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Microstructure and properties of transparent glass-ceramics

Part 1 *The microstructure of spinel transparent glass-ceramics*

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The variation of the microstructure with heat-treatment of transparent glass-ceramics based on the $ZnO–Al_2O_3–SiO_2$ system has been investigated using X-ray diffraction and transmission electron microscopy. The principal crystalline phase was found to be $ZnAl_2O_4$, gahnite, when a minimum amount of nucleating agent, ZrO_2, was present. The dependence of mean particle size, volume fraction and mean crystal spacing on the heat-treatment was also studied. It was found that the microstructural parameters were relatively sensitive to the time at the crystallization temperature of 950° C.

1. Introduction

Glass-ceramics are polycrystalline materials produced by the controlled nucleation and crystallization of special glass compositions. The preparation of a satisfactory glass-ceramic depends on devitrifying or crystallizing a suitable glass composition under strictly controlled conditions in order to provide a closely interlocking microcrystalline structure and a smooth uncrazed surface. In order to do this it has generally been necessary to include in the glass a material which will provide nuclei for subsequent crystal growth or control of crystal formation in such a manner that many crystals of the desired form grow simultaneously in the glass.

For the most part, glass-ceramics are non-transparent, i.e. opaque. However, a number of glass-ceramics containing not less than two crystalline phases have been prepared which are transparent, due to the absence of voids, and also due to the small crystal size and the absence of light scattering at the crystal boundaries which require good matching between the indices of refraction for the crystals and glassy phase [1].

The present paper reports upon the variation of the microstructure of zirconia-nucleated glass-ceramics derived from the $ZnO–Al_2O_3–SiO_2$ system as a function of time at the crystallization temperature. Subsequent papers will describe the relationships between physical properties and microstructure, and also a process of monitoring the crystallization process by electron spin resonance.

2. Materials and methods

The composition of the glasses studied are shown in Table I. Glass 1 has been previously studied by Beall and Duke [1]. All glasses were made up from batch materials of greater than 99.6% purity. The glasses were prepared from Brazilian quartz, ground so as to pass through a 30 mesh sieve, aluminium oxide, zinc oxide, magnesium oxide, calcium oxide (or calcium carbonate), barium oxide, and zirconium dioxide.

The starting materials were thoroughly dried, weighed and mixed in a rotary ball-mill for two hours. The batch was melted in a platinum crucible at 1650° C in an electrically heated furnace until bubble-free, quenched in 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 glasses were melted for approximately 24 h and poured into slabs on a cast iron plate coated with a graphite suspension to prevent adhesion of the glass. The glasses were annealed at 780° C and subsequently heat-treated in static air in an electric furnace, and rapidly cooled to room temperature at the end of the heat-treatment period.

The microstructure of the glass-ceramics was studied using a JEM 200 transmission electron microscope. Crystalline phases were identified by the conventional X-ray diffraction technique. For microscopy the method of ion-beam machining was used which proved to be more successful than carbon replication or fragmentation for the study of glass-ceramics where the crystals present are extremely small (less than 50 nm). Preliminary thinning was performed by cutting 3 mm diameter cylinders from a bulk sample using an ultrasonic drill with a stainless steel tip fed with 220 mesh Carborundum powder. The cylinders were subsequently sliced into discs, approximately 250 μm in thickness, on a diamond saw. The discs were then heat-treated at the required temperature for the required time. The discs were thinned by abrading them with a stream of alumina particles carried in nitrogen. The sample was held by the edges, and the jet of gas-borne particles allowed thinning of the centre of both sides of the disc. Thinning was complete when a small perforation occurred through the disc. The samples were then thoroughly washed with trichloroethylene, ether and methanol and transferred to an Edwards ion-beam machining equipment. The discs were mounted at an angle of 20° and sputtering with argon ions was continued for a period of 8 h. Suitable operating conditions were found to comprise a total current density of 100 μA cm^{-2} at a voltage of 6 kV. Finally the specimen was thinned at an angle of 10°, with liquid nitrogen cooling the specimen to prevent sputtering atoms re-depositing on it. This was continued for about 4 to 6 h until interference fringes could be observed in an optical microscope. The samples were thoroughly washed and dried, and the area around the hole, but not the thinned area, was coated with a conducting paint to prevent charging in the electron beam. The sample was then ready for transfer into the electron microscope.

