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Glass-ceramics with random and oriented microstructures

Part 1 *The microstructure of a randomly oriented glass-ceramic*

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The variation of the microstructure with the heat-treatment of a glass-ceramic based on the Li_2O–SiO_2 system has been investigated using a scanning electron microscope. The principal crystalline phase was found to be lithium disilicate. The dependence of the volume fraction and mean crystal spacing on the heat-treatment was also studied. It was found that while the volume fraction of crystalline phase was relatively insensitive to the heat-treatment temperature employed, the mean inter-crystal spacing appeared to provide a sensitive indicator of microstructural changes.

1. Introduction

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses. This is accomplished by subjecting suitable glasses to a carefully regulated heat-treatment which results in the nucleation and growth of crystal phases within the glass. The influence of heat-treatment conditions upon the glass-ceramic microstructure is of interest and it is also important to establish the relationships between microstructural parameters and physical properties of the materials.

In general, the crystal phases in glass-ceramics are randomly oriented [1] but it is possible to produce materials having a microstructure in which a high degree of crystal alignment occurs [2]. Hence the influence of microstructural orientation upon glass-ceramic properties is also of interest.

The present paper reports upon the variation of the microstructure of phosphate-nucleated glass-ceramics, derived from the Li_2O–SiO_2 system, as a function of heat-treatment temperature. Subsequent papers will describe the relationships between physical properties and microstructure for these randomly oriented materials and for glass-ceramics of the same chemical composition having aligned microstructures.

2. Materials and methods

The composition of the glass studied is shown in Table I and has been previously studied by the authors [2]. The glass was prepared from Brazilian quartz, ground to pass through a 60 mesh sieve, high purity lithium carbonate and A.R. lithium orthophosphate, potassium carbonate, aluminium oxide and boric oxide. The materials were thoroughly dried, weighed and mixed by milling in a rotary ball mill for 2 h. The glass was melted and refined in a platinum crucible at 1400° C until bubble-free, quenched into a melting mixture of ice and water, and then crushed and dried. This process was repeated twice with the object of achieving good homogeneity. The glass was remelted for 2 h and cast into moulds with a graphite suspension to prevent sticking.

TABLE I Glass composition (mol %)

SiO_2	Li_2O	K_2O	Al_2O_3	P_2O_5	B_2O_3
61	30.5	1.5	1.0	1.0	5.0

Specimens of the glass were heat-treated by placing small samples on a platinum sheet in a muffle furnace at the heat-treatment temperature and rapidly cooling to room temperature at the end of the heat-treatment period. Thermo-

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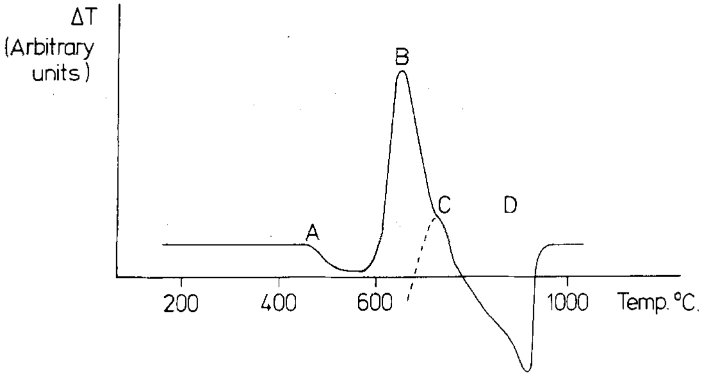

Figure 1 DTA thermogram of the glass.

couples of Pt and Pt–13% Rh were used to control and monitor the temperature. The range of temperature over which the glass devitrified was determined by a heat-treatment schedule and by differential thermal analysis (Fig. 1).

The microstructure of the glass-ceramic was studied using a scanning electron microscope (SEM). Specimens approximately 3 mm thick were prepared for SEM by polishing to a 1 μm finish and etching in a 3% solution of hydrofluoric acid for 30 sec; the surfaces were coated with a layer of gold/palladium approximately 10 nm thick.

The volume fraction of the crystalline phases in the glass-ceramic was evaluated by a point counting technique [3, 4]. A grid consisting of 100 points was drawn onto positive prints of the SEM micrographs and the number of grid points falling on crystalline phases in the glass-ceramic was counted.

The mean free distance λ, was also evaluated [5]. This parameter may be considered as the mean edge-to-edge distance along a straight line between particles or second phase regions. It is defined as:

$$\lambda = \frac{1 - V_\alpha}{N_\alpha}$$

where V_α is the volume fraction of the α phase and N_α is the number of intersections of the α phase per unit length of test line.

