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A transmission electron microscope study of glass-ceramics

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A technique for preparing thin foils of glass-ceramics for transmission electron microscopy has been developed, using a combination of chemical, abrasion and ion-beam machining. This has permitted a study of the microstructural development in a number of glasses of different chemical compositions subjected to various heat-treatments. Results are presented and discussed for materials based on the Li_2O-SiO_2 system and on a more complex Li_2O-K_2O-ZnO-SiO_2 material employing phosphorus pentoxide as a nucleation catalyst.

1. Introduction

The controlled crystallization of glasses, usually achieved by the inclusion in the materials of a nucleating agent, has enabled useful glass-ceramics to be developed with properties that can be varied by changes of chemical composition or of crystallization heat-treatment. Some of the processes underlying the development of the glass-ceramic microstructures and the relationships between microstructural parameters are not well understood, however, and further work in these directions is necessary. Progress along these lines requires an unambiguous technique for characterizing the microstructures of glasses in various stages of crystallization. In earlier work [1], a technique for examining the microstructure of partially crystallized glass by transmission electron microscopy using thin foils prepared by a chemical etching technique was described. This method is useful for materials in which the volume fraction of the crystalline phase is low. When the glass-ceramic under examination is highly crystalline, however, the chemical thinning technique is unsatisfactory because large differences in the rates of chemical attack for the different phases cause certain crystals to be dissolved selectively. This results in disintegration of the specimens before satisfactory thinning has been accomplished.

Transmission electron microscopy, however, is considered to be one of the most powerful methods for the investigation of glass-ceramic microstructures since it permits detailed examination of the morphology of the structure and also enables various regions of the microstructure to be characterized as either amorphous or crystalline by selected-area electron diffraction. Furthermore, in many cases individual crystals can be identified by the diffraction technique. For these reasons, it was considered necessary to develop techniques by which highly crystalline glass-ceramics could be examined.

2. Experimental techniques

2.1. Glass preparation

Glasses having the molecular compositions given in Table I were prepared from high-purity lithium carbonate, lithium phosphate, zinc oxide and Brazilian quartz. The appropriate compositions were melted in 500 g quantities in a platinum-2% rhodium crucible in an electrically-heated furnace at 1450°C for 3 h. The molten glasses were quenched into water and the resulting "frit" after drying was crushed, mixed and re-melted at 1450°C until it was homogeneous and bubble-free.

2.2. Specimen preparation for transmission electron microscopy

Using a vertical drawing process, rods about 3 mm in diameter were drawn directly from the molten glass; this process ensures fairly rapid chilling of the glass. After the rod specimen had been subjected to the desired heat-treatment, discs of thickness less than 0.3 mm were sliced from them using a diamond saw.

For materials which contained only a small volume fraction of crystals, the chemical thinning

TABLE I Mol % compositions of the experimental glasses

Glass no.	1	2	3	4
Li_2O	30	30	29	29
K_2O	—	—	—	1
ZnO	—	—	1	1
SiO_2	70	69	69	68
P_2O_5	—	1	1	1

process was applied as a first stage of the preparation technique. In this, the edges of the discs were coated with "Lacomit" varnish and the discs were immersed with agitation in a solution comprising 5 parts HF, 2 parts HCl and 93 parts H_2O by volume. The etching was continued until the glass thickness had been reduced to about 50 µm. The acid-resisting varnish was then removed, leaving a glass disc with a sufficiently strong rim and a central thin area.

For the more highly crystalline glass-ceramics, it was decided to use a mechanical thinning process as the first stage of the technique. In this the edges of the disc specimen were glued onto a perforated glass slide and thinning was accomplished by successively directing a jet of 10 μm alumina powder onto the centres of each face of the disc. By this means a thin central area again of about 50 µm in thickness was produced.

