

# The Electron Microscopic and X-ray Diffraction Examination of a Lithium Zinc Silicate Glass-Ceramic

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This paper describes a crystallographic study of an experimental glass-ceramic. The crystallisation of the glass has been followed by electron microscopy, both of bulk specimens and of thin films, and by electron and X-ray diffraction.

Comparisons have been made between the structures observed in the bulk samples and the thin films. The importance of microstructure in determining the mechanical strength of the glass-ceramic has been shown and the effect of heat treatment on the microstructure demonstrated.

## 1. Introduction

Glass-ceramics produced by the controlled devitrification of special glasses characteristically possess an extremely fine-grained structure, and therefore, in their study, increasing use is being made of the electron microscope. Replica techniques, in which a polished and etched sample of the block material is examined, have given useful results on the crystallisation mechanisms of these materials, but more recently thin-film studies have been undertaken by several workers in an attempt to obtain a fuller understanding of the nucleation and crystallisation processes. The present paper is concerned with the study of an experimental glass-ceramic by electron microscopy, both of bulk samples and of thin films, by electron diffraction and by X-ray diffraction.

## 2. Composition and Heat Treatment of the Glass

The weight percentage composition of the glass was: 78.1, SiO<sub>2</sub>; 12, Li<sub>2</sub>O; 2.5, K<sub>2</sub>O; 5.5, ZnO; 1.9, P<sub>2</sub>O<sub>5</sub>. The glass was available as cast, ½ in. cubes and also film approximately 100 μm thick, blown from the melt at 1100°C.

Eight of the cubes were heat treated as follows:

As cast (i.e. not heat treated)

480°C for 1 h

480°C for 1 h followed by 600°C for 1 h

480°C for 1 h followed by 600°C for 1 h followed by 800°C for 1 h

500°C for 1 h

500°C for 1 h followed by 600°C for 1 h

500°C for 1 h followed by 600°C for 1 h followed by 800°C for 1 h

500°C for 1 h followed by 600°C for ½ h followed by 800°C for 1 h.

The heat-treated cubes were sectioned and polished by conventional metallographic techniques to a final, 1 μm, diamond finish and were etched in a 2% HF solution for 10 sec. Direct, carbon replicas self-shadowed at 2:1 were prepared by evaporation and were removed from the etched surfaces by flotation in distilled water to which a few drops of the etching solution had been added. The replicas were finally washed in distilled water. The blown films in the original condition were chemically thinned to a thickness of about 2500 Å units using a 5% HF, 2% HCl, 93% H<sub>2</sub>O solution [1]. After thinning, the films were collected on platinum supports and subjected to the same heat treatments as the block samples.

The electron microscopic examination of the

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replicas and of the thin films was carried out in a Siemens Elmiskop 1 electron microscope, as also was the electron diffraction, using the "selected area" technique.

X-ray diffraction examination of samples from the heat-treated cubes was performed in a 9 cm powder camera using  $\text{CuK}\alpha$  radiation.

### 3. Results

#### 3.1. X-ray Diffraction

The X-ray diffraction results are given in table I.

No trace of crystallinity was detected in the as-cast sample nor in those heat treated for 1 h at  $400^\circ\text{C}$  and at  $500^\circ\text{C}$ . All the samples heat-treated at  $600^\circ\text{C}$  gave a strong lithium di-silicate pattern with no other crystalline phases present. All the samples heat-treated at  $800^\circ\text{C}$  gave strong patterns of lithium di-silicate and silica together with a possible trace of lithium zinc silicate, but the form of silica present was not the same in all samples. In the samples heat-treated (i)  $480^\circ\text{C}/1\text{h} - 600^\circ\text{C}/1\text{h} - 800^\circ\text{C}/1\text{h}$  and (ii)  $500^\circ\text{C}/1\text{h} - 600^\circ\text{C}/\frac{1}{2}\text{h} - 800^\circ\text{C}/1\text{h}$ , the form of silica present was cristobalite, whilst in the remaining sample heat-treated  $500^\circ\text{C}/1\text{h} - 600^\circ\text{C}/1\text{h} - 800^\circ\text{C}/1\text{h}$ , the greater part of the silica present was quartz with only a small amount of cristobalite showing.

#### 3.2. Electron Microscopic Examination

##### 3.2.1. As-Cast Glass

The structure of this specimen as observed by replica techniques consisted of numerous, rounded areas or "globules" up to  $500\text{ \AA}$  in diameter set in a more readily etching matrix (fig. 1). The structure observed by transmission electron microscopy of thin films was similar to that observed in the replicas (fig. 2). In the thin films, the globules appeared to vary in size up to about  $1000\text{ \AA}$ .

No electron diffraction pattern could be obtained from the thin films.

##### 3.2.2. $480^\circ\text{C}/1\text{h}$

No difference was detected between the structure of this specimen and that of the as-cast specimen, the globule structure again being present. This was also true of the thin films, which again gave no electron diffraction pattern.