3. Microstructure

Figs. 2 and 3 are a series of representative micrographs of the glass-ceramic microstructure produced by heat-treating samples of the glass for a period of 1 h at temperatures between 650 and 900° C.

Devitrification at 650° C (Fig. 2a) produced a single crystalline phase which was identified as lithium disilicate by X-ray powder diffraction. The majority of the crystals are needle-shaped, approximately 10 μm long and 2 μm in width; a second crystal morphology can be seen in which the crystals are "star" shaped with three, four or

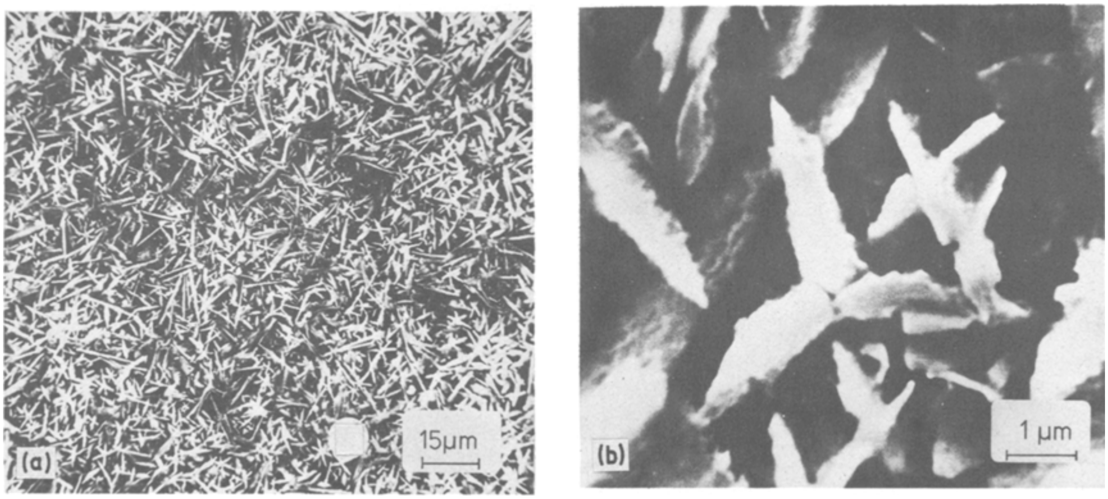

Figure 2 The glass after devitrification at 650° C for 1 h.

