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Transmission Electron Microscopy of Partially Crystallised Glasses

P. F. JAMES*, P. W. MCMILLAN
School of Physics, University of Warwick, Coventry, UK

The early stages of crystallisation in a Li_2O–SiO_2–P_2O_5 glass were studied by transmission electron microscopy using thin sections prepared from the bulk material by chemical thinning. Small crystalline regions of lithium disilicate were formed, often as several small single crystals joined together around a central core. Possible explanations of the core are discussed in terms of a region of different chemical composition or a central region of disorder. The observations are also compared with the growth of crystal spherulites in polymers.

1. Introduction

The development of glass-ceramics in recent years has led to considerable interest in the process of controlled crystallisation of glasses. Glass-ceramics are fine-grained materials which are of increasing technological importance owing to their many useful and controllable properties, for example high mechanical strength. The more fundamental processes in the formation of glass ceramics, including the precise role of nucleation catalysts and the effects of glass-in-glass phase separation prior to crystallisation, are only imperfectly understood, however.

A powerful technique for studying crystallisation is direct transmission electron microscopy and diffraction. This has the advantage over the surface carbon replica method of providing a direct image of the structure and the ability to distinguish glass and crystalline phases easily by selected area diffraction. Direct transmission is thus particularly valuable in investigating the early stages of phase separation and crystallisation.

A successful method has been developed for preparing thin films of glass from bulk material by chemical thinning [1], which has enabled the morphology of phase separation in lithia-silica glasses to be determined. Particle-size distributions, concentration and volume fractions were measured by using a quantitative stereo technique. Hence the kinetics of phase separation were obtained [2]. Attempts to thin crystallised glasses and glass-ceramics in the same way by chemical means were less successful, however, owing to the difference in etching rates of the glass and crystalline phases, which resulted in disintegration of specimens. Fortunately it was possible to thin glasses in which the degree of crystallisation was small and some preliminary results are presented in this paper. In spite of the promise shown by the more sophisticated technique of ion-bombardment, the chemical thinning method has still a great deal to offer in simplicity and speed. Another technique which the authors have been using for glass-ceramics with some limited degree of success involves bombarding the specimen with a controlled-velocity stream of very fine abrasive particles. This will be described in a later publication.

2. Experimental

Samples of a glass of molecular percentage compositions $30Li_2O$–$69SiO_2$–$1P_2O_5$ were partially crystallised by heat-treatment, cut into thin slices (about 200 μm in thickness) on a diamond wheel, and chemically thinned in a solution of volume percentage composition $5HF$–$2HCl$–$93H_2O$, using the method previously described [1, 2]. Heat-treatment temperatures between 550 and 600°C for times of up to 1 h were used in order to produce only slight volume-crystallisation. Some of the specimens were given a prior heat-treatment at 500°C for 1 h since this is known to produce a maximum number of crystal nuclei on subsequently heating at a higher temperature [3]. Observations were

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*Now at the Department of Glass Technology, University of Sheffield.

made at 100 kV and 200 kV in JEM 7 and JEM 200 electron microscopes.

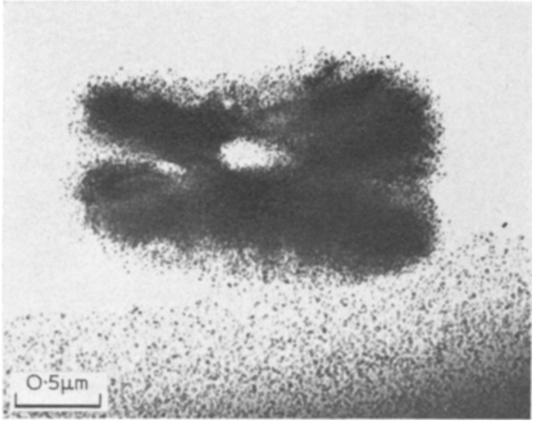

Figure 1 Transmission electron-micrograph of $30Li_2O$–$69SiO_2$–$1P_2O_5$ glass heat-treated at 500° C for 1 h and 550° C for 30 min, 100 kV.

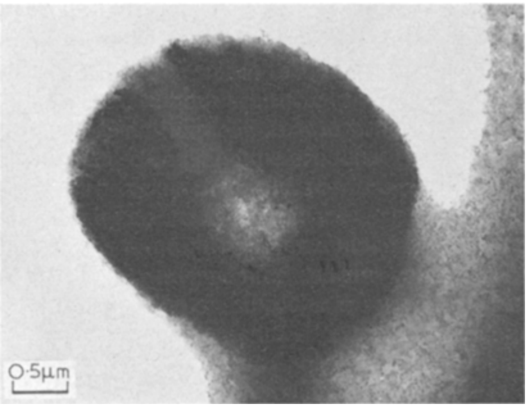

Figure 2 Transmission electron-micrograph of $30Li_2O$–$69SiO_2$–$1P_2O_5$ glass heat-treated at 500° C for 1 h and 550° C for 1 h, 200 kV.