The volume fractions of the crystalline phases in the glass-ceramics were evaluated by a point-counting technique [2], on positive prints of the electron micrographs. It should be pointed out that the measurements were carried out on transmission electron micrographs of thin foils and not two-dimensional sections, as strictly required. Nevertheless, the measurements obtained still provide a reliable guide to the relationship between the properties and the microstructure of the materials, which will be reported in a subsequent paper. For point-counting a grid consisting of 324 holes was constructed from Perspex by drilling a regular array of 1 mm holes at 1 cm intervals.

The average particle size was measured using a Carl-Zeiss Particle Size Analyser. The mean free path, λ, was also determined [3]. This parameter may be considered as the mean interparticle spacing. It is defined as

$$\lambda = d\left[\frac{1-(V_f)_\alpha}{(V_f)_\alpha}\right]$$

where $(V_f)_\alpha$ is the volume fraction of α-particles and d is the mean particle size.

TABLE I Glass compositions (wt %).

Glass	SiO_2	Al_2O_3	ZnO	MgO	CaO	BaO	ZrO_2
1	64.8	17.6	5.6	4.6	–	–	7.4
2	63.6	17.3	5.5	4.5	–	–	9.1
3	63.6	17.3	5.5	–	4.5	–	9.1
4	63.6	17.3	5.5	–	–	4.5	9.1

3. Microstructure: X-ray diffraction and transmission electron microscopy

The initial glass 1 was prepared from a composition by Beall and Duke [1]. The heat-treatment by Beall and Duke of this glass at 800° C for 4 h, produced the initial crystalline phase of tetragonal zirconia, followed by the growth of a spinel solid solution, $MgAl_2O_4$ s.s. after a crystallization treatment of 950° C for 4 h.

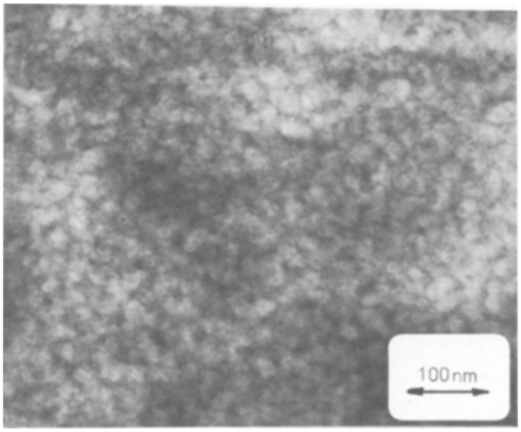

Figure 1 Transmission electron micrograph of phase separation in annealed glass 1.

This was not the case for the final crystalline species when glass 1 prepared in the present study was subjected to the same heat-treatment. During the annealing process a phase separation occurs which is believed to be caused by the diffusion of zirconium ions into zirconium rich regions, as studied by Neilson [4–6]. Fig. 1 shows the phase separation in the annealed glass. The initial minor crystalline phase after the nucleation heat-treatment at 800° C for one hour, was tentatively assigned as tetragonal zirconia, since there was very close agreement of the observed *d*-spacings of the most intense reflections with those reported in the ASTM card index for this structure, but there were differences in the relative intensities of these reflections from those reported. Fig. 2 shows the tetragonal zirconia nuclei present. After the crystallization heat-treatment of 950° C for 4 h, a β-quartz s.s. phase was identified. Fig. 3 shows these β-quartz crystals.