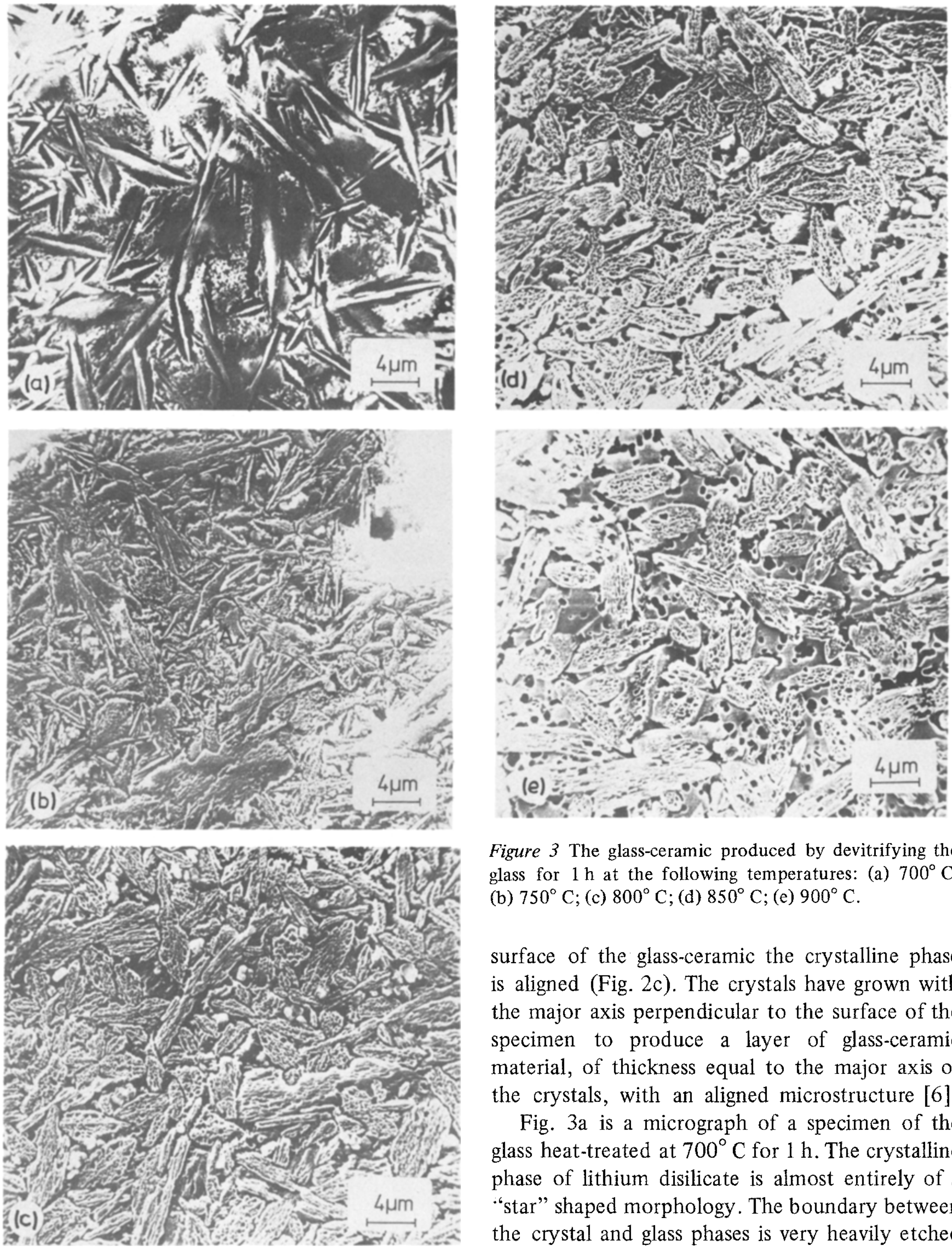

Figure 3 The glass-ceramic produced by devitrifying the glass for 1 h at the following temperatures: (a) 700° C; (b) 750° C; (c) 800° C; (d) 850° C; (e) 900° C.

six "arms" visible in the micrograph. Fig. 2b shows one of these crystals with three visible "arms"; a volume of the material between the crystals has been removed by the etching process to reveal the intersection of the "arms". In the bulk material the crystals are randomly oriented whereas at the surface of the glass-ceramic the crystalline phase is aligned (Fig. 2c). The crystals have grown with the major axis perpendicular to the surface of the specimen to produce a layer of glass-ceramic material, of thickness equal to the major axis of the crystals, with an aligned microstructure [6].

Fig. 3a is a micrograph of a specimen of the glass heat-treated at 700° C for 1 h. The crystalline phase of lithium disilicate is almost entirely of a "star" shaped morphology. The boundary between the crystal and glass phases is very heavily etched and this is thought to be due to high stresses in this area. High stresses will be produced in these regions by a mismatch of the thermal expansion coefficients of the two phases.

Heat-treating the glass at 750° C for 1 h produces a glass-ceramic with two crystalline phases. The microstructure of this sample (Fig. 3b) consists of a major phase of needle-shaped lithium disilicate crystals and a minor phase which was identified as tridymite. The appearance of this phase is consistent with the occurrence of the second exotherm in the differential thermal analysis of the glass composition (Fig. 1).

The microstructure of the glass-ceramics which result from heat-treating a specimen of the glass at 800° C (Fig. 3c) and 850° C (Fig. 3d) for 1 h are very similar to the microstructure of its material produced by the 750° C heat-treatment. The glass-ceramics contain a needle-shaped lithium disilicate phase and a minor phase of tridymite, together with a residual glassy phase. Fig. 3e is a micrograph of the glass-ceramic produced by devitrifying the glass at 900° C for 1 h. X-ray powder diffraction showed that the only crystalline phase present was lithium disilicate.

Samples of the glass heat-treated for 2 h at the above temperatures produced glass-ceramics with crystal phases and microstructures very similar to those of the 1 h heat-treatment.

4. The volume fraction and mean particle spacing

The variation in the volume of the crystalline phases as a function of heat-treatment of the glass was determined and is shown in Figs. 4a and b for 1 and 2 h heat-treatments respectively. For the 1 h heat-treatment the volume fraction shows a maximum of 90% for a temperature of 750° C. This temperature corresponds to that at which the second crystalline phase of tridymite was first detected. The volume fraction of the crystalline phases for a 2 h heat-treatment is approximately constant at 85%.

Figs. 5a and b shows the variation of the mean crystal spacing λ, with the temperature of the heat-treatment for times of 1 h and 2 h respectively. Both heat-treatment times show a minimum in the value of λ at approximately 750° C; this corresponds to the first appearance of the second crystalline phase in the glass-ceramic.

