JOURNAL OF MATERIALS SCIENCE 10 (1975) 911–917

Anisotropic glass-ceramics produced by extrusion through opposed dies

K. H. G. ASHBEE
H. H. Wills Physics Laboratory, University of Bristol, UK

Oriented glass-ceramics have been produced in two morphologically different systems by extruding the green glasses through opposed dies at temperatures near their respective crystallization temperatures. The principal crystalline phase is a mica for one system and an asbestos for the other and, by using the crystals as markers, it has been possible to explore the pattern of flow and its effect on crystal orientation at various stages of the extrusion process. It is demonstrated that crystal alignment occurs during extensional flow between the dies and is modified by plug flow through the dies. Oriented glass-ceramics are expected to exhibit marked anisotropy in properties and, as far as mechanical properties are concerned, this has been confirmed by measurements of tensional modulus, fracture stress and indentation strength. The oriented crystals remain aligned during subsequent drawing down to fibres and by suitable heat-treatment can be complemented by a population of randomly oriented crystals.

1. Introduction

The development of a new fibre was recently briefly reported by the author [1]. The fibre is a glass-ceramic in which the main crystalline phase, fluorophlogopite (mica), has a preferred orientation introduced by extruding the green glass through opposed dies before the fibre-drawing operation. Extrusion is carried out at the crystallization temperature and the extrusion geometry is similar to that proposed by Frank (see Mackley [2] and Frank *et al.* [3]) as a method for creating pure extensional flow in polyethylene solution. There are three regions of the apparatus within which crystal alignment could conceivably take place, namely the region of near-spherical radial compression in the fluid approaching the dies, that of extensional flow between the dies and that of shearing flow within each die.

To investigate the nature of the alignment process, opposed dies extrusion experiments have now been carried out on the green glasses of glass-ceramics characterized by different morphologies for the principal crystalline phase. Using the techniques of X-ray diffraction and scanning electron microscopy to determine crystal orientations at various locations within the extrusion press, it has been possible to identify the physical mechanisms responsible for crystal alignment.

2. Methods and materials

Fig. 1 shows an isometric drawing of the extrusion press and a vertical section taken through the line of centres of the dies. The container, ram, base plug and die retaining plugs are all machined from EN 58B stainless steel and the dies from pyrolytic graphite. Before introducing an as-cast glass billet into the container, diametrically opposed dimples for locating the dies are machined into it using an ultrasonic tool immersed in a water-slurry of carborundum powder. The dies and die-retaining plugs are inserted and the complete assembly is placed inside the coil of an induction furnace and between the cross-head and base-plate of a mechanical testing machine. The temperature of the press is measured using an optical pyrometer.

The principal crystalline phases of the three different glass-ceramics used in the present experiments are a disilicate, an asbestos and a mica respectively. The linkages between adjacent SiO_4 tetrahedra within these three crystalline structures are conveniently represented by the Kagomé patterns shown in Fig. 2. The respective green glasses are a glass derived from the SiO_2–Li_2O–ZnO system which crystallizes to lithium disilicate, Corning 119 MCY the main crystalline phase for which is fluor-magnesio-richterite and Corning 119 SCR which crystallizes