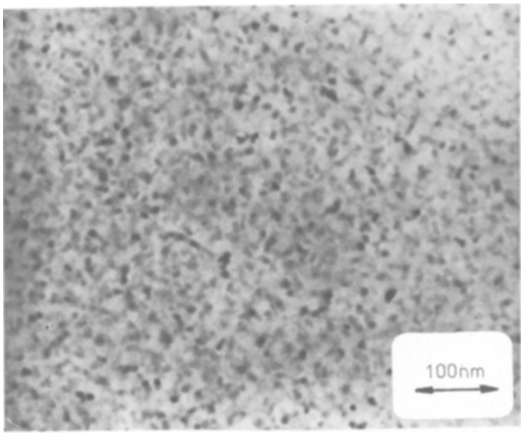

Figure 2 Transmission electron micrograph of tetragonal zirconia nuclei in nucleated glass 1 at 800° C for 4 h.

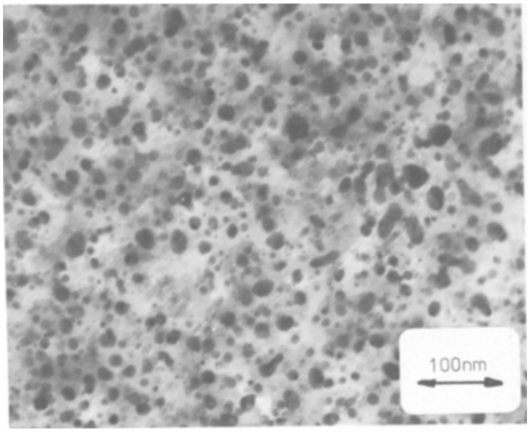

Figure 3 Transmission electron micrograph of β-quartz crystals in fully crystallized glass 1 at 800° C for 4 h and 950° C for 4 h.

To establish a microstructure comprising spinel ($MgAl_2O_4$) as the main crystalline phase the composition of glass 1 was changed by introducing more MgO at the expense of SiO_2 and then more Al_2O_3 also at the expense of SiO_2. X-ray analyses of these glasses, however, showed the same results as for glass 1 i.e. after a heat-treatment of 800° C for 4 to 6 h and 950° C for 4 h tetragonal zirconia and β-quartz s.s. crystals were formed.

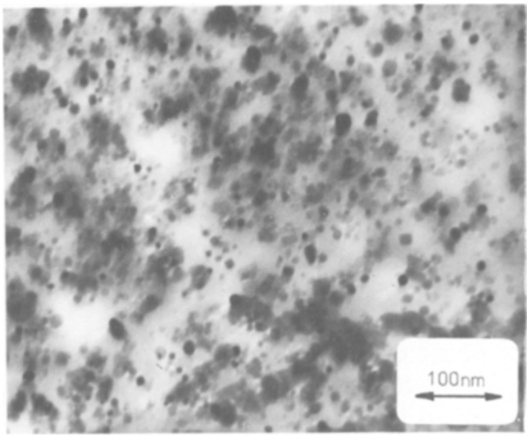

Figure 4 Transmission electron micrograph of gahnite crystals in fully crystallized glass 2 at 800° C for 4 h and 950° C for 4 h.

Further attempts to produce the spinel phase by heat-treating the glasses at 800° C and then at different crystallization temperatures of 950, 975 and 1000° C for periods of 4 to 6 h still resulted in the formation of a β-quartz s.s.

It was concluded, therefore, that for the particular composition, the only crystalline species formed were tetragonal zirconia and a β-quartz s.s., and that the temperatures necessary for nucleation and crystal growth were 800 and 950° C respectively.

The next step was to investigate the role of the nucleating agent ZrO_2. Nucleation in these materials is supposedly accomplished by the addition of zirconia which produces uniform internal nucleation. Even though in glass 1 tetragonal zirconia crystals were present, it was thought that maybe too few nuclei were available to promote the growth of spinel crystals and that the presence of the zirconia was essential for the growth of these spinel crystals.