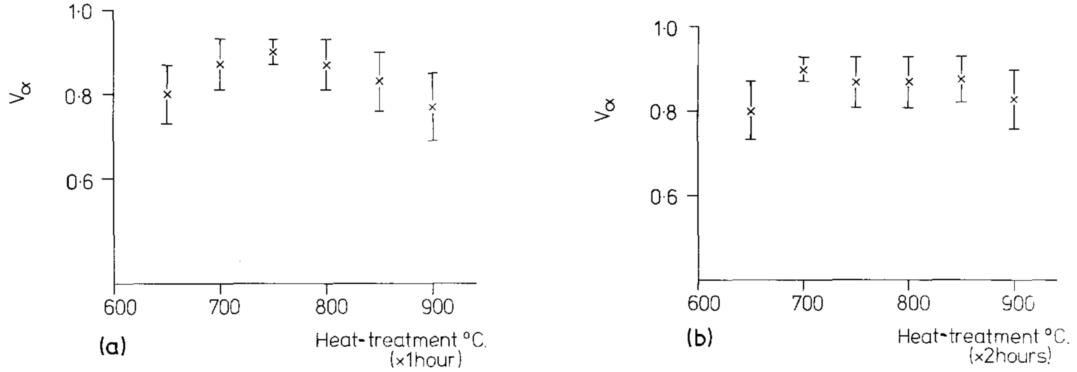

Figure 4 The variation in the volume fraction of the crystalline phases of the glass-ceramic as a function of heat-treatment; (a) 1 h and (b) 2 h heat-treatment.

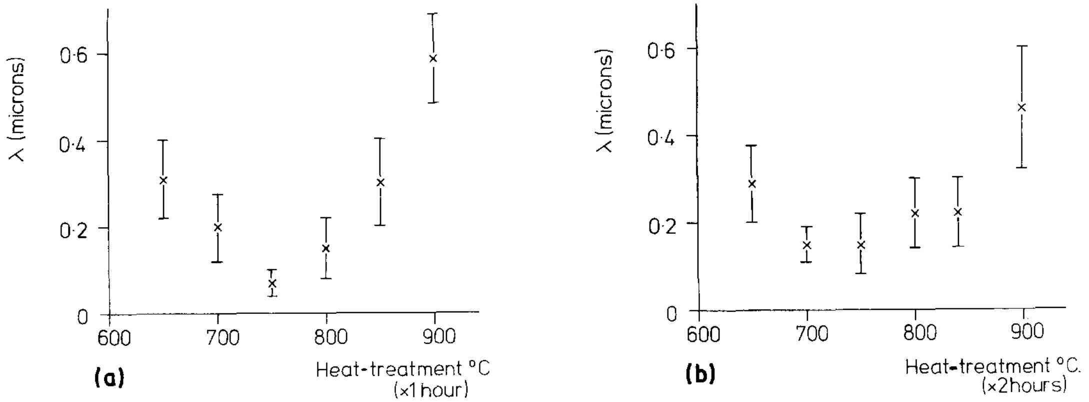

Figure 5 The variation in the mean crystal spacing λ, with the temperature of heat-treatment of the glass for (a) 1 h and (b) 2 h.

5. Discussion and conclusions

The investigation showed that a phosphate-nucleated glass-ceramic derived from the Li_2O–SiO_2 system could be converted to glass-ceramic by single-stage heat-treatments in the temperature range 650 to 950° C. The major phase was lithium disilicate which occurred in a needle-like morphology. At temperatures in the region of 750° C a second phase, identified as tridymite, was detected but this was apparently not formed at higher temperatures in the region of 900° C.

Investigation of microstructural parameters as a function of heat-treatment showed that while the volume fraction of crystalline phase was relatively insensitive to heat-treatment temperature, a flattened maximum (corresponding to a volume fraction of about 90%) occurs at approximately 750° C in the volume fraction versus heat-treatment temperature curve. This effect was more apparent for material heat-treated for 1 h than for that heat-treated for 2 h. The mean intercrystalline spacing, λ, appears to be a highly sensitive parameter for monitoring microstructural changes and distinct minima occurred for a heat-treatment temperature of 750° C irrespective of whether the duration of treatment was 1 or 2 h.

It is concluded that the 'optimum' microstructure in the sense of maximum volume fraction of crystalline phase combined with minimum interparticle spacing was developed by heat-treatment at 750° C. The microstructural analysis has enabled a series of well characterized glass-ceramics suitable for the investigation of microstructure-property relationships to be produced. The results of such a study will be reported in a subsequent paper.

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