After washing in distilled water, methyl alcohol and ether the specimens were transferred to an Edwards ion-beam machining equipment. The discs were mounted at an angle of 15° and sputtering with argon ions was continued until a perforation occurred through the glass. Suitable operating conditions were found to comprise a total current density of 200 µA cm^{-2} at a voltage of 6 kV. Under these conditions the risk of overheating the specimen, particularly at the point of impingement of the ion-beam, was minimized. Efficient machining required the voltage to be stabilized over long periods and to ensure this it was found essential to clean the ion guns regularly, to maintain a critical distance between the pierced anode and cathode plates and to ensure that the hole in the cathode plate did not become excessively enlarged by erosion. To avoid over-frequent replacement of the cathode plate an additional multi-hole plate was installed which could be rotated to align a fresh hole with that in the original cathode plate. Using these conditions, it was found that glass specimens having thin areas in the region of 1000Å (100 nm) thick could be prepared using machining times typically of 30 h.

2.3. Transmission electron microscopy and X-ray diffraction

The electron microscope was carried out using a JEM 200 microscope operating at 200 kV and hot-stage microscopy at temperatures up to 550°C was undertaken using a JEM 7 microscope operating at 100 kV. Selected-area electron diffraction studies were made and powder specimens of the crystallized glasses were also examined by X-ray diffraction.

3. Results

3.1. Li_2O-SiO_2 system

The influence of phosphorus pentoxide in promoting internal crystal nucleation in Li_2O-SiO_2 glasses was illustrated by examination of glasses 1 and 2 (Table I). The binary glass 1

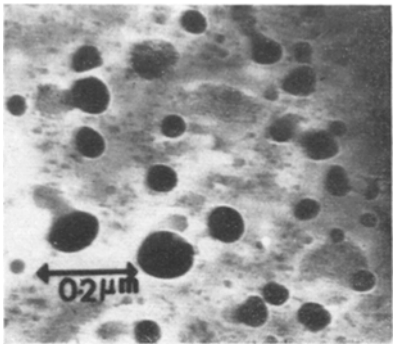


Figure 1 Phase separation in glass 1 after 1 h at 500°C.

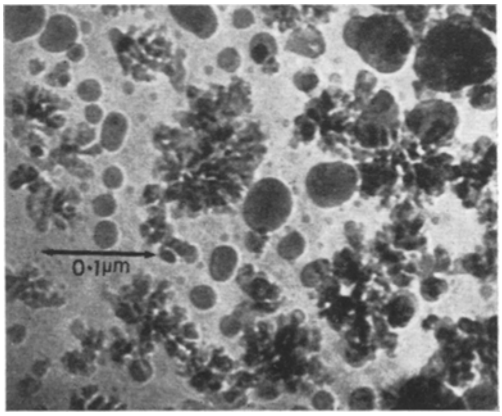


Figure 2 Crystalline phase in glassy matrix between phase-separated droplets in glass 2 after 1 h at 480°C.

showed no evidence of crystallization after heat-treatment at 500° C (Fig. 1) but glass-in-glass phase separation had occurred. Between the phase-separated droplets there appears to be some fine structure, but the nature of this has not been elucidated so far. The inclusion of 1 mol % of phosphorus pentoxide in glass 2 promotes crystal nucleation at 480° C (Fig. 2) as well as modifying the morphology of phase-separation, resulting in a significant increase in the numbers of droplets per unit volume. It is to be noted that the crystallites appear to have nucleated within the matrix phase and not at the interface between the two glassy phases. A selected-area electron diffraction pattern for the region shown in Fig. 3a is given in Fig. 3b and this permitted identification of the crystallites as lithium disilicate. The crystallites, which could not be detected by X-ray diffraction at this stage, had sizes ranging between 50 and 200Å.

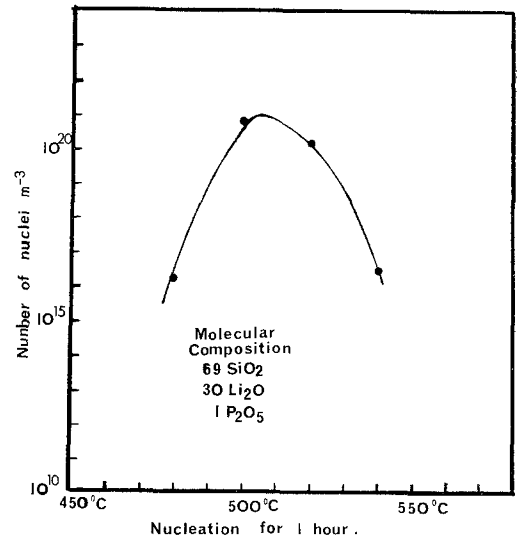


Figure 4 Concentration of lithium disilicate crystallites for different nucleation temperatures.