Glass 2 was subsequently prepared which contained 9.1% ZrO_2 (Table I). The glass was given the same heat-treatment as glass 1 i.e. 800° C for 4 h and 950° C for 4 h. X-ray diffraction showed that during the nucleation stage fine crystals of tetragonal zirconia were present, due to the broad reflections obtained. After the crystallization heat-treatment spinel-type crystals were present, as can be seen in Fig. 4. A glass prepared with 8.3 wt% ZrO_2 still showed the same β-quartz phase as glass 1.

It can be seen that for the particular system under study, there appears to be a minimum amount of ZrO_2 needed to induce the growth of spinel crystals. This amount is around 9% ZrO_2.

At this stage, it could not be deduced whether this spinel phase was spinel s.s. $(Zn, Mg)Al_2O_4$ or gahnite $ZnAl_2O_4$, since both give very similar X-ray diffraction reflections. A glass-ceramic known to have gahnite as the main phase, according to Beall and Duke [1] was prepared. The diffraction of this glass produced exactly the same reflections as glass-ceramic 2. This result was, however, still inconclusive. To determine whether the dominant phase was a spinel s.s. or gahnite, the assumption was made that if the MgO in glass 2 took part in crystal formation to produce spinel $MgAl_2O_4$, then a completely different phase would be obtained on replacement of the MgO by another alkaline earth metal oxide. If, however, the MgO did not take part in the crystal formation, with the Mg^{2+} ion acting as an interstitial ion in the residual glass phase, then gahnite would be formed.

Glasses 3 and 4 were prepared (Table I). The same heat-treatments were employed as for previous glasses; 800° C for 4 h and 950° C for 4 h. The same X-ray diffraction reflections were produced as for glass 2, indicating that the main crystalline phase was in fact gahnite. Fig. 5 shows the presence of a small number of tetragonal zirconia crystals with a very small background phase separation. Fig. 6 shows the fully nucleated glass and Fig. 7 shows the fully crystallized glass-ceramic containing gahnite crystals.

The gahnite crystals initially took the form of spherical particles (as was seen in glass 2) but structural changes caused the particles to take on a rod-shaped formation after a one hour crystallization treatment. Fig. 8 shows gahnite crystals formed in glass-ceramic 4. Again the structural appearance of these crystals seems to be slightly different.

The alkaline earth metal oxides present in all the glasses do not, therefore, take part in the crystal formation, and the ions must reside in interstitial positions in the glass network. X-ray patterns were taken of the complete nucleation stage, and it was noticed that tetragonal zirconia appeared within a few minutes of the glass being held at 800° C, and was even present after annealing of the glass. Since the nucleation of glass 3 appeared quite spontaneously, it was wondered whether gahnite crystals would grow when the temperature was taken directly to 950° C, through the nucleation temperature of 800° C. Fig. 9 shows the micrograph of glass 3 heat-treated at 950° C only. X-ray diffraction patterns showed exactly the same reflections as for the two stage treated specimens and electron microscopy shows no difference in the microstructure. Again it can be seen that rod-shaped gahnite crystals are present.

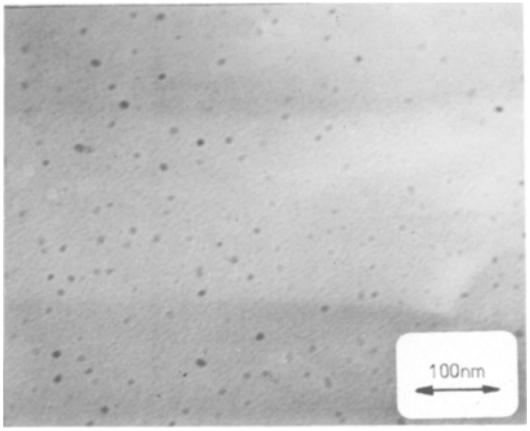

Figure 5 Transmission electron micrograph of tetragonal zirconia nuclei in annealed glass 3.