##### 3.2.3. $500^\circ\text{C}/1\text{h}$

The structure observed in replicas of block specimens subjected to this heat treatment appeared similar to that of the as-cast sample

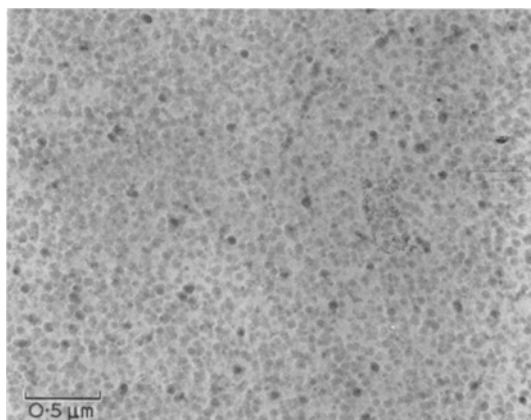


Figure 1 Block sample as cast; etched 15 sec in 2% HF.

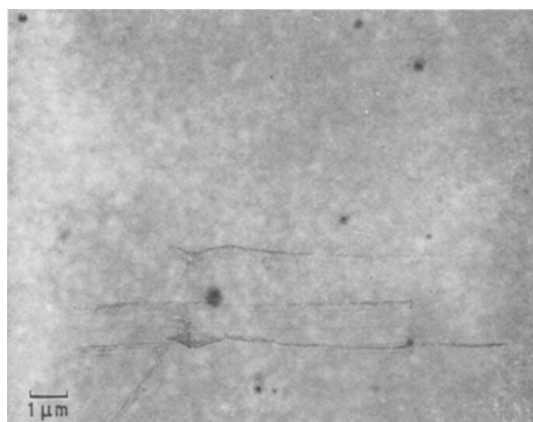


Figure 2 Thin film prior to heat treatment.

and the sample heat-treated at  $480^\circ\text{C}$  for 1 h. The globule structure observed in this specimen, however, appeared slightly more pronounced than in the other two samples (fig. 3). No evidence of crystallisation was observed in this specimen nor did it give any X-ray diffraction pattern. In the thin films heat-treated at  $500^\circ\text{C}$  for 1 h, however, crystallisation had commenced, the structure observed consisting of rather indistinct, light and dark areas randomly oriented (fig. 4). Selected-area electron diffraction from these crystals showed them to be lithium di-silicate.

##### 3.2.4. $480^\circ\text{C}/1\text{h} - 600^\circ\text{C}/1\text{h}$

The structure of this specimen as observed from replicas consisted of numerous, needle-shaped crystals containing well-defined globules. These crystals were set in a background containing a higher density of globules which were not so well defined and only half the size of those within the

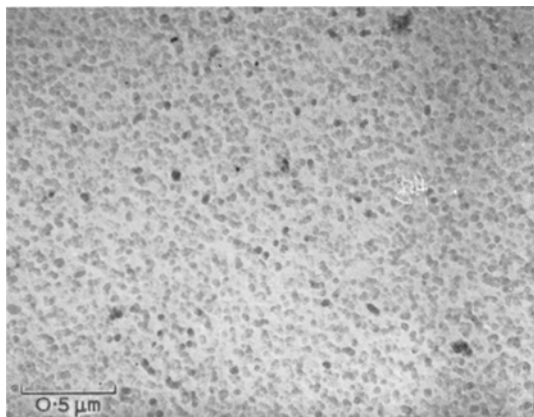


Figure 3 Block sample heat-treated for 1 h at 500°C; etched 10 sec in 2% HF.

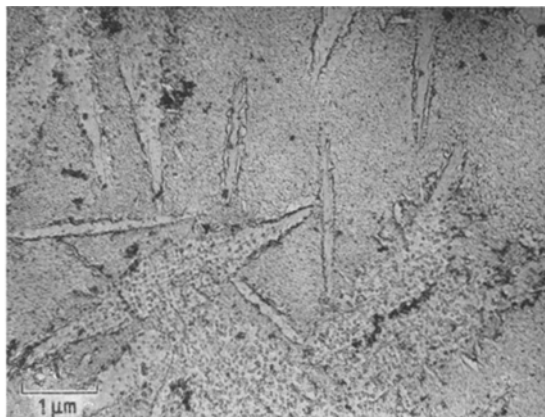


Figure 5 Block sample heat-treated for 1 h at 480°C and 1 h at 600°C; etched 10 sec in 2% HF.