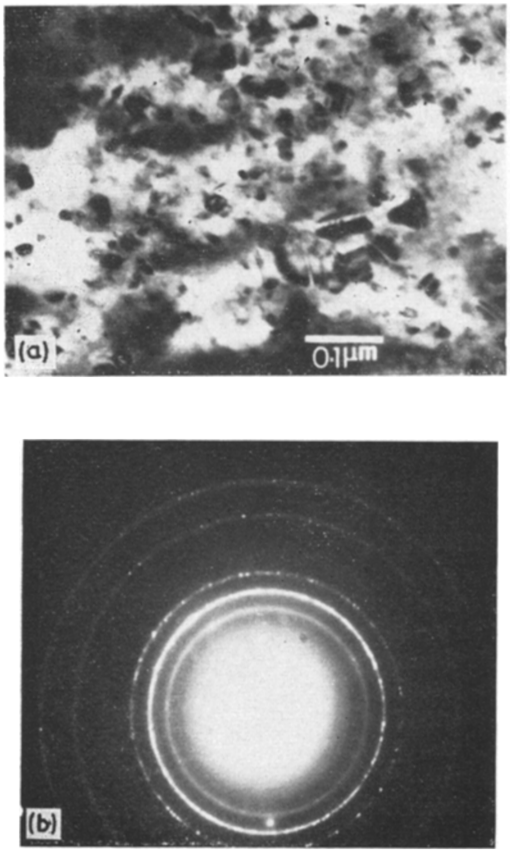


Figure 3 (a) Lithium disilicate crystallites in glass 2 after 1 h at 520° C. (b) Selected-area diffraction of (a).

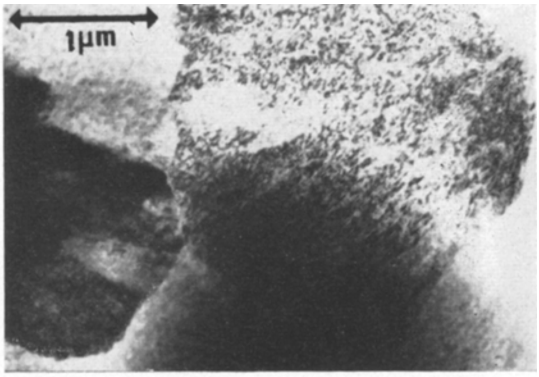


Figure 5 Lithium disilicate crystals in glass 2 after 1 h at 500°C and 1 h at 550° C.

Since crystal nucleation occurred in glass 2 at the comparatively low temperature of 480° C it was thought of interest to determine the influence of temperature in this region on nucleation rate. Fig. 4 illustrates the results and indicates that optimum nucleation occurs at a temperature in the region of 500° C. On the basis of this, examination of glasses that had received a nucleation treatment of 1 h at 500° C followed by isothermal treatment at 550° C to promote crystal growth was undertaken. Treatment at 550° C for 1 h of glass 2 resulted in the development of characteristic spongy crystalline areas containing fine scale heterogeneities, as shown in Fig. 5. These

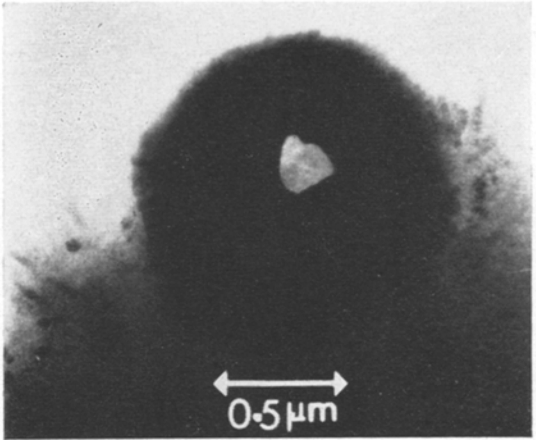


Figure 6 Core region in lithium disilicate spherulite in chemically thinned specimen of glass 2 after 1 h at 500°C and 1 h at 550°C.