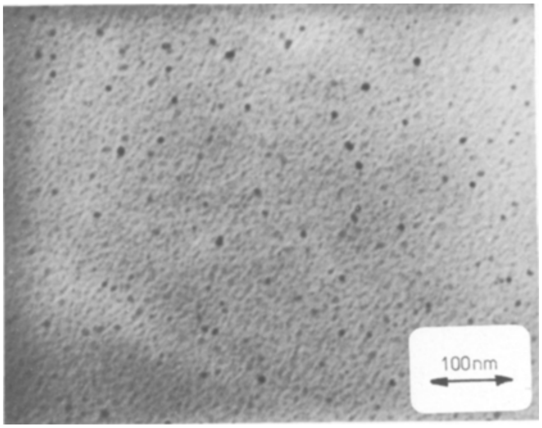

Figure 6 Transmission electron micrograph of tetragonal zirconia nuclei in nucleated glass 3 at 800° C for 4 h.

4. Microstructural parameters

The most detailed investigation of microstructural parameters, namely volume fraction, particle size and mean free path was performed on glass 3.

TABLE II Microstructural parameters of glasses 1, 2, 3 and 4 after various heat-treatments.

Glass-ceramic	Particle size (nm)	Volume fraction (%)	Mean free path (nm)
1 – 800° C 4 h – 950° C 3 h	10.0 ± 1.5	–	–
1 – 800° C 4 h – 950° C 4 h	12.5 ± 2.0	34 ± 2	–
2 – 800° C 4 h – 950° C 4 h	10.0 ± 1.5	22 ± 2	–
4 – 800° C 4 h – 950° C 4 h	15.5 ± 8	22 ± 2	–
3 – annealed 780° C 2 h	5.0 ± 0.5	4.0 ± 0.8	–
3 – nucleated 800° C 1–4 h	7.0 ± 0.8	9.0 ± 1.0	–
3 – 800° C 4 h – 950° C 12 min	8.0 ± 1.0	10.0 ± 1.0	–
3 – 800° C 4 h – 950° C 30 min	8.5 ± 1.5	11.0 ± 1.0	–
3 – 800° C 4 h – 950° C 1 h	19.5 ± 2.5	12.0 ± 2.0	143 ± 7
3 – 800° C 4 h – 950° C 2 h	21.0 ± 3.0	14.0 ± 2.0	129 ± 7
3 – 800° C 4 h – 950° C 3 h	22.0 ± 4.0	17.0 ± 2.5	107 ± 8
3 – 800° C 4 h – 950° C 4 h	23.0 ± 4.0	18.0 ± 1.8	105 ± 8
3 – 800° C 4 h – 950° C 5 h	24.0 ± 4.0	20.0 ± 1.5	96 ± 8
3 – 800° C 4 h – 950° C 6 h	28.0 ± 4.0	21.0 ± 1.5	105 ± 8

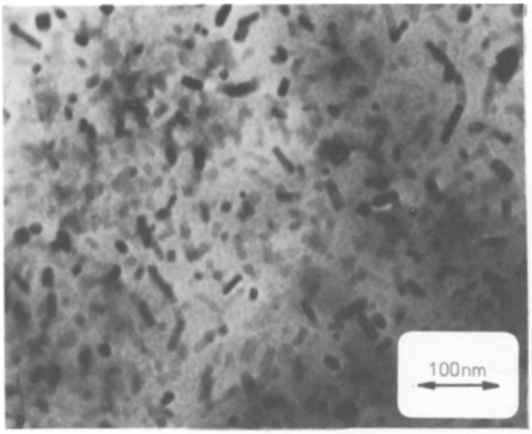

Figure 7 Transmission electron micrograph of gahnite crystals in fully crystallized glass 3 at 800° C for 4 h and 950° C for 6 h.