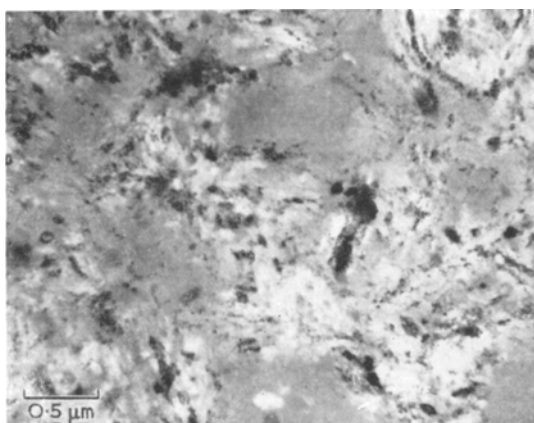


Figure 4 Thin film heat-treated for 1 h at 500°C.

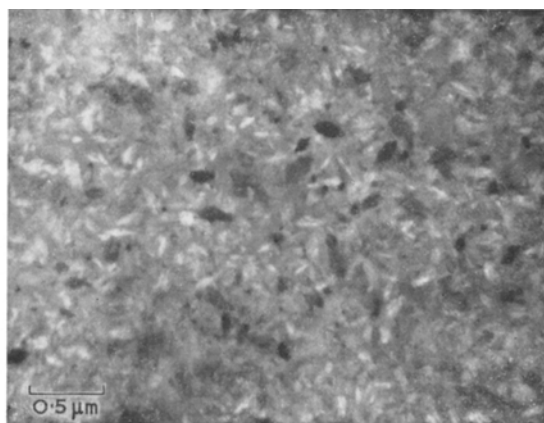


Figure 6 Thin film heat-treated for 1 h at 480°C and 1 h at 600°C.

needles, being 200 to 300 Å in diameter. The needle-shaped crystals, shown by X-ray diffraction to be lithium di-silicate, formed aggregates with a radial tendency. Towards the tips of the needle-like crystals, the density of the globules was very low and the needles appeared to contain longitudinal striations. The amount of crystalline material present in the specimen was approximately 50 to 60% of the total volume (fig. 5). The size of the needle-shaped crystals in this specimen varied up to about  $\frac{1}{2}$  to 1 μm wide by 7 to 8 μm long.

The structure observed in comparable thin films consisted of masses of lozenge-shaped crystals embedded in a background of non-crystalline material (fig. 6). The size of the lozenge-shaped crystals appeared to vary slightly but was approximately 2000 Å long by 1000 Å wide at their widest point. These lozenge-shaped crystals frequently appeared to occur in star-

like aggregates, and were rather similar in morphology to the crystals observed in the block sample.

The lozenge-shaped crystals observed in this specimen were identified by electron diffraction as lithium di-silicate.

### 3.2.5. 500°C/1 h – 600°C/1 h

Block samples of this specimen were found to consist of aggregates of needle-like crystals forming an almost continuous network with large, relatively structureless areas enclosed within the network structure. The network of aggregates of crystals, lithium di-silicate according to X-ray diffraction, showed very few striations but contained a considerable number of globules which were well defined. Towards the edges of the structureless regions, a smaller number of globules was observed, indicating

that migration of the globules was occurring by some mechanism (fig. 7). These large, structureless patches, presumably residual glass, occupied approximately 40% of this structure and were approximately 4  $\mu\text{m}$  in diameter. The average size of the acicular crystals was approximately 5  $\mu\text{m}$  long by 1  $\mu\text{m}$  wide; some crystals up to 8  $\mu\text{m}$  long were also observed.

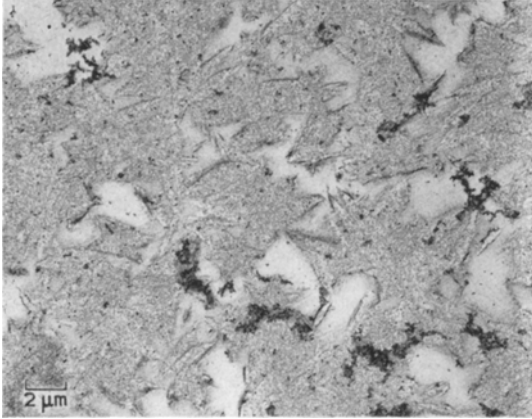


Figure 7 Block sample heat-treated for 1 h at 500° C and 1 h at 600° C; etched 10 sec in 2% HF.

Examination of thin films showed their structure to consist of lozenge-shaped crystals of lithium di-silicate surrounded by some residual glass (i.e. somewhat similar to the morphology of the block samples but with crystals of a lower aspect ratio). Crystal-size differences were noticed between specimens prepared on separate occasions, the difference being as much as a factor of 2. This discrepancy was believed to be due to film thickness. The lozenge-shaped crystals were found to vary in size from 3000 to 6000 Å and appeared striated parallel to their length (fig. 8), but showed no clear evidence of the globule structure present in the block sample.

### 3.2.6. 480° C/1 h - 600° C/1 h - 800° C/1 h

The structure of the block sample of this material consisted of a network of striated, lithium di-silicate crystals varying in size from about 1 to 3  $\mu\text{m}$  long by  $\frac{1}{4}$  to 1  $\mu\text{m}$  wide. Dispersed throughout this network were small, rounded crystals of cristobalite approximately 0.2 to 0.5  $\mu\text{m}$  in diameter and frequently forming aggregates. Some residual glass was associated with this cristobalite (fig. 9).

