References

1. A. R. PATEL and JACOB KOSHY, *J. Crystal Growth* 2 (1969) 128.
2. A. R. PATEL and R. P. SINGH, *ibid* 5 (1969) 70.
3. A. R. PATEL and H. L. BHAT, *ibid* 8 (1971) 156.
4. A. R. PATEL and S. K. ARORA, *ibid* 18 (1973) 156.
5. E. NICKLAUS and F. FISCHER, *ibid* 12 (1972) 337.

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Additives causing internal bias in TGS crystals

The recent interest in triglycine sulphate for infrared detectors has re-stimulated work on this material and has led to the interesting and useful discovery that doping with alanine can cause permanent polarisation in one direction [1]. This effect has been explained in terms of modification of the hydrogen bonding by the substitution of small amounts of the larger alanine molecule for certain of the glycine units. Similar but less useful effects have been obtained by doping with sarcosine and other amino acids [2].

Numerous other dopants have been used in TGS growth in attempts to modify the Curie temperature, resistivity, dielectric constant and loss of the material. Generally the only effective additives are those which form isostructural compounds and complete solid solution ranges, such as selenates and fluoberyllates or the equivalent deuterated compounds. Many other additives cause habit modification, but do not give any significant changes in properties. However, this failure to cause property modification may partly be due to the fact that TGS substantially rejects most impurities and very high concentrations in solution are necessary before significant quantities are incorporated in the crystals.

In the present work we report on the effect of incorporation of Ru^{3+}, Fe^{3+} and Cr^{3+} in TGS; in the last two cases, much higher concentrations of additives have been used than have hitherto been reported [3].

Ruthenium red (Johnson Matthey Chemicals Ltd) was used as one of the very few water soluble ruthenium salts available. $FeCl_3 \cdot 6H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$ (both Hopkin and Williams Ltd) were used for the other dopants.

In most cases the crystals were grown in 1 litre beakers suspended in a temperature-controlled silicone oil bath similar to that described by Moravec and Novotny [3]. Seed crystals were mounted in silicone rubber on perspex platforms which rotated at 70 rpm; the latter also served to stir the solutions. The direction of rotation was reversed every 30 sec to promote uniformity of growth. In some cases crystals for preliminary studies were grown by evaporation in beakers using similar seed mounting and stirring arrangements.

The compositions of the solutions grown were:

"standard" solution: 1 M TGS in water (saturated approximately at room temperature)
Dopants added: Ru red 2 to 5 $g\,l^{-1}$.
$FeCl_3 \cdot 6H_2O$, 0.08, 0.27, 0.64, 1.32, 2.64 and 5.28 M
$KCr(SO_4)_2 \cdot 12H_2O$, 0.2 M
HCl, 0.24 M.

The addition of HCl was made for control purposes to determine the effect of Cl^- alone.

The Ru-doped crystals from several runs showed a consistent habit modification compared with undoped TGS [3]. However, on different occasions some degree of decomposition was noted in the solutions during growth with the production of a brown precipitate. The crystal products were slightly brown-green in colour and showed an internal bias which varied in different specimens, to a maximum of $\sim 2\,kV\,cm^{-1}$, which is comparable with that obtained for TGS grown from 20% L-alanine doped solutions. Analysis indicated that the crystals showing the highest bias contained 10 ppm of Ru.

The reasons for the variable results obtained are thought to be due to the very complex and not well understood chemistry of Ru compounds. Commercial ruthenium red is not a simple substance and evidently degrades when added to TGS solutions. The reaction products vary –