heterogeneities persisted even after treatment for 16 h at 550° C though the morphology of the crystal phase had changed to give well-defined lozenge-shaped crystals (Fig. 7a). The heterogeneities within the lithium disilicate crystals consist of spherical inclusions about 500Å in diameter and with a concentration of the order of 10^{21} m^{-3} (Fig. 7b).

Spherulites of lithium disilicate were found in some areas of the specimens and in some cases, these apparently had an amorphous core region as shown in Fig. 6. It was observed however that this microstructural feature only occurred with specimens that had undergone the chemical thinning treatment and was absent from specimens thinned by a combination of abrasion and ion-beam machining.

3.2. Li_2O-K_2O-ZnO-SiO_2 system

Glass 3 (Table I) was derived by substituting 1 mol % ZnO for Li_2O in glass 2. Electron microscopy showed that this compositional change appeared to promote coarse and extensive glass-in-glass phase separation (Fig. 8a). An enlarged view of the spongy crystalline regions shows that they consist of a large number of crystallites. Occasionally twinning in the crystallite can be seen (Fig. 8b). It was also observed that specimens given a nucleation treatment of 1 h at 500° C followed by isothermal treatment at 550° C exhibited multiple cracking during this treatment. This suggested the development of high internal strains in the material and it was therefore decided to prepare glass 4, which was derived by replacing 1 mol % SiO_2 by K_2O in glass 3. It was believed that the K_2O would be concentrated in the glass phase of the glass-ceramic, thereby lowering its viscosity at the heat-treatment temperature and enabling stress relief to occur by viscous flow during the crystallization process.

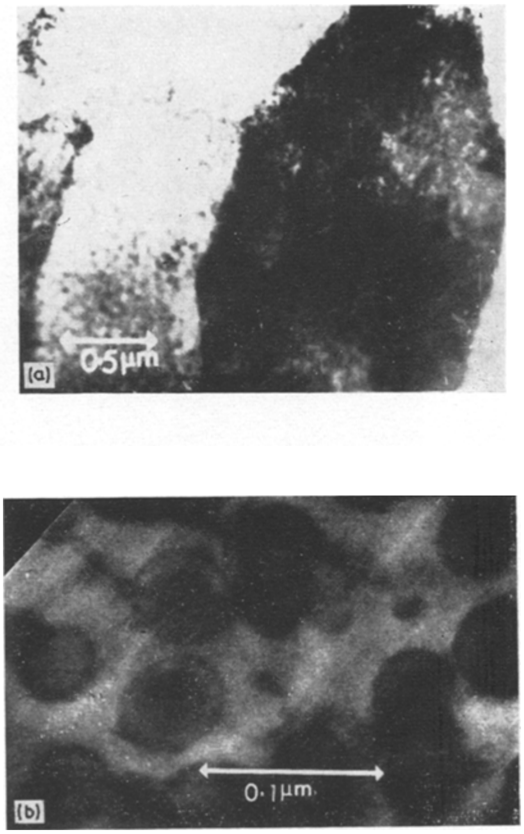
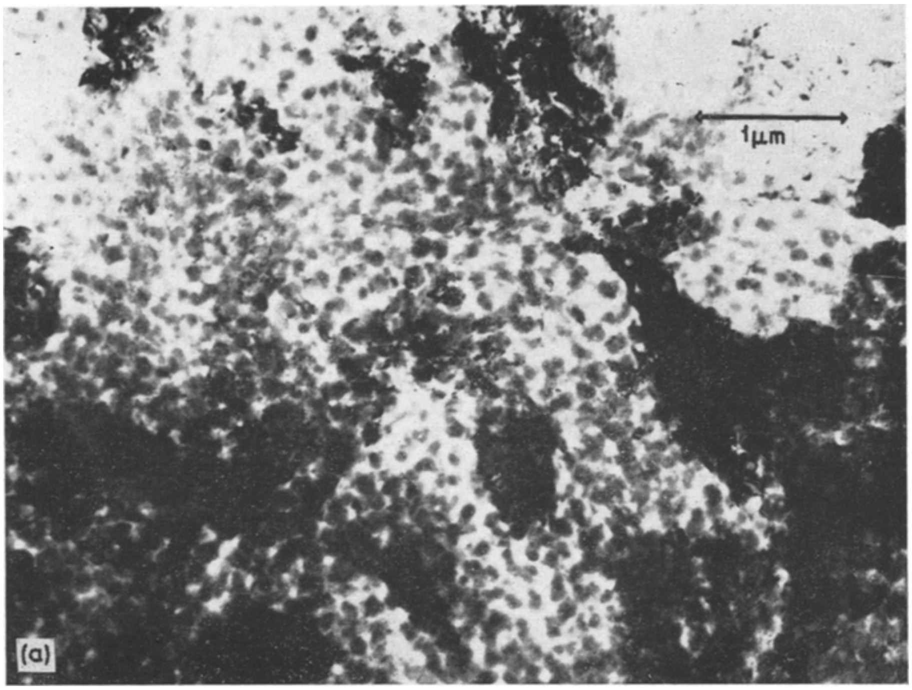