The structure of the thin film bore similarities to that of the block sample and was found to

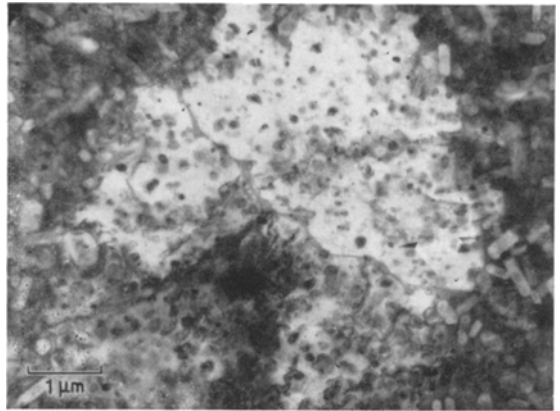


Figure 8 Thin film heat-treated for 1 h at 500° C and 1 h at 600° C.

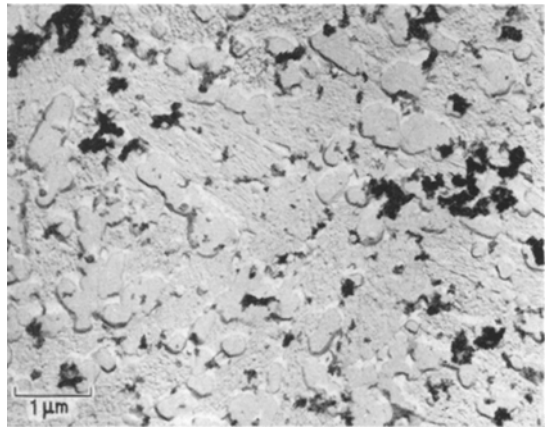


Figure 9 Block sample heat-treated for 1 h at 480° C, 1 h at 600° C, and 1 h at 800° C; etched 10 sec in 2% HF.

consist of relatively large, featureless areas in a background of randomly oriented, lath-shaped crystals (fig. 10).

The large, relatively featureless areas were up to 10  $\mu\text{m}$  in diameter and were found to consist of polycrystalline aggregates, the size of the individual crystals being approximately 2  $\mu\text{m}$  in diameter (fig. 11). A small amount of a phase, believed from its electron-scattering behaviour to be residual glass, was also observed at the grain boundaries within these polycrystalline aggregates. On the basis of single-crystal, electron diffraction patterns obtained from the individual crystals of the aggregates, it is thought that they may be tridymite, but this interpretation was not unambiguous. The background structure present in this specimen consisted of a network of interpenetrating, lath-shaped crystals varying in size up to 0.6  $\mu\text{m}$  long by 0.2  $\mu\text{m}$  wide. These

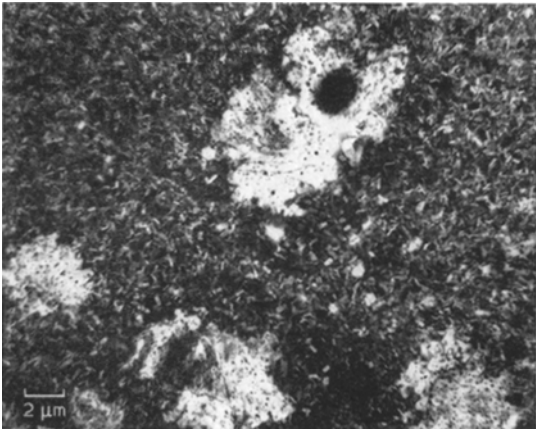


Figure 10 Thin film heat-treated for 1 h at 480° C, 1 h at 600° C, and 1 h at 800° C.

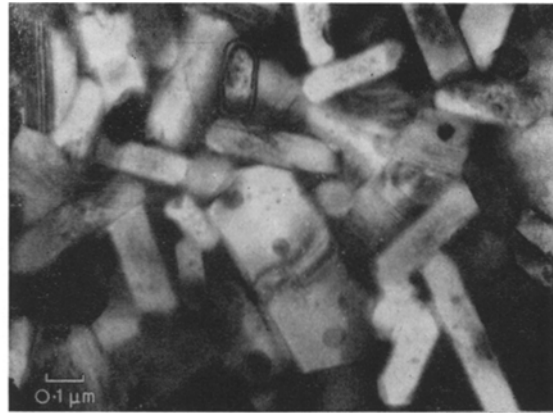


Figure 12 Thin film heat-treated for 1 h at 480° C, 1 h at 600° C, and 1 h at 800° C.

crystals appeared randomly orientated, and many were striated in a direction parallel to the major axis (fig. 12). Fig. 12 also shows that in some crystals there are alternate, dark and light bands or strips parallel to both the major and the minor axes of the crystals. These features are believed to be due to twinning of the crystals. Electron diffraction patterns obtained from these lath-shaped crystals in the matrix showed that they were lithium di-silicate.

comparatively resistant to etching, possibly quartz; the other phase was more readily etched, and is believed to be a residual glass phase. The quartz crystals varied in size from  $\frac{1}{4}$  to 2  $\mu\text{m}$  in diameter and were rather irregular in shape. Some small, rounded areas 1000 to 3000 Å in diameter which were scattered throughout the structureless quartz may be entrapped pockets of residual glass (fig. 13).