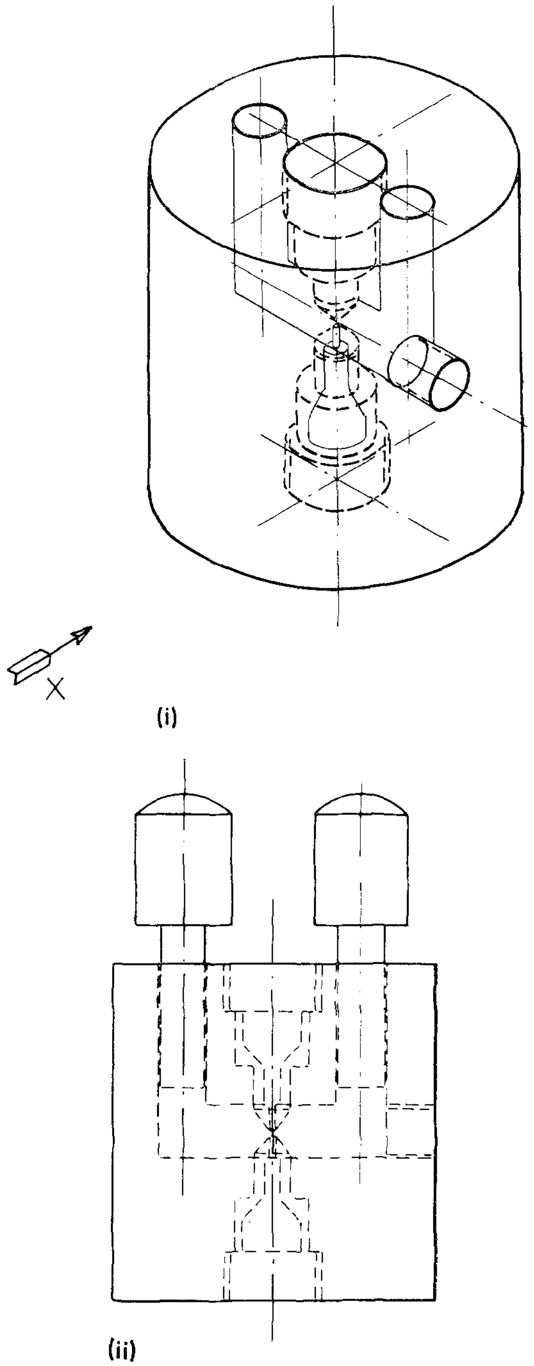


Figure 1 The extrusion press.

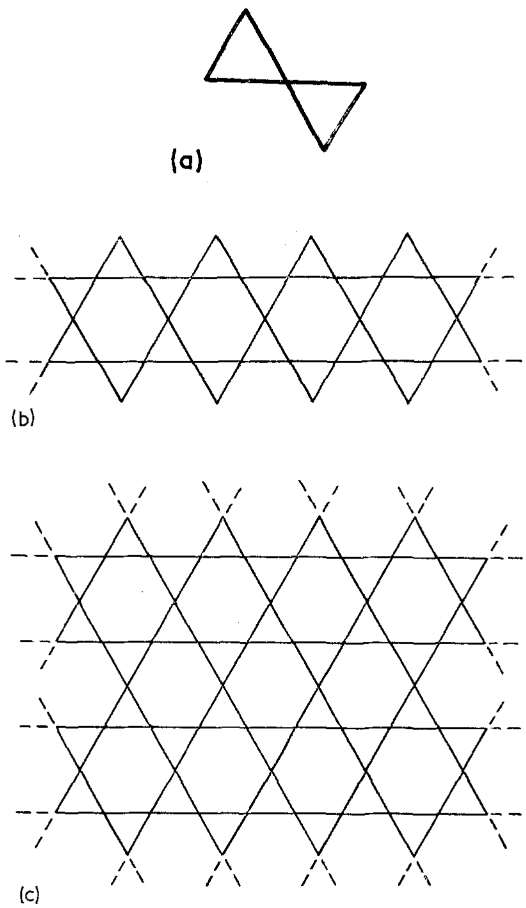


Figure 2 Kagomé patterns representing the corner-sharing faces of adjacent SiO_4 tetrahedra in (a) disilicates $(Si_2O_7)^{6-}$, (b) amphiboles $[(Si_4O_{11})^{6-}]_n$, (c) micas $[(Si_2O_5)^{2-}]_n$.

to the 1M modification of synthetic fluorophlogopite.

3. Textures

3.1. Lithium disilicate

1 mm diameter rod obtained by extruding the green glass at 800° C was crystallized but Laue transmission X-ray diffraction patterns showed the crystals to be randomly oriented. Extrusions obtained at higher temperatures were not crystallized, they did exhibit longitudinal zones of optical birefringence but subsequent crystallization did not yield a texture.