Figure 7 (a) Well-developed crystals in glass 2 after 16 h at 550° C. (b) Spherical inclusions in lithium dislicate crystals shown in (a).

Heat-treatment of glass 4 at 550° C, after the nucleation treatment, resulted in a fine-grained white material which showed no sign of cracking even after several days at this temperature. The microstructure and selected-area diffraction patterns for a glass-ceramic produced by heat-treatment for 3 h at 550° C are given in Fig. 9. It is also found that the mean size of the phase-separated droplets in this material is much smaller than in glass 3, an effect which must be attributed to the presence of K_2O. The major crystalline phase present is again lithium disilicate as evidenced from the electron diffraction pattern (Fig. 9b) and from X-ray diffraction analysis.



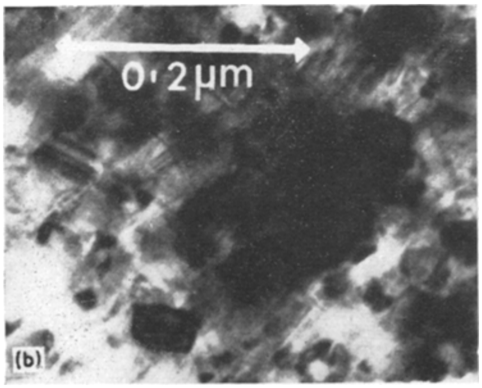


Figure 8 (a) Heavy phase separation and irregularly-shaped crystalline phase in glass 3 after 1 h at 500°C and 10 min at 550°C. (b) Enlarged view of irregularly-shaped crystalline region.

It was found for glass 4, that twinning of the lithium disilicate crystals was a common feature as illustrated by the diffraction pattern and corresponding micrograph in Fig. 10. It has been possible to identify a $[12\bar{2}]$ twinning axis in this material. Even after prolonged heat-treatment this morphology of the crystalline phase appears to be maintained (Fig. 11).

The direct observation of the crystallization process while the crystals were actually being formed was thought likely to yield useful results. Hot-stage electron microscopy of glass 4 during isothermal treatment was therefore carried out. Considerable difficulty in obtaining suitable images was experienced owing to thermal drift of the specimen.

4. Discussion

4.1. Phosphorus pentoxide as a nucleating agent

Glass 2, heat-treated for 1 h at 500°C developed lithium disilicate crystals in a volume fraction of about 0.06 whereas the corresponding P_2O_5 free glass 2 showed no evidence of crystallization after this treatment. Clearly, as shown in earlier work [3], phosphorus pentoxide promotes the nucleation of lithium disilicate in such glasses.