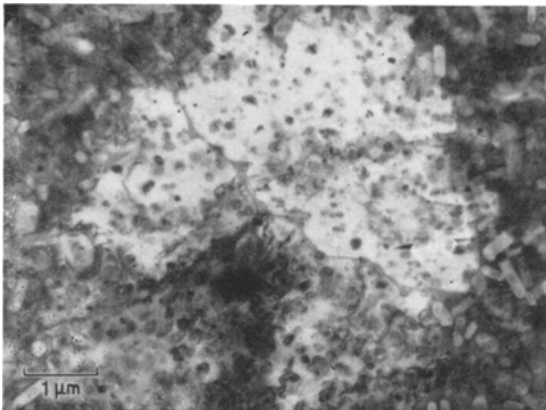


Figure 11 Thin film heat-treated for 1 h at 480° C, 1 h at 600° C, and 1 h at 800° C.

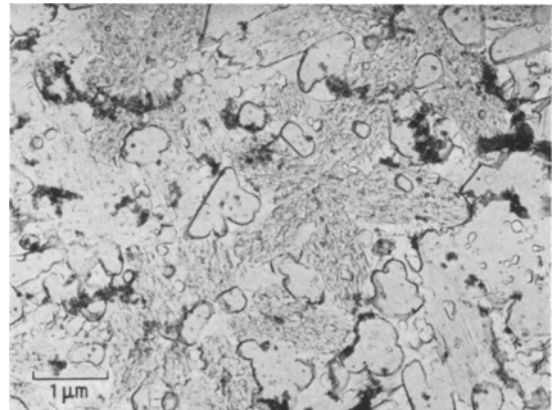


Figure 13 Block sample heat-treated for 1 h at 500° C, 1 h at 600° C, and 1 h at 800° C; etched 10 sec in 2% HF.

### 3.2.7. 500° C/1 h – 600° C/1 h – 800° C/1 h

The structure observed in replicas of this material consisted of an almost continuous matrix of lithium di-silicate surrounding a considerable number of irregularly shaped areas of duplex structure. In these duplex areas, one phase was

Two crystalline phases were observed in the thin films subjected to this heat-treatment cycle, the structure consisting of relatively large, clear patches embedded in a background structure of randomly oriented, lath-shaped crystals, identified by electron diffraction as lithium di-silicate (fig. 14). The structure of this thin film was similar to that observed in the specimen

heat-treated  $480^{\circ}\text{C}/1\text{ h} - 600^{\circ}\text{C}/1\text{ h} - 800^{\circ}\text{C}/1\text{ h}$ , with the exception that a definite increase in the number of clear areas was observed in this specimen, and the lath-shaped crystals appeared to have a much greater length-to-width ratio than those previously observed. The average size of the lath-shaped crystals was  $0.6\ \mu\text{m}$  long by  $0.1\ \mu\text{m}$  wide giving an aspect ratio of 6 as opposed to 3 in the previous sample.

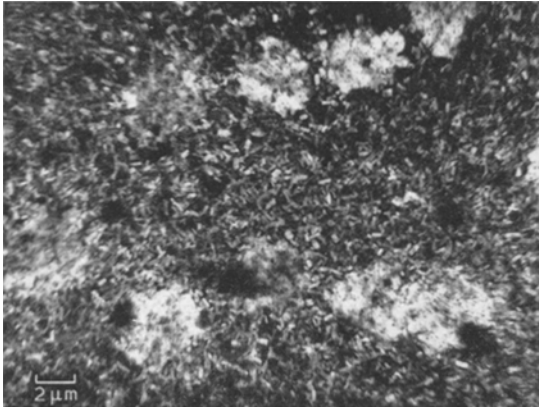


Figure 14 Thin film heat-treated for 1 h at  $500^{\circ}\text{C}$ , 1 h at  $600^{\circ}\text{C}$ , and 1 h at  $800^{\circ}\text{C}$ .

The clear areas in this specimen were found to consist of numerous grains, probably of tridymite (fig. 15). These polycrystalline aggregates were very similar to those observed in the specimen heat-treated  $480^{\circ}\text{C}/1\text{ h} - 600^{\circ}\text{C}/1\text{ h} - 800^{\circ}\text{C}/1\text{ h}$ , the individual grains being approximately  $1.5\ \mu\text{m}$  in diameter, and some residual glass remaining at the grain boundaries.

