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## *Orientation dependence of l-alanine incorporation in TGS crystals*

Ferroelectric triglycine sulphate (TGS) crystals are presently grown on a large scale so that the pyroelectric properties of this material may be utilized in single and multi-element infra-red detectors, and in the pyroelectric vidicon thermal imaging device. The crystals are grown from aqueous solution on seeds which are cut and cleaved from existing crystals perpendicular to the ferroelectric *b*-axis and which have a growth face area ~1 cm$^2$. The seeds are mounted with silicone rubber on large horizontal perspex plates carried on each end of four cross-pieces on a central, reversing stirrer. Because each seed is set into the plate so that the single exposed face $\{0\,1\,0\}$ is flush with the top surface, growth perpendicular to the plane of the seed can only take place vertically upwards, and the grown cystal is a truncated pyramid, with its base resting on the seed plate. This crystal is effectively one half of the crystal which would have grown had the seed been suspended freely in the solution.

TGS has the space group $P2_1/m$ above its Curie point (49.5° C) and the transition to the ferroelectric state is order/disorder, brought about principally by the switching of glycinium ions at one type of site in the lattice [1]. In an unpoled TGS crystal, with equal numbers of positive and negative domain terminations at an $\{0\,1\,0\}$ surface, the mirror plane persists macroscopically at temperatures below the Curie point and the positive coordinate end of the *b*-axis is indistinguishable from the negative end. In practice this means that the crystal grown on one $\{0\,1\,0\}$ face of a cleaved seed is the mirror image of the crystal grown on the opposite $\{0\,\bar{1}\,0\}$ face, but is otherwise identical. Thus the orientation of a seed mounted for growth need not be specified for pure TGS solutions.

It has been found [2] that it is advantageous to grow TGS crystals from solutions doped with *l*-alanine since the alanine substitutes to a small extent for glycine in the lattice and, because it has an asymmetric molecule, causes the ferroelectric domains to be locked in a single direction; this effect can be expressed in terms of the field required to overcome domain locking, which is known as the internal bias field. Since the crystal is permanently poled the plane of symmetry perpendicular to the *b*-axis no longer exists.

It would seem, *a priori*, that the alanine concentration in the growth solution would govern the proportion incorporated by crystals and hence their internal bias but the growth of alanine doped crystals of a required bias on $\{0\,1\,0\}$ seeds was complicated by the fact that, as has been reported [3], TGS crystals grown from solutions containing *l*-alanine developed a habit which was asymmetric about the $(0\,1\,0)$ plane. Seeds mounted with one orientation gave crystals whose growth rate was extremely slow (compared to the growth rate in comparable conditions in an undoped solution) which were termed "short"; while seeds mounted with the other face exposed to the solution gave crystals whose growth rate was comparatively fast though still slow compared to growth in an undoped solution, which were termed "tall". It was also found that the short crystals, grown on the $(0\bar{1}0)$ face, contained an appreciable amount of alanine, while the tall crystals contained very much less.

A measure of the amount of alanine incorporated in a crystal is given by the internal bias, determined from the ferroelectric hysteresis loop displayed on an oscilloscope screen via a Sawyer–Tower circuit. The relationship of this measurement to the sample's alanine content was demonstrated by a set of enzymatic analyses [4] performed by Dr M. P. Esnouf of the Radcliffe Infirmary, Oxford, on a number of samples of TGS of known internal bias. The results of these analyses are summarized in Fig. 1, in which the alanine content determined is plotted against the measured internal bias. These results show that the amount of alanine incorporated in the material, which was grown in solutions containing 13 to 30 mol % alanine, was very small.

When measurements of the internal bias of a number of crystals grown on large area $(0\bar{1}0)$ seeds were made on a routine basis it was found that while the exact amount of alanine incorporated depended on factors which will be discussed more fully elsewhere [5] there was a clearcut difference between the bias of tall and short crystals. For example, when grown from a solution containing 18 mol % *l*-alanine tall crystals showed a bias of 0.1 to 0.2 kV cm$^{-1}$ and short crystals a bias of 3 to 6 kV cm$^{-1}$. During investigations of the variation of alanine content within $\{010\}$ slices taken from individual crystals, in which bias measurements were made at regularly spaced points on the surface of the slices, double and triple hysteresis loops indicated the existence of distinct regions of different bias near the edges of the samples. It was assumed that these regions originated through growth on different habit faces at the sides of the crystal, but a particular bias value could not be attributed unambiguously to material grown on a particular face from the information available. In addition, it was not clear whether an exceptionally high bias value occasionally obtained, usually from a very restricted area, was due to anomalous growth kinetics at a particular face, or possibly to some strain effect in the lattice.