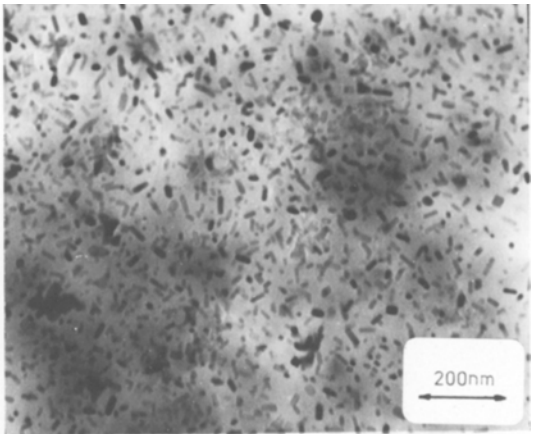

Figure 9 Transmission electron micrograph of gahnite crystals in glass 3 heat-treated at 950° C for 6 h.

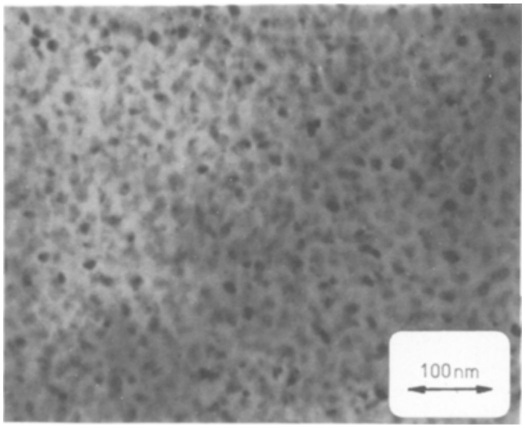

Figure 8 Transmission electron micrograph of gahnite crystals in fully crystallized glass 4 at 800° C for 4 h and 950° C for 4 h.

Table II summarizes the complete analysis on glass-ceramics 1, 2, 3 and 4.

In measuring particle sizes the main difficulty arose in measuring the average size of the rod-shaped particles in glass-ceramic 3. Since the rod-shaped particles are randomly oriented, measuring their lengths on a two-dimensional micrograph could indicate the projection of long particles at various angles. Since a small percentage of particles could be expected to lie in a plane of the micrograph, these would indicate the maximum size of particles present in the glass-ceramics. Absolute values of particles size were impossible to calculate, the relative average length of the particles resulting from each treatment were determined.

The variation of particle size, d, with heat-treatment for glass-ceramic 3 is shown in Fig. 10. An initial size of 5 nm after a 30 min crystallization heat-treatment increases rapidly to 20 nm after a 1 h treatment and then increases slowly to 22 nm after the 6 h treatment.

Fig. 11 shows the variation of volume fraction, V_f, with heat-treatment. Here a steady increase is noticeable from 12% after the 1 h treatment to 20% after the 6 h treatment, where the volume fraction appears to stabilize. Measurements of particle size and volume fraction on samples heat-treated for 24 h at the crystallization temperature showed no change from measurements performed on samples treated for 6 h.

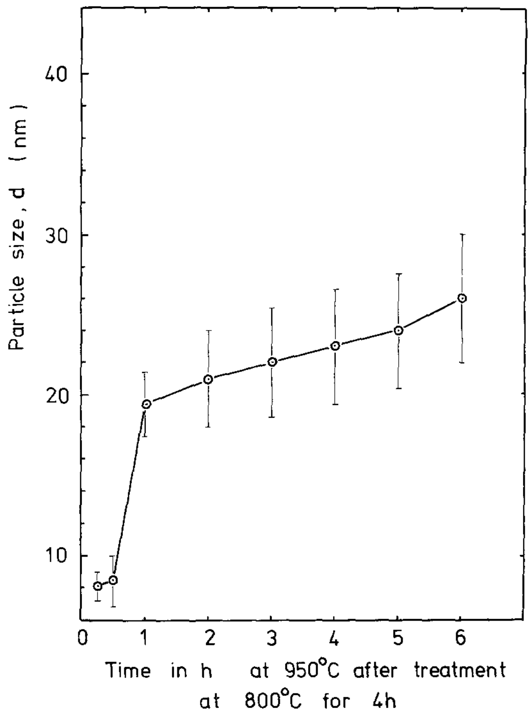

Figure 10 The variation of particle size, d, with heat-treatment for glass-ceramic 3.