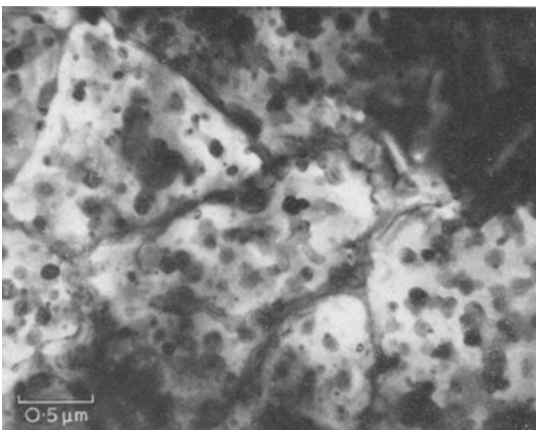


Figure 15 Thin film heat-treated for 1 h at  $500^{\circ}\text{C}$ , 1 h at  $600^{\circ}\text{C}$ , and 1 h at  $800^{\circ}\text{C}$ .

### 3.2.8. $500^{\circ}\text{C}/1\text{ h} - 600^{\circ}\text{C}/\frac{1}{2}\text{ h} - 800^{\circ}\text{C}/1\text{ h}$

The structure observed in direct, carbon replicas of this specimen were similar to those of the previous specimen, with the exception that the structureless areas were smaller, more numerous, and exhibited a more regular morphology in this specimen. The structure consisted of a continuous network of aggregates of lithium di-silicate crystals which, although showing a slight tendency towards being striated, appeared to consist mainly of masses of small nodules up to  $500\ \text{\AA}$  in diameter (fig. 16). It was not clear whether this nodule effect was some form of etch pitting or whether the crystals were made up of a large number of sub-grains in parallel orientation. Dispersed throughout this network were numerous, featureless areas, mainly at the interstices of the lithium di-silicate crystals. These areas were approximately  $0.2$  to  $0.8\ \mu\text{m}$  in diameter and probably consisted of cristobalite. They were generally set in more deeply etching material which is believed to have been residual glass (fig. 17).

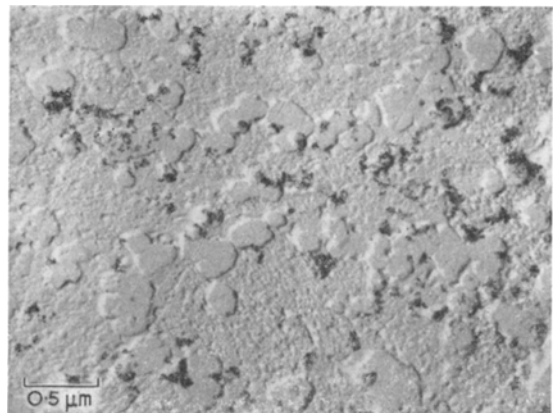


Figure 16 Block sample heat-treated for 1 h at  $500^{\circ}\text{C}$ ,  $\frac{1}{2}\text{ h}$  at  $600^{\circ}\text{C}$ , and 1 h at  $800^{\circ}\text{C}$ ; etched 10 sec in 2% HF.

The structure observed in the thin films subjected to this heat treatment consisted of large, clear areas embedded in a background structure of interpenetrating, lath-shaped crystals varying in size up to  $2\ \mu\text{m}$  long by  $\frac{1}{2}\ \mu\text{m}$  wide, as opposed to the  $0.6\ \mu\text{m}$  long by  $0.1\ \mu\text{m}$  wide crystals observed in the specimen heat-treated  $500^{\circ}\text{C}/1\text{ h} - 600^{\circ}\text{C}/1\text{ h} - 800^{\circ}\text{C}/1\text{ h}$ . A considerable number of crystals of hexagonal outline were present in the background structure interspersed with the lath-shaped crystals (fig. 18). These hexagonal-shaped crystals were  $0.3$  to  $0.8\ \mu\text{m}$

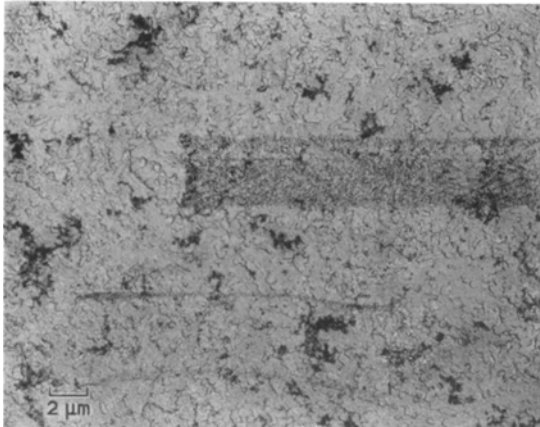


Figure 17 Block sample heat-treated for 1 h at 500° C, ½ h at 600° C, and 1 h at 800° C; etched 10 sec in 2% HF.