3. Experimental Results

Figs. 1 and 2 are transmission electron-micrographs of the glass heated at 500° C for 1 h and 550° C for 30 min and 1 h respectively. Many crystalline regions, with typical dimensions of 5 to 10 μm, were observed distributed uniformly in the thin glass film, which had extensive areas with a thickness of about 1500Å near the edges. The crystals were frequently much thicker than the thin glass film, except in very thick regions of the film which did not transmit electrons. Also the crystals often protruded from the edges of the specimen, as can be seen in figs. 1 and 2. This was because the crystalline phase dissolved in the thinning solution at a slower rate than the glass.

The fine droplet background structure surrounding the dark crystalline region represents glass-in-glass phase separation. This has been studied in detail for the present system [2] and consists of silica-rich droplets within a matrix of approximate composition $Li_2O.2SiO_2$.

Fig. 3 is an electron diffraction pattern taken by selecting an area including the crystal in fig. 2. The diffuse rings are due to the glass. Indexing of this pattern and others revealed that the crystals were of lithium disilicate. Many of the patterns were produced by several distinct crystal orientations showing that the crystalline regions observed were not always single crystals but were often composed of two or more smaller crystals of disilicate joined together to form an aggregate. This fact is illustrated in fig. 1 which shows that the crystalline region has several distinct "arms" or branches around the central "core". The central "core" region seen in figs. 1 and 2 was observed for a large proportion of the crystals. Careful selected area diffraction revealed that there was no other crystalline phase present in the "core" and stereo pairs of micrographs indicated that the "core" was essentially hollow but with some glassy phase present. It is interesting to note that such cored crystals have also been observed in replicas and an example is shown in fig. 4. This is a platinum-carbon shadowed replica of a glass of composition 31.5 Li_2O–67.5 SiO_2–1 P_2O_5 heated at 560° C for 1 h, polished and etched slightly in hydrofluoric acid.

4. Discussion

The above observations suggest several interesting possibilities for crystal nucleation and growth in the lithia-silica and other glass systems. It is probable that the early stages of growth of crystal spherulites are being observed in this glass. Spherulites are not single crystals but consist of polycrystalline aggregates and in later stages of development are composed of a radiating array of crystalline fibres, these fibres being able to form branches of slightly different crystallographic orientations [4]. Such spherulite formation is a characteristic of liquid melts with high viscosity and comparatively slow rates of crystallisation and is therefore expected to occur

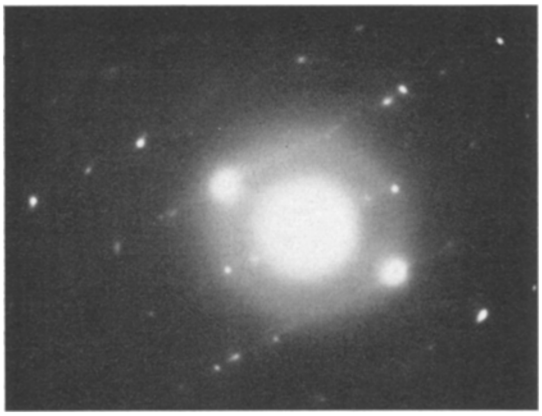

Figure 3 Selected-area electron diffraction pattern of region shown in fig. 2.

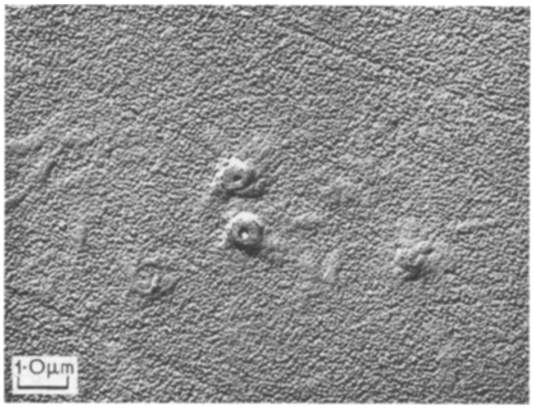

Figure 4 Platinum, carbon-shadowed replica of 31.5 Li_2O-67.5SiO_2-1P_2O_5 glass heated at 560°C for 1 h.

during the crystallisation of glasses. Spherulites usually originate from a single nucleus and this may be identified perhaps with the "core" region observed on the micrographs.

4.1. Chemical Composition Theory of the "Cores"

One explanation for the core regions is that a central localised part of the crystal (or small aggregate of crystals) has a different chemical composition from the remainder, and dissolves at a faster rate in the thinning solution. This would be the case if the lithium disilicate phase had nucleated and grown on a nucleus of a different crystalline phase. One possibility is that the nucleating particles were small lithium metasilicate crystals. Although there was no evidence for the presence of this phase from electron diffraction, it would dissolve very rapidly once the central core was exposed to the thinning solution and hence would be difficult to detect. The probable small size of the nucleus would also make detection difficult.