For mean free path or intercrystalline spacing measurements of rod-shaped particles in glass-ceramic 3, the value of mean particle size was taken to be the average particle length. Fig. 12 shows the variation of mean free path, λ, as a function of heat-treatment. The mean free path decreases until a minimum occurs after the 5 h treatment, indicating that maximum crystallization had occurred.

5. Glass appearance

All glasses when poured, had good transparency. The glass-ceramics varied in transparency; glass-ceramic 2 was translucent rather than transparent. Glass-ceramic 1 with the β-quartz s.s. phase produced a very good transparent material, as did glass-ceramics 3 and 4, which had the gahnite phase. Obviously the excellent transparency in these materials is due to the extremely small size of the crystals constituting the glass-ceramics. The overall transparency of the glasses and glass-ceramics in the i.r. region and visible region will be discussed in a subsequent paper.

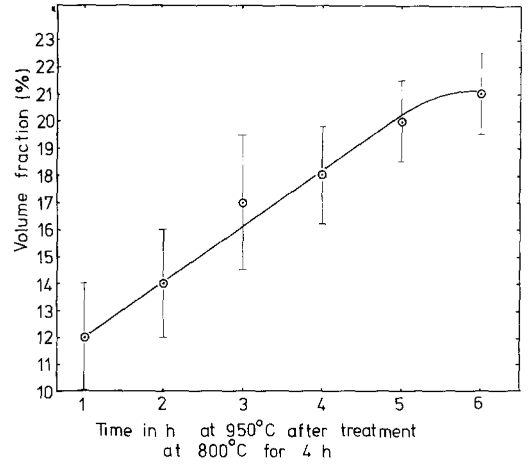

Figure 11 The variation of volume fraction, V_f, with heat-treatment for glass-ceramic 3.

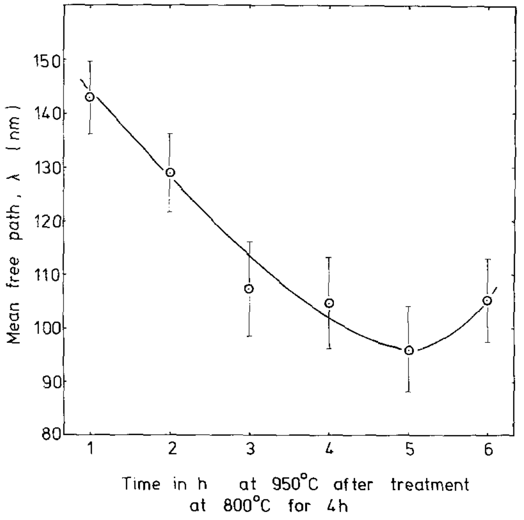

Figure 12 The variation of mean free path, λ, with heat-treatment for glass-ceramic 3.

6. Discussion and conclusions

The investigation showed that zirconia-nucleated glass-ceramics derived from the $ZnO-Al_2O_3-SiO_2$ system could be converted to transparent glass-ceramics comprising very small crystals of β-quartz if less than 9 wt % ZrO_2 is present and gahnite if more than 9% is present. Alkaline earth metal oxides present in these materials have been shown not to take part in crystal formation and therefore to be incorporated in the residual glass phase. The optimum heat-treatment for the development of a fully crystallized glass-ceramic was shown to comprise a nucleation heat-treatment of 800° C for 4 h and a crystallization heat-treatment of 950° C for 4 to 6 h.

Investigations of microstructural parameters as a function of heat-treatment time showed that the mean intercrystalline spacing, λ, was as sensitive to heat-treatment as particle size and volume fraction. For glass-ceramic 3 a distinct minimum occurred for a heat-treatment of 950° C for 5 h.

Particle size analysis of the glass-ceramics showed that the overall grain size did not exceed 30 nm. Similarly, the volume fraction of crystalline phases was low, not exceeding 25% for glass-ceramics containing gahnite.

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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