3.2. Fluor-magnesio-richterite

Extrusion at temperatures above 900° C results in oriented crystallization. Fig. 3 is the Laue X-ray transmission pattern obtained at 1000° C with an inter-die strain rate of 165 sec^{-1}. Equatorial arcs corresponding to at least four different interplanar spacings can be resolved. Fluoramphiboles are acicular crystals with monoclinic structure and, using X-ray powder data for synthetic fluor-magnesio-richterite [4],

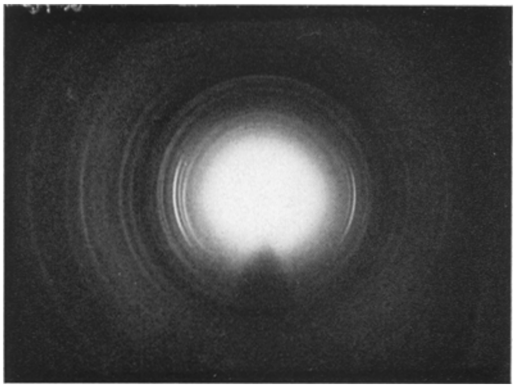
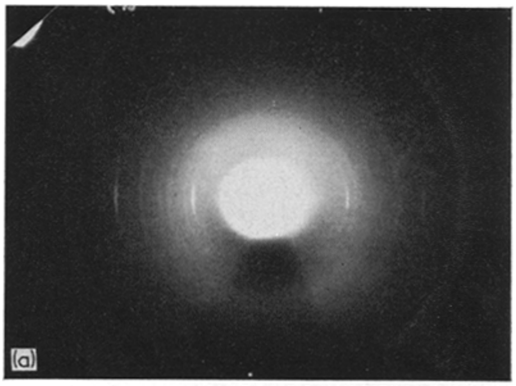


Figure 3 Extruded 119 MCY. The arcs are due to diffraction from the vertically oriented $\{hk0\}$ planes. The aspect ratio for this material is between 5:1 and 10:1 (Chyung [12]).



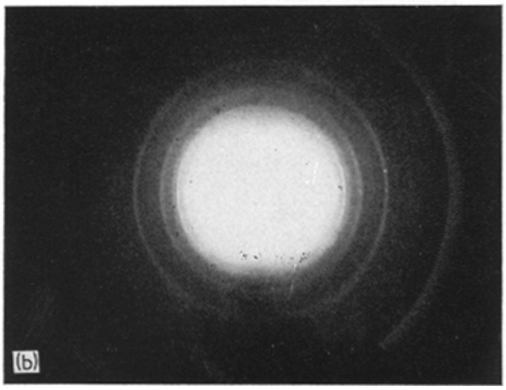


Figure 4 (a) Laue transmission diffraction pattern obtained from extruded 119 SCR. The rod axis is vertical, (b) same specimen after drawing at 850°C.

the arcs have been indexed as (310), (330), (170) and (350) reflections. Since [001] is the axis of the crystals, it is evident that the rods are aligned more or less parallel to the direction of