The form of the nucleation rate versus temperature curve given in Fig. 4 is qualitatively in agreement with that predicted by classical nucleation theory [4] in which two important parameters are σ, the interfacial energy between the crystal nucleus and the surrounding glass, and ΔG_V, the volume free energy change resulting from the conversion of the disordered glass

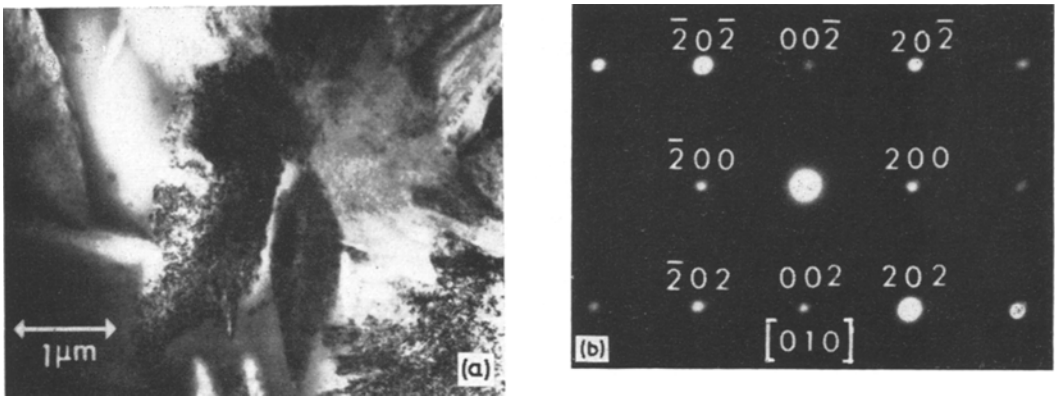


Figure 9 (a) Morphology of lithium disilicate in glass 4 after 1 h at 500°C and 3 h at 550°C. (b) Selected-area diffraction of lithium disilicate in (a).

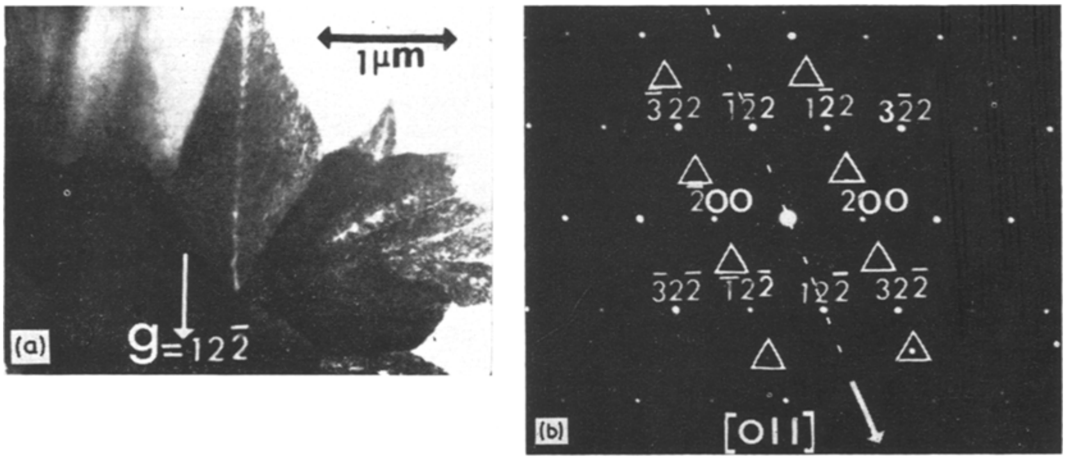
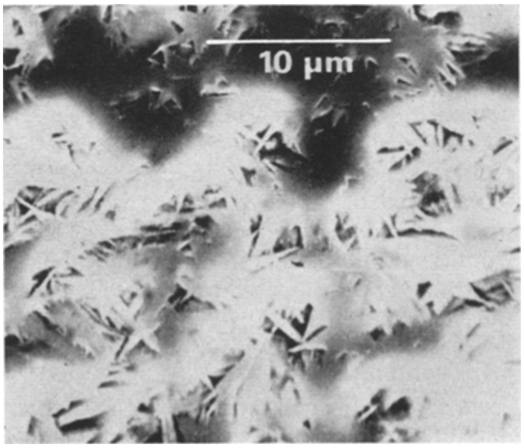


