of two linear regions of differing gradients. The expansion of the specimen was described by two coefficients of thermal expansion α_1 and α_2 , measured from these linear regions. The temperature range over which α_1 and α_2 were measured is given approximately by: α_1 , 150 to 350°C; α_2 , 500 to 650°C. Fig. 11 shows

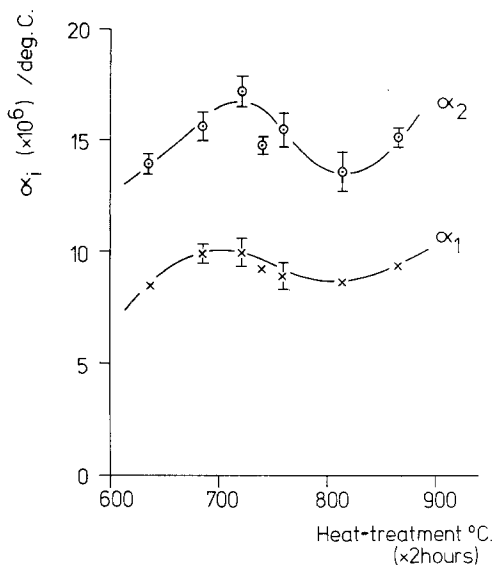


Figure 11 The variation of the thermal expansion coefficients, α_1 , with the temperature of a 2h heat-treatment for the glass-ceramic.

the variation of α with the temperature of a 2h heat-treatment for the glass-ceramic. The two expansion coefficients α_1 and α_2 show the same variation with heat-treatment temperature; both have a maximum value at a temperature of approximately 720°C.

4. Discussion and conclusion

The various physical properties of the glass-ceramics have in general been shown to be strongly dependent upon the crystallization temperature employed to produce the glass-ceramic and it is

of interest to consider how far these variations are explainable in terms of microstructural changes.

It is notable that a number of the properties attain maxima or minima for glass-ceramics produced by crystallization heat-treatment at a temperature in the region of 750°C. Because of the diverse nature of the properties studies, it seems reasonable to suppose that these observations are explainable, at least partly, in terms of microstructural effects. At this point it should be recalled that, as shown previously [1], the volume fraction of crystalline phase attains a flattened maximum and the mean free path in the residual glass phase, λ , a distinct minimum for material heat-treated at about 750°C. We also note that in addition to the major crystalline phase, lithium disilicate, which is formed in varying amounts throughout the whole heat-treatment range, a second minor phase identified as tridymite appears during heat-treatment at temperatures above about 740°C but that formation of this phase appears to cease at the upper end of the heat-treatment range.

Considering the various properties in turn: the maximum in the value of Young's modulus for a heat-treatment temperature of 750°C shown in Fig. 1 corresponds with the maximum volume fraction of crystalline phase, V_α . Since the crystalline phases are likely to have higher elastic moduli than the residual glass phase, the occurrence of the maximum value for E would be expected from a simple additive relationship. It should be noted, however, that the maximum in the elastic modulus data is much more pronounced than that shown by the volume fraction values. Also, the apparent increase in elastic modulus when the heat-treatment temperature was increased above about 820°C is difficult to explain purely in terms of variation of the volume fraction of crystalline phase present.

The maximum strength, σ_f , occurs after heat-treatment at 750°C (Fig. 2) and this coincides with a maximum V_α and minimum λ . Analysis of the results established a linear relationship between σ_f and $\lambda^{-1/2}$ and supported the view that the strength of the glass-ceramic is controlled by microflaws in the residual glass phase; the severity of these is limited by the presence of crystal-glass interfaces.

The indentation hardness measurements (Fig. 5) indicated that the Vickers Hardness may be slightly microstructure-sensitive as shown by

the flattened maximum for heat-treatment temperatures in the region of 700 to 750°C but the Knoop Hardness was not dependent on heat-treatment temperature. These differences are possibly due to the different geometries of the indenters employed in the two tests.

The volume resistivity versus heat-treatment temperature curve (Fig. 6) shows a sharp maximum at about 740°C. The conductivity of the glass-ceramic arises because of migration of lithium ions through the structure and since the mobility of these will be far greater in the residual glass phase than in the crystal phase, a minimum in resistivity would be expected when the minimum volume fraction of glass phase is present. The sharpness of the resistivity peak suggests, however, that there may be other contributing factors. One of these is that the chemical composition of the residual glass phase is changing as its volume fraction changes. Indeed, the changes in the values of the pre-exponential constant A (Fig. 7b) strongly suggest that the composition of the residual glass phase is dependent on heat-treatment conditions. The pre-exponential constant is given by:

$$A = \frac{e^2 \lambda^2 nb}{2KT}$$

where e is the electronic charge, λ is the "jump distance" between potential wells, n is the number of ions taking part in the conduction process, and b is the vibrational frequency of the ion in its well.

While the values of λ and b may be slightly influenced by the glass composition, the major effect of compositional change will be upon n . The minimum in A , therefore, may indicate that heat-treatment at $\sim 740^\circ\text{C}$ results in a minimum density of mobile Li^+ ions in the glass phase.

Kuznetsov [10] has shown that the activation energy of conduction for simple $\text{Li}_2\text{O}-\text{SiO}_2$ glasses decreases almost linearly as the lithium oxide content is increased, presumably due to the increase in the concentration of ionic current carries and to changes in the glass structure. Although the residual glass phase in the present glass-ceramic is probably not a simple $\text{Li}_2\text{O}-\text{SiO}_2$ composition, it is likely to be sufficiently close to this to suggest that a similar trend will occur. Hence the maximum in E (Fig. 7a) for material heat-treated at $\sim 740^\circ\text{C}$ also suggests a minimum concentration of mobile Li^+ ions.

The variation of loss tangent as a function of crystallization temperature (Fig. 10) is not surprising in the light of the results obtained for the d.c. conduction measurements. At the measurement temperature and frequencies employed the dominant loss mechanisms are ionic conduction losses and ion migration losses [12] and those factors that result in maximum resistivity will also result in minimum loss tangent values, as observed.

It is to be noted that the values for the dielectric constant of the glass-ceramic do not follow the pattern of the other electrical data since they increase steadily as a function of heat-treatment temperature (Fig. 9). Although the exact form of the relationship is not clear from the available data, from simple mixture rules [11] one might expect some change in the trend of the data at the heat-treatment temperature giving the maximum volume fraction of crystalline material. If this effect does occur, it is obscured by other effects such as changes in the composition of the glass phase and ionic polarizability resulting from structural changes in the glass phase.

The thermal expansion values (Fig. 11) also show indications of a microstructural dependence in that maxima occur for heat-treatment temperatures similar to but slightly lower than that giving the maximum volume fraction of crystalline phase. The relationship does not appear to be well defined, however, and in particular, the increase of thermal expansion coefficient for higher heat-treatment temperatures is not easy to explain.

In conclusion, the work has shown that a number of physical properties of the glass-ceramic are dependent on microstructural effects. This dependence is especially marked for modulus of rupture and is significant for electrical properties such as d.c. conductivity and loss tangent but for these, compositional changes in the residual glass phase are also important. For other properties, the microstructural dependence is much less well defined.

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