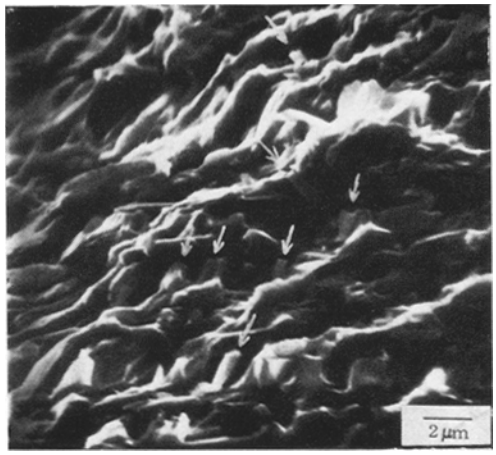


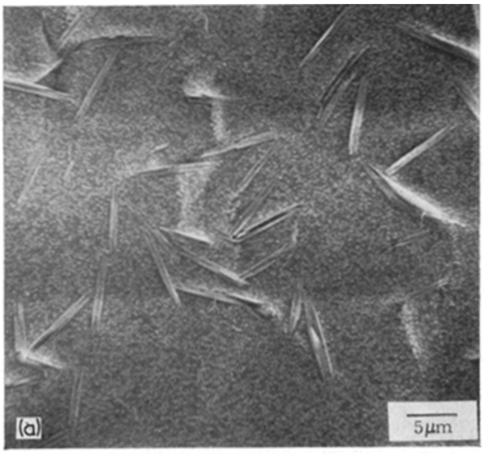
Figure 5 Scanning electron micrograph of extruded 119 MCY fractured in tension. Individual amphibole crystals are indicated by arrows.

extrusion. The arc lengths in Fig. 3 are larger by a factor of 3 than those for oriented fluorophlogopite crystals (Fig. 4a), from which it is inferred that the texture is not as well developed. This conclusion is confirmed by the scanning electron micrograph of a fracture surface of oriented amphibole rods reproduced in Fig. 5. Although the crystals are small, the acicular habit is revealed, the aspect ratio being about 5:1.

3.3. 1M fluorophlogopite

Using an inter-die strain rate of 165 sec^{-1}, extrusion at 950°C produces a partially crystallized material. Laue transmission X-ray diffraction (Fig. 4a), and scanning electron microscopy of polished and etched transverse sections (Fig. 6a and b), demonstrate that the fluorophlogopite plates are strictly aligned parallel to the extrusion direction. Fluorophlogopite crystals grown from 119 SCR are the monoclinic 1M polymorph [5] and not the hexagonal 3T form previously reported [1]. Hence, the three sets of equatorial diffraction arcs in Fig. 4a should be indexed as 003, 004 and 005 rather than 0009, 00012 and 00018. Incidentally, 004 is usually too weak to be observed and is not listed in the powder diffraction record of 1M synthetic fluorophlogopite [6]. The small rounded regions of light contrast also evident in Fig. 6 have not been identified; they are not observed in scanning electron micrographs of fracture surfaces [1].

The crystal alignment is maintained during subsequent drawing down to diameters of 50 µm



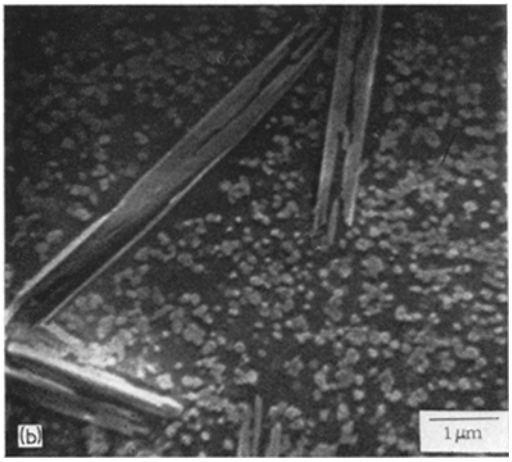


Figure 6 (a) and (b) Scanning electron micrographs showing the fluorophlogopite plates edge-on in transverse sections polished and etched in a water solution of NaOH (0.1 %) plus a trace of ethylenediaminetetraacetic acid (Chyung [12]).

or less (approximately five crystal diameters, Fig. 4b). The drawing process creates significant hollows in the fibre surface, the presence of which may be expected to enhance the frictional transfer of shear stress if the fibres are incorporated into composite materials.

Subsequent annealing at 950°C to complete the crystallization, reveals the nucleation of unoriented crystals (see Fig. 7). This is an important observation since it paves the way for exploiting the degree of anisotropy. Randomly crystallized 119 SCR is known commercially as Corning 9658 and is remarkable for its machineability and toughness. Both properties are attributed to cleavage of the fluorophlogopite crystals and both may now be tailored to suit specific requirements by adjusting the proportions of preferred and randomly oriented crystals. To manufacture a fully oriented material, it would be necessary to ensure that all the crystals are nucleated during extrusion. The kinetics of crystal nucleation and growth can be significantly altered by adjusting the composition of the green glass [7] and, with a suitable time for heating and extruding the billet, it may be possible to achieve nearly total alignment.