Figure 10 (a) Morphology of lithium disilicate crystals in glass 4. (b) Selected-area diffraction showing twinning in lithium disilicate crystals. Heat treated at 500°C for 1 h and at 500°C for 3 h.



structure to the regular crystalline lattice. However, present theory is insufficient to predict the influence of composition and thermal history on the nucleation rate of complex glasses. This arises because of difficulties in measuring σ and ΔG_V. Reduction of the interfacial energy, σ, would lead to an increase of the nucleation rate and one possible mode of action of nucleating agents such as phosphorus pentoxide is that they cause a reduction of this parameter. Another possibility, discussed by James and McMillan [5] is that nuclei of a crystalline phosphate, such as lithium

Figure 11 Scanning micrograph of the lithium disilicate after 1 h at 500°C and 6 h at 550°C in glass 4 (× 2200).

orthophosphate, are precipitated by homogeneous nucleation and these then heterogeneously nucleate the crystallization of lithium disilicate. In the present study, however, no evidence was obtained of the presence of crystalline phosphates. If these were present and acting as nucleating particles they would probably have dimensions of the order of a few unit cells. High resolution electron microscopy is necessary to solve this problem and this is being undertaken with glasses containing higher concentration of phosphorus pentoxide.

It is interesting to note that the number densities of lithium disilicate crystallites determined in the present study after a nucleation treatment of 500° C for 1 h are higher than those reported by Harper, James, and McMillan [2] by a factor of 10^6. The difference between these results undoubtedly arises because in the present work the numbers of crystallites were determined for specimens which had received only the nucleation treatment whereas in the earlier investigation the numbers of nuclei were estimated by determining the number densities of crystals present after a further treatment to cause the crystals to grow to sizes which could be resolved in the optical microscope. Clearly, large numbers of the nuclei formed at temperatures in the region of 500° C are ineffective in promoting the development of crystals at 750° C either because they redissolve or are otherwise incorporated in rapidly growing crystals in the near vicinity. This result points out a possible danger of determining the number densities of nuclei in experiments in which a crystal growth stage is incorporated. It should be mentioned, however, that despite the discrepancies in the numerical values the general forms of the nucleation rate curves, including the occurrence of a maximum at around 500° C, were the same for the two methods.

4.2. Phase-separation and crystallization

The presence of spherical inclusions in a concentration of about 10^{21} m^{-3} and approximately 500Å in diameter in the lithium disilicate crystals (Fig. 7) indicates that these are incorporated during the growth of the crystal. The precise effects of prior glass-in-glass phase separation on the crystallization process are imperfectly understood but it is likely that the crystal growth process is impeded by these inclusions. If this is the case, a certain amount of phase separation appears desirable in preventing coarsening of the crystalline phase. There is evidence that the nucleation efficiency is considerably improved when prior glass-in-glass phase separation has occurred [6], resulting in the formation of a glass-ceramic microstructure having a significantly finer grain size.

It seems possible, however, that there may be a critical balance in the extent of phase separation. In the present study it was observed for the phosphorus pentoxide-nucleated Li_2O-ZnO-SiO_2 glass that multiple cracking occurred owing to severe internal strains set up during crystallization. This glass showed extensive and coarse phase separation prior to crystallization. The inclusion of a small proportion of potassium oxide reduced the extent and coarseness of phase separation and at the same time eliminated the cracking of the material. The beneficial effect of the K_2O addition may be due, at least partly, to its marked influence on the morphology of phase-separation. Another effect, however, will be that the viscosity of the residual glass phase, in which this oxide is presumed to concentrate, will be lowered. This would enable stress relief by viscous flow to occur more readily.