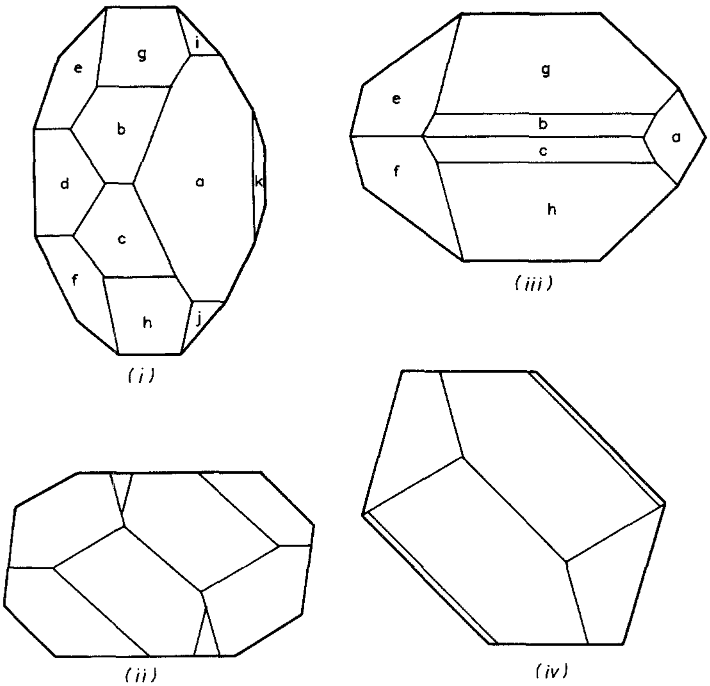

Figure 1 Habit modification in Fe-doped TGS. (i) Undoped TGS viewed perpendicular to the *b*-axis; (ii) undoped TGS viewed down the *b*-axis; (iii) Fe-doped TGS viewed perpendicular to the *b*-axis; (iv) Fe-doped TGS viewed down the *b*-axis. (a) 0 0 1, (b) $\bar{1}\,1\,1$, (c) $\bar{1}\,\bar{1}\,1$, (d) 1 0 0, (e) $\bar{1}\,1\,0$, (f) $\bar{1}\,\bar{1}\,0$, (g) $\bar{1}\,2\,1$, (h) $\bar{1}\,\bar{2}\,1$, (i) 0 2 1, (j) $0\,\bar{2}\,1$, (k) 1 0 1.

probably as a result of temperature differences during the preparation of the solutions – and hence the concentration of the active species producing the effect varies in the crystal products.

Since Fe is in the same sub-group as ruthenium it was decided to investigate the effect of this additive in detail. Preliminary experiments using $Fe_2(SO_4)_3$ and $FeCl_3 \cdot 6H_2O$ showed that Fe^{3+} produced a similar crystal habit modification to Ru addition (Fig. 1). Solutions of increasing concentrations of $FeCl_3 \cdot 6H_2O$ gave crystals of increasing pale brown colour and increasing acicular habit. Since experiments with Cl^- added as HCl in comparable concentrations had no detectable effect on the TGS crystal produced, it was evident that any changes in habit or properties were due solely to Fe^{3+}, and all subsequent experiments were made with $FeCl_3 \cdot 6H_2O$ as additive.

The colour of the TGS/$FeCl_3$ solutions was deep red-brown (comparable $FeCl_3$ solutions were yellow brown) which was taken as an indication of complex formation in solution. Evidence for the formation of a diglycinate $-Cr^{3+}$ chelate [4] and a Cu^{2+} chelate [5] in TGS solution has been reported, suggesting that a similar Fe^{3+} complex exists in Fe doped TGS solutions.

The Fe doped crystals showed an internal bias of up to 5 kV cm^{-1}.

To test whether other trivalent ions would give similar bias effects, Cr^{3+} incorporation was investigated. Small pale mauve crystals were obtained from the $KCr(SO_4)_2 \cdot 12H_2O$ doped solutions. These showed a small degree of bias of between 100 and 500 V cm^{-1}.

Esr investigations of Cr doped TGS have been reported [4] to give evidence of a shift of the ligands surrounding the Cr^{3+} when ferroelectric switching occurs. We have found that incorporation of sufficient M^{3+} ions can cause bias, which is consistent with a modification of the ligands by the M^{3+} ion. The Cr^{3+} ion is reported to be on a site between G II and G III in TGS crystals [4, 6]; these are glycine–glycinium units which are reputed to reverse when the dipoles switch [6]. It is suggested that the M^{3+} ions lock these glycine molecules in position and hence make the reversal difficult to accomplish due to the strong bonding of the units with Fe^{3+}.

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.

Acknowledgement

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References

1. P. J. LOCK, *Appl. Phys. Letters* **19** (1971) 390.
2. K. T. KEVE, K. L. BYE, P. W. WHIPPS and A. D. ANNIS, *Ferroelectrics* **3** (1971) 39.
3. F. MORAVEC and J. NOVOTNY, *Kristall und Technik* **6** (1971) 335.
4. K. NISHIMURA and T. HASHIMOTO, *J. Phys. Soc. Japan* **35** (1973) 1699.
5. A. LOSCHE and W. WINDSCH, *Phys. Stat. Sol.* **II** (1965) 455.
6. S. HOSHINO, Y. OKAYO and R. PEPINSKY, *Phys. Rev.* **115** (1959) 323.

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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

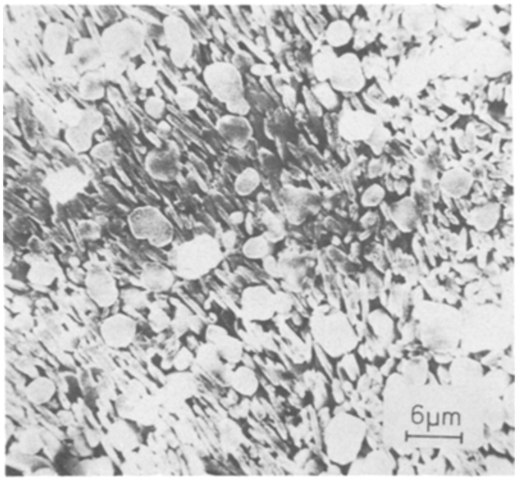

Figure 1 **SEM of an etched surface of an extruded glass-ceramic; the extrusion axes is parallel to a diagonal.**