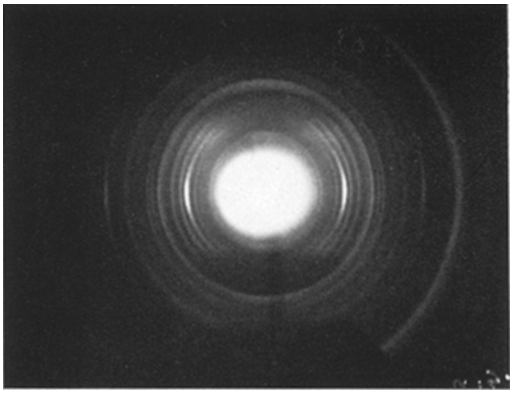


Figure 7 Diffraction pattern obtained after annealing extruded 119 SCR. The {001} arcs are complemented by Debye-Scherrer rings.

4. The alignment mechanism

X-ray diffraction has shown that crystallization commences during heating of the extrusion press, that is, before the extrusion process is under way. This means that at least some of the alignment is attributable to rotation of crystals already present. To investigate the occurrence of crystal alignment, the horizontal channel including dies has been trepanned from the press after quickly cooling at the end of an extrusion experiment on Corning 119 SCR. 1 mm thick slabs machined from this material have been examined by X-ray diffraction.

4.1. Spherical radial flow towards the dies

To achieve very high extensional strain rates, it is necessary to sink the dies into the charge, as a consequence of which the inflowing fluid experiences approximately spherical radial flow. The expected pattern of flow lines in a vertical section containing the axis is sketched in Fig. 8. There exists a nearest distance of approach of flow lines so the in-going crystal nuclei will tend to become radially aligned, that is, aligned more or less perpendicular to the extrusion direction

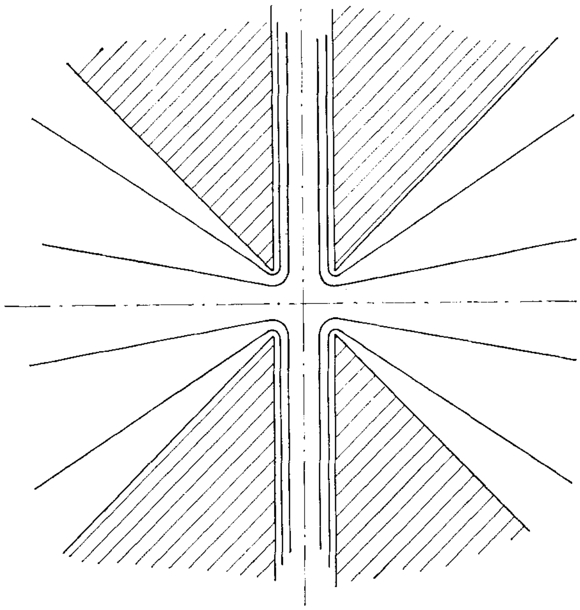


Figure 8 Schematic diagram of the pattern of flow lines expected during extrusion between opposed dies.

That such a preferred orientation has not been confirmed is attributed to the fact that the X-ray beam used for the present orientation determinations is 250 μm in diameter and, therefore, samples a relatively large solid angle.

4.2. Extensional flow

Between the dies, the fluid along the axis is subjected to pure extensional flow [3]. The strain rate is $\dot{\epsilon} \sim -2v/d$, where v is the speed of the extruded material and d is the bore diameter of the dies. Fig. 9 shows the Laue X-ray transmission pattern obtained from material just entering the lower die, it contains equatorial arcs similar but longer than those seen in Fig. 4a and verifies that the crystals become fairly well aligned parallel to the axis of symmetry during extensional flow. If alignment parallel to the flow lines also exists during the spherical radial flow, a rapid change in alignment direction must occur at the abrupt changes in flow direction associated with entry into the dies.