4.3. Core-regions in lithium disilicate crystals

It was observed that a core-region occurred in lithium disilicate spherulites which had been exposed to the chemical thinning solution but were absent from specimens that had not been chemically etched. This suggests that the central areas originally contained crystalline material which was more rapidly attacked by the etchant than the surrounding structure. It was suggested [1] that the core could be more disordered than the outer regions owing to the presence of dislocations. An interesting possibility is that the central region is less pure than the surrounding regions, with partial replacement of silicon ions by phosphorus ions. Saalfield [7] has shown that such a substitution is possible over a large composition range in single crystal Ca_2SiO_4. If a similar substitution occurred in the central core regions of the lithium disilicate crystals, the replacement of Si^{4+} by P^{5+} ions would require omission of a corresponding number of Li^+ ions from the crystal lattice to preserve local electroneutrality and this would be expected to change the chemical resistance.

4.4. Twinning

Twin crystals are commonly found in nature but it is not usually possible to determine whether this results from a growth fault or because of deformation. The twinning observed in the lithium disilicate crystals in the present study may be more likely to result from a growth fault since large strains in the crystal would not be expected to arise because viscous deformation of the surrounding glass phase could occur. However, the extent to which the strain can be relieved will depend on the rate of crystal growth and on the composition of the surrounding glass. During growth of the crystals, the glass phase becomes depleted of lithium oxide and therefore becomes progressively more viscous. It would be useful to investigate whether the addition of minor amounts of oxides that tend to concentrate in the glass phase, thereby changing its thermoviscous behaviour, affect the incidence of twinning.

The twin spots observed from the electron diffraction pattern (Fig. 10a) are characteristic of a simple case of twinning with the twin plane parallel to the [011] beam direction. The twin axis is then parallel to the plane of the diffraction pattern along the $[12\bar{2}]$ direction. Rotation of the twin diffraction spots through 180° causes them to coincide with the main diffraction spots. The weak twin spots could probably arise from a damaged lattice in the twins or small dimensions of the twinned crystals.

4.5. Hot-stage transmission electron microscopy

Observation of the crystallization of glass 4 *in situ* indicated that nucleation occurred on the surface of the thin foils at a lower temperature than observed during heat-treatment of the bulk material. Thus while no crystals phases could be detected for the bulk material after heat-treatment at 500° C for 1 h, crystalline nuclei appeared when the thin foils were heated to 480° C on the hot-stage of the microscope.

The numbers and sizes of the crystals varied depending on the temperature and duration of heat-treatment. In the early stages, the crystallite sizes ranged between 60 and 600Å but after 3 h at 550° C the crystals, identified as lithium disilicate, attained sizes in the region of 2 μm. The hot-stage study of nucleation and crystallization was hampered since thermal drift caused considerable difficulty in achieving satisfactory images.

This limited study shows that *in situ* measurements made using thin foils, while they can yield useful information concerning surface nucleation and crystallization processes, are of limited value in the investigation of structural changes within the bulk of the material. Hench and Kinser [8] have reported similar results from the *in situ* observation of nucleation at 480°C in a glass of the molecular composition 30 parts Li_2O 70 parts SiO_2.

5. Summary and conclusions

A successful technique using a combination of chemical, abrasion and ion beam thinning has been developed for preparing thin foils of partially crystallized glasses and glass-ceramics.

Transmission electron microscopy of specimens prepared in this way has provided clear evidence that the inclusion of phosphorus pentoxide in Li_2O-SiO_2 glasses promotes nucleation of lithium disilicate crystals within the bulk of the material. It was also apparent that nucleation occurs within the matrix phase of the two-phase glasses and is not associated with the boundary between the two glass phases.

During crystal growth at 550° C silica-rich droplets are incorporated in the lithium disilicate crystals and this is likely to influence the kinetics of crystal growth. There were indications that while some glass-in-glass phase separation prior to crystallization is beneficial in assisting the development of a fine-grained glass-ceramic microstructure, excessive and coarse phase separation may be harmful in leading to the development of high internal strains.

Twinning of the lithium disilicate crystals arising most probably from growth faults is frequently observed.

Observation of the crystallization process *in situ* for thin foils showed that surface nucleation predominates for specimens of this geometry and the results are therefore of limited value for the study of bulk nucleation processes.

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