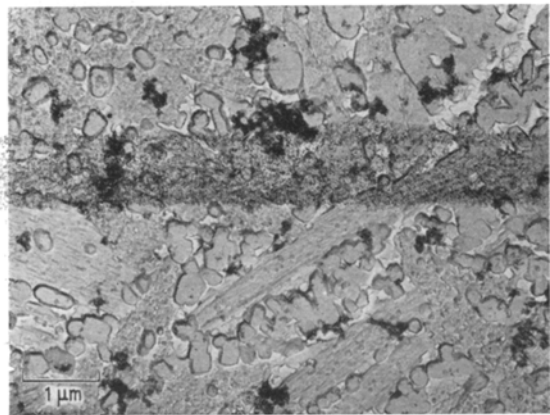


Figure 19 Block sample heat-treated for 1 h at 500° C, ½ h at 600° C, and 1 h at 800° C; etched 10 sec in 2% HF.

in diameter, and it is thought that they may be correlated with the smaller, structureless areas seen in the replicas from block samples as shown in fig. 19. A small amount of residual glass was still present at the boundaries of the lath-shaped crystals and some evidence of twinning occurring in these crystals can also be seen.

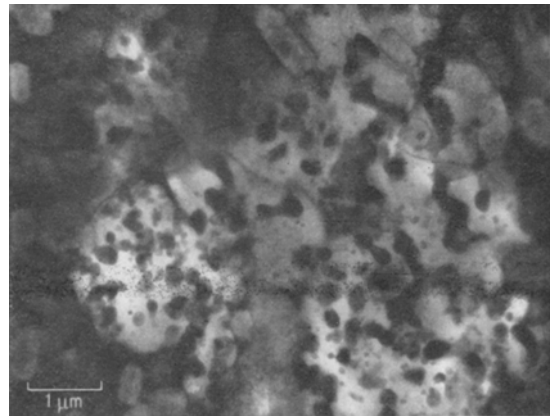


Figure 20 Thin film heat-treated for 1h at 500° C, ½ h at 600° C, and 1 h at 800° C.

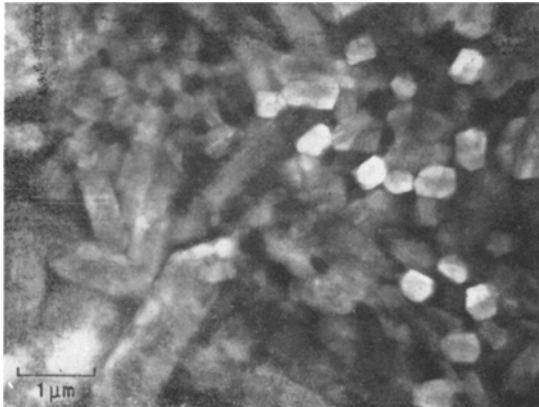


Figure 18 Thin film heat-treated for 1 h at 500° C, ½ h at 600° C, and 1 h at 800° C.

The large, clear areas in this specimen, as shown in fig. 20, consisted of polycrystalline aggregates as previously observed in high heat treatments. The individual grains, probably of tridymite, were of the same order of size as those previously observed, 1.5 μm diameter. The number of aggregates observed in this specimen however were fewer than in the high heat-treatment specimens discussed in the preceding section. This may be due to the occurrence of

some of the silica as smaller, hexagonal crystals dispersed throughout the matrix.

#### 4. Discussion of Results

##### 4.1. X-ray Diffraction

The most interesting feature from the X-ray diffraction results was the form of silica present in the three, fully heat-treated samples. Although all three had had the same, final, heat treatment of 800° C for 1 h, and, although no trace of silica was detected after heat treating at the lower temperatures, the form of silica differed between the three heat treatments, the 480° C/1 h – 600° C/1 h – 800° C/1 h sample and the 500° C/1 h – 600° C/½ h – 800° C/1 h sample having cristobalite, whilst the 500° C/1 h – 600° C/1 h – 800° C/1 h one had quartz accompanied by only a small amount of cristobalite.

The low-temperature stages of the heat-treatment cycles to which the glass is subjected therefore must have an important bearing on the mineralogical form of the crystallising silica. This suggests that, if cristobalite is the form of silica which one would expect to separate from this glass, the presence of quartz in the 500° C/1 h – 600° C/1 h – 800° C/1 h sample is due to inversion of this cristobalite. Nevertheless, it is difficult to appreciate how this inversion has taken place, since it has taken place at the lower temperature and must therefore correspond to an ordering in material which is in fact in a glassy state.

#### 4.2. Electron Microscopic Examination

Differences observed in the background structures of the three samples heat-treated at 600° C may be connected with the cristobalite/quartz relationship. In the sample heat-treated 480° C/1 h–600° C/1 h, a large number of globules were observed both in the lithium di-silicate crystals and in the glass, whereas in the 500° C/1 h–600° C/1 h sample these globules are present in the lithium di-silicate and at the margins of the glass lakes only, suggesting some form of globule migration or absorption. It is possible that this globule migration is related to the cristobalite quartz inversion.