In the case of polyethylene, extensional flow is known to induce crystallization (see, for example, Frank [8]). It is possible that, by way of extension of corner-sharing SiO_4 tetrahedra, extensional flow also promotes crystallization in glasses. Oriented nucleation during extrusion may be the origin of some of the oriented crystals grown during post extrusion annealing.

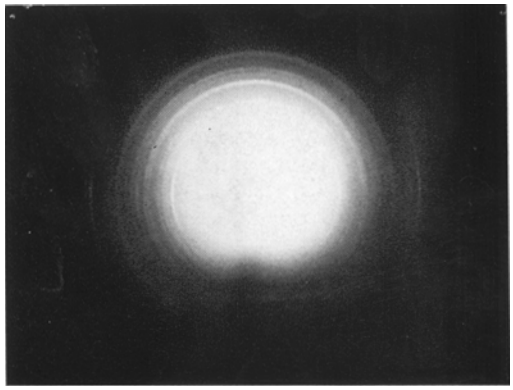


Figure 9 Sample of 119 SCR removed from the entry side of lower die. The exposure time was 1.5 h compared with 1 h (Fig. 4a).

4.3. Rotation of ellipsoidal particles in a shearing fluid

The observation that the arcs due to fluorophlogopite basal plane reflections are shorter for material emerging from than for material entering the dies indicates that shear within the dies enhances the crystal alignment. Jeffery [9] has calculated the motion of ellipsoidal particles immersed in a viscous fluid. Under conditions of laminar flow, a possible motion is that in which any one of the three axes of the ellipsoid lies permanently perpendicular to both the direction

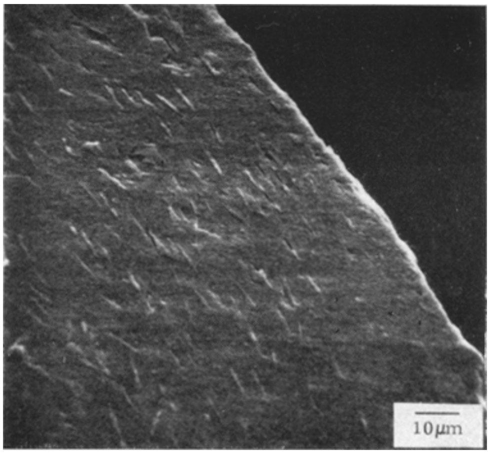


Figure 10 Scanning electron micrograph of a transversely fractured as-extruded rod of 119 SCR.

of flow and the direction of the velocity gradient, while the ellipsoid rotates about this axis with a variable spin. In the case of an ellipsoid of revolution rotating about its axis of revolution, the equations of motion are tractible and reveal that the motion is periodic. The axis of revolution describes a cone about the perpendicular to both the direction of flow and the direction of the velocity gradient. Intuitively, one might expect a disc to spin its way along the direction of shearing flow, the spin being fastest when the disc lies perpendicular to the direction of fluid shear so that, statistically, there is a preferred orientation parallel to this direction. A rod, on the other hand, might be expected to roll along the direction of shearing flow. Of the various motions possible under conditions pertaining to Jeffery's equations, these special motions for a disc and a rod do, in fact, correspond to the least dissipation of energy. Moving from extensional to shearing flow, adoption of the motion corresponding to least dissipation of energy would require a change in orientation for a rod and is not observed (Section 3.2).

Shear within the dies does, however, modify the alignment of plate-shaped particles. Although mica crystals in 119 SCR are parallel to the extrusion direction before entering the dies those near the surface of the extruded rod are also parallel to the surface, see Fig. 10. The radial distribution of disc axes observed in Fig. 10 is confined to the outermost layers and could be evidence of plug flow. Since the shear rate is highest at the die surface, thixotropy (a large fall in viscosity due to shearing) is most likely to occur in the outermost layers and rotation of the mica plates into parallelism with the die surface may well play an important role in this process.

