Good internal ferroelectric bias can be induced in TGS crystals, by growing from solutions containing Ru and Fe and to a lesser extent with Cr. Of these additives, Ru and Fe give the largest effect, but Fe gives much more reproducible results than Ru.

The effect is tentatively explained by the association of M^{3+} with glycinium ions in the structure; the ligand formation makes dipole reversal difficult. Further studies on Fe-doped crystals using Mössbauer spectroscopy are being carried out, which should help to elucidate the exact mechanism.

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J. SILVER
E. A. D. WHITE
V. M. WOOD
*Electrical Engineering Department,
Imperial College,
London, UK*

Glass-ceramics with an aligned microstructure

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses; this results in a material with a random arrangement of crystals as a dispersed phase. The physical properties of this material are isotropic [1].

In this letter we describe some of the results obtained from hot-extruding a glass-ceramic; this technique has been used to produce a material with aligned crystal microstructures in $Li_2O–SiO_2$ glass-ceramics (compositions given in [2]). The extruded material consists of a glass matrix and two crystalline phases; one of these phases is aligned morphologically and crystallographically parallel to the extrusion axis (Fig. 1).

The apparatus for the hot-extrusion experiments, shown in Figs. 2 and 3, consists of a stainless steel plunger with a water jacket which is attached to the cross-head of an Instron Universal Testing Machine. The plunger descends into a die which is heated by high frequency induction and stands on the load cell of the Instron Machine. The temperature of the die can be monitored by optical pyrometry or by a thermocouple which is situated in the die. The induction coil is electrically insulated from the die by a fused silica tube. When the extruded material is clear of the die it enters a water-cooled collection zone; the die is a loose fit on the stand at room temperature and can be lifted off to collect the extruded material.

The microstructure of the extruded material was analysed statistically in terms of the volume fraction of the crystalline phases (~ 85%), the mean crystal–crystal spacing and the distribution function of the number of crystals $N(\theta)$, making an angle θ with a reference direction. The degree of orientation of the crystal phases was found to be independent of the quantity of material

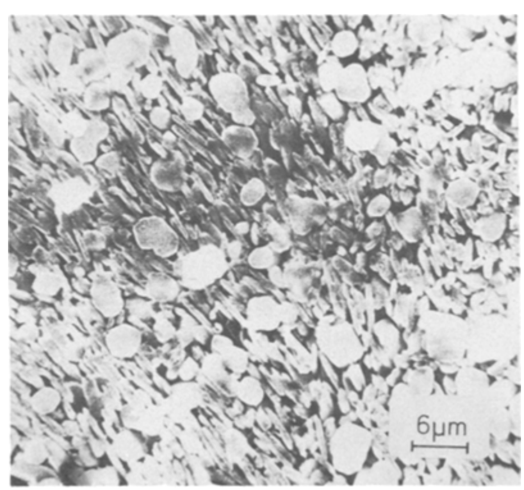

Figure 1 **SEM of an etched surface of an extruded glass-ceramic; the extrusion axes is parallel to a diagonal.**

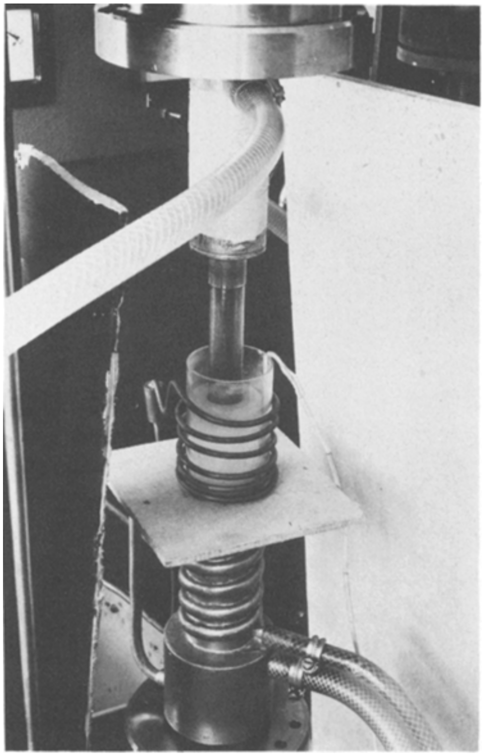

Figure 2 Photograph of the extrusion apparatus.