Kinser and Hench [5] have detected both the metasilicate and disilicate in a 30 mol. % Li_2O–70 mol. % SiO_2 glass crystallised as a thin film *in situ* in the electron microscope. They found that the metasilicate occurred only in the early stages of heat-treatment, and concluded that the nucleation sequence involves first the precipitation of the metasilicate followed by the disilicate. However, surface crystallisation tends to predominate in experiments with thin films and therefore the same sequence does not necessarily apply to the internal bulk crystallisation observed in the present experiments. McMillan, Phillips, and Partridge [6], on the other hand, have found evidence that lithium metasilicate forms as a transient phase prior to the disilicate in a complex glass-ceramic based on the lithia-silica system.

Another possible nucleating phase is a crystalline phosphate. This is reasonable since previous work [2] suggested that the phosphorous pentoxide associates with the lithium ions in the glass. These phosphate groupings might form clusters and precipitate as tiny crystals. Again, however there was no evidence of phosphates from diffraction.

4.2. Disordered Region Theory of the "Cores"

The alternative explanation of the "cores" is that the crystals are of uniform composition, i.e. lithium disilicate, but have a region of disorder or strain near their centres due, for example, to the presence of one or more dislocations. Localised regions of this kind would possess enhanced chemical reactivity and etch at a faster rate in the thinning solution, producing a small hole which would subsequently enlarge rapidly. In fact such central regions have been revealed by etching in small silver bromide crystals grown from solution [7]. In view of the importance of screw dislocations in promoting crystal growth from solution, it is likely that dislocations will also occur in crystals nucleated in glasses and that they will influence growth in a similar manner.

The problem of the origin of such dislocations presents no great difficulty as Frank [8] has pointed out for the case of growth from solution.

There should be little difference in the ease of nucleation within the glass of a dislocated crystal and a perfect one. If however only perfect crystals are nucleated within the glass, then dislocations could be produced at an early stage by the impingement of two or more crystal nuclei with imperfect lattice registration. The presence of such dislocations would then greatly enhance the subsequent growth rates of these small crystal aggregates. Such a possibility may explain the observation that the lithium disilicate regions on the micrographs were often composed of several small crystals joined together.

It is interesting to note that Verma [9] observed distinct cores in silicon carbide crystals which were not given an etching treatment. Frank [10] suggested that a hollow tube with a diameter of 1 or 2 μm exists along the central dislocation in these crystals. He has shown that such hollow dislocations may occur for substances in which the dislocation Burgers vectors are large ($\sim$ 10Å), for example some silicates.

It is not known whether hollow dislocations do occur in lithium disilicate but the thinning solution used in the present experiments could easily have enlarged such a hollow tube to produce the observed "core" structure. Thus both hollow and non-hollow dislocations could give rise to a similar central "core" in the crystals.

At present there is insufficient evidence to distinguish between the "chemical composition" and "disordered region" theories. However, the detection of only the disilicate phase would tend to favour the latter theory. It is hoped that a non-chemical method of thinning may resolve the difficulty and reveal the exact nature of the crystal "core".

4.3. Relation to Polymer Systems

Before leaving the question of the origin of the "cores" it is relevant to consider the case of crystallised polymers where spherulites with unusual central structures are observed. These observations have been accounted for in terms of the branching of the constituent crystal fibres of the spherulite [11]. In the early stages this branching causes a sheaf of fibres to form at the centre and as growth proceeds the edges of the sheaf gradually curve backward until the two opposite sides meet. This leads to the formation of spherical or "double leaf" shaped structures of a different texture near the centre. At a later stage of growth the whole crystal aggregate gradually approximates to a circle with radiating fibres in all directions, but the "irregularities" remain close to the centre of the spherulite. However, it is unlikely that a similar mechanism could explain the "core" effects in the present glass system since the crystals are being observed at a very early stage of development before appreciable branching has occurred. Whether the crystals develop later into sheaf-like structures awaits further study.

4.4. Effect of Phase-Separation

One result from the present study is the apparent lack of any direct connection in the present glass between the glass-in-glass phase separation and crystal nucleation. Thus the numbers of phase-separated droplets greatly exceed the numbers of crystals, as can be clearly seen from figs. 1 and 2. An approximate estimate of the number of crystals from the electron-micrographs was 10^9/cm^3, whereas the number of droplets was of the order of 10^{16}/cm^3. This would suggest that crystal nucleation at the individual droplet interfaces is unlikely. Also the crystals are able to grow to large dimensions despite the presence of a high density of silica-rich droplets.

5. Conclusions

Transmission electron microscopy has shown that lithium disilicate crystals grown in a lithia-silica glass containing phosphorous pentoxide as a nucleating agent, possess a central "core" region having either a different chemical composition or a different structure from the surrounding regions. It was not possible in the present study to distinguish between these two possibilities but elucidation of this matter using non-chemical thinning methods should result in a better understanding of the nucleation step in the crystallisation of lithia-silica glasses.

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