5. Anisotropy of mechanical properties

The tensional (Young's) modulus of the fluorophlogopite material in the green glass, extruded and in the randomly fully crystallised conditions was obtained from dead load tests in which extension is measured axially using a d.c.-d.c. linear variable differential transformer mounted inside a cage which is itself in series with the test-piece [10]. Measurements for individual specimens are reproducible to an accuracy of $< 1\%$ and are listed in Table I. In the case of extruded material, the modulus is very sensitive to the volume fraction of oriented crystals and, since this volume fraction is small, it is not reproducible from one extrusion experiment to the next. Comparison of the highest values determined suggests that a low density of oriented mica crystals raises the modulus of 119 SCR by 33% compared with 11% for the improvement produced by the highest possible density of randomly oriented crystals. The absolute magnitude, 0.81 Mbar is still short of that for synthetic fluorophlogopite, 1.72 Mbar [11].

Crystal orientation also produces a significant enhancement of fracture stress. For example, a 1% volume fraction of mica crystals aligned parallel to the axis of a 1 mm diameter rod increases the tensile strength from < 0.22 kbar for the green glass to 0.61 to 0.74 kbars. This compares with < 0.69 kbar for a 0.5 volume fraction of randomly oriented crystals.

TABLE I Tensional modulus of oriented mica glass-ceramic

Identification	Volume fraction of principal crystalline phase	Young's modulus (Mbar)
Green glass (119 SCR)	0	0.58, 0.61
Extruded between opposed dies at 950°C	7.5×10^{-3}	0.53, 0.63, 0.81
Fully randomly crystallized (Corning code 9658)	0.6 (Chyung [12])	0.59, 0.62, 0.68

Knoop microhardness indentations on polished transverse and longitudinal sections of as-extruded 119 SCR reveal a factor of nearly two difference in indentation length. For example, using a 100 g load in a GKN microhardness tester, indentations 0.15 $\pm$ 0.08 mm long were obtained in transverse sections compared with 0.26 $\pm$ 0.06 mm for longitudinal sections, the latter being irrespective of indenter orientation. The residual glass has a high boron content [12] and is likely to have an open structure. Assuming that, as a consequence, it is amenable to compaction when subjected to a hydrostatic pressure, the hardness observations should be interpreted in terms of a resistance to compaction parallel to the mica plate orientation.

Acknowledgements

This work was stimulated by Professor F. C. Frank's discussion in 1970 with M. R. Mackley and Professor A. Keller on the subject of extensional flow in polyethylene. The benefit of Professor Frank's comments during the preparation of this paper is also very much appreciated. H. N. Young built the apparatus and its precursors and, together with Dr Mackley and H. G. S. Havard, contributed many ideas during the development work. In selecting and obtaining glasses likely to be amenable to the orientation of crystal nuclei, the author received generous help from Drs G. H. Beall, C. K. Chyung and D. G. Grossman of the Corning Glass Works. The author thanks Corning Glass Works for permission to publish work on materials supplied by them. This work is the subject of patent applications.

References

1. K. H. G. ASHBEE, *Nature* **252** (1974) 469.
2. M. R. MACKLEY, University of Bristol Ph.D. Thesis (1972).
3. F. C. FRANK, A. KELLER and M. R. MACKLEY, *Polymer* **12** (1971) 467.
4. G. V. GIBBS, J. L. MILLER and H. R. SHELL, *Amer. Mineral.* **47** (1962) 75.
5. D. G. GROSSMAN, private communication (1974).
6. F. D. BLOSS, G. V. GIBBS and D. CUMMINGS, *J. Geol.* **71** (1963) 537.
7. C. K. CHYUNG, G. H. BEALL and D. G. GROSSMAN, "Electron Microscopy and Structure of Materials" (University of California Press, Berkeley, 1972) pp. 1167-94.
8. F. C. FRANK, *Proc. Roy. Soc. A* **319** (1970) 127.
9. G. B. JEFFERY, *ibid* **102** (1923) 161.
10. R. MORRELL, *J. Phys. E* **5** (1972) 465.
11. H. R. SHELL and K. H. IVEY, "Fluorine Micas" (U.S. Department of Interior Bulletin 647, 1969) p. 187.
12. C. K. CHYUNG, private communication (1974).

Received 29 January and accepted 31 January 1975.