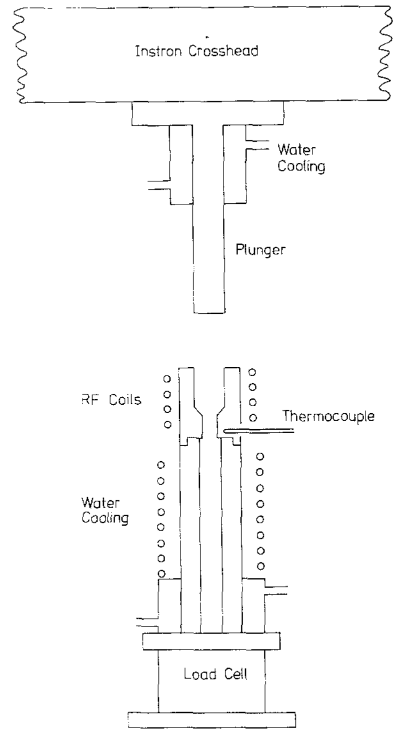

Figure 3 Details of the extrusion die.

extruded and decreased in a radial direction from the surface to the axis of the extruded material.

Control specimens of the same compositions, heat-treated at the same temperature and for the same time as the extruded samples were also analysed statistically. The microstructures of the glass-ceramics were observed using a scanning electron microscope in the secondary electron and cathodoluminescence modes [2].

In the following, the main features of the physical property measurements for the control and extruded glass-ceramic samples are briefly summarized and compared. A degree of anisotropy, DA, can be evaluated by considering the ratio of a physical property measurement in two perpendicular directions; for an isotropic system this ratio would be unity.

The mechanical properties of the extruded material were anisotropic; the maximum value of the Young's modulus and rupture strength (three-point loading) of this material was attained when the samples were loaded perpendicular to the extrusion axis. The minimum values of these moduli were approximately the same as the equivalent results for the control samples; the degree of anisotropy for these moduli was approximately 2.

The Knoop hardness number of the extruded material was found to vary with the orientation of the indenter relative to the extrusion axis (Fig. 4).

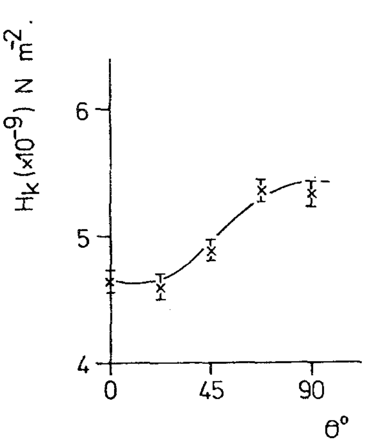

Figure. 4 Knoop hardness as a function of orientation of indenter.

Two coefficients of thermal expansion were measured for each glass-ceramic; a low temperature coefficient was isotropic for the extruded material and had a value approximately three times that measured for the control samples. A high temperature coefficient was found to be anisotropic for the extruded material and greater in a direction perpendicular to the extrusion axis than parallel to it. The average value of this coefficient for the extruded samples was approximately twice that measured for the randomly oriented material. It is believed that the anisotropy in this coefficient is partly due to differences in the expansion coefficient of a crystalline phase (lithium disilicate) with crystallographic direction.

The electrical properties of the control and extruded glass-ceramics were also measured; the volume resistivity of the latter material was anisotropic, being greater when measured perpendicular to the extrusion axis. The degree of anisotropy for this property was found to vary between 1.8 and 38. The anisotropy of the resistivity measurements was reflected in the variation of the activation energy for conduction and the pre-exponential constant of an Arrherius equation.

The dielectric properties of the extruded material showed no anisotropy.

It is intended to describe the results of these investigations in full detail in later publications.

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D. I. ATKINSON
P. W. MCMILLAN
Department of Physics,
University of Warwick,
Coventry, UK