Comparing the block sample and thin-film samples which were examined on the electron microscope, it is clear that some measure of correlation may be made. Thus, for the as-cast and the low-temperature treated samples, the globule structure of the block specimens appears fairly similar to the contrast effects observed in the thin films. In the samples which have been heat treated to higher temperatures, there appears to be a close relationship between the morphology of the crystalline phases developed both in the block samples and in the thin films, although there does appear to be major differences in size. These size differences may be related to the constraint imposed on the growing crystals by the thinness of the films.

An interesting feature of the thin-film work was the manner in which some of the films given high heat treatments cracked. This cracking took place after heat treatment and was probably due to handling difficulties of the films. An examination of these cracks showed a tendency for the crack to propagate through silica and through the intercrystalline glass, but an even more marked reluctance for it to crack through a

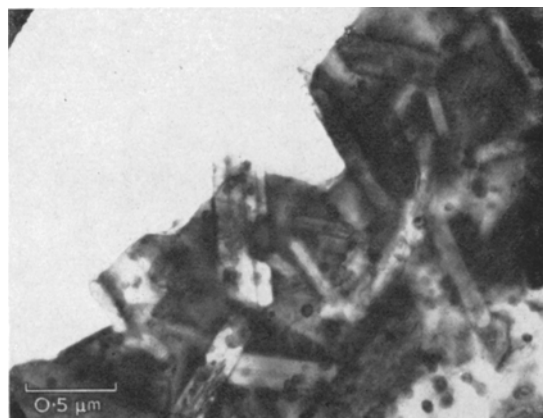


Figure 21 Fracture in a thin-film specimen of the fully heat-treated glass-ceramic.

lithium di-silicate crystal (fig. 21). This suggested, as had already been suspected, that the silica and the glass were weak members of the material and the lithium di-silicate was strong. An explanation of this may be found in the manner of fracture of the silica minerals, of the glass, and of the lithium di-silicate. The silica minerals and the glass possess no good cleavage (quartz has one cleavage but this is in fact a very poor one), hence an applied stress on the crystal will produce the same tendency to fracture irrespective of the relative orientations of crystal and stress. Lithium di-silicate, however, possesses three, good, mutually perpendicular cleavages along which fracture will proceed only so long as the applied stress normal to the cleavage plane exceeds the fracture stress. If the applied stress is not normal to the cleavage plane, then in this system of three mutually perpendicular cleavages it will be resolved into two perpendicular components each acting on two separate cleavages, but with a diminished stress on each. This resolved stress may be insufficient to cause fracture. Thus a random network of lithium di-silicate crystals would form an intrinsically strong material. If, distributed throughout this network, there is a weaker material, the units of the weaker material being interconnected, then fracture would be expected to take place in the weaker member, and because of the interconnection would propagate readily throughout the specimen. If, on the other hand, the weaker material is finely disseminated throughout the network, its effect would be negligible and the strength of the glass-ceramic will be in fact the strength of the lithium di-silicate network.



TABLE I X-ray diffraction results.

Heat treatment	Crystalline phases present
As-cast	None detected
480° C/1 h	None detected
500° C/1 h	None detected
480° C/1 h, 60° C/1 h	Lithium di-silicate strong pattern
500° C/1 h, 600° C/1 h	Lithium di-silicate strong pattern
480° C/1 h, 600° C/1 h, 800° C/1 h	Lithium di-silicate very strong, cristobalite very strong
500° C/1 h, 600° C/1 h, 800° C/1 h	Lithium di-silicate very strong, quartz strong, cristobalite weak
500° C/1 h, 600° C/½ h, 800° C/1 h	Lithium di-silicate very strong, cristobalite strong, ?Li <sub>2</sub> OZnOSiO <sub>2</sub> weak

## 5. Conclusions

A lithium zinc silicate glass-ceramic which separated into two glass phases on casting crystallised at a temperature between 500 and 600° C with the formation of crystals of lithium di-silicate. Subsequent heat treatment of the material caused growth of the lithium di-silicate to form a continuous network within which most of the residual glass crystallised to form silica.

Variations in the low and intermediate heat treatments given to this material produced marked variations in the structure and mineralogical composition of the final material. Although the silica did not crystallise until the highest temperature, the early stages of the heat treatment had an effect on the morphology and mineralogical composition of the silica produced. A comparison can be made between block samples of this material and thin films heat-treated at a thickness of approximately 2500 Å.

Examination of cracks in thin films of fully heat-treated material suggest that silica and residual intercrystalline glass are weak members of the material, and that high mechanical strength can be attained by obtaining a finer dispersion of these materials throughout the bulk glass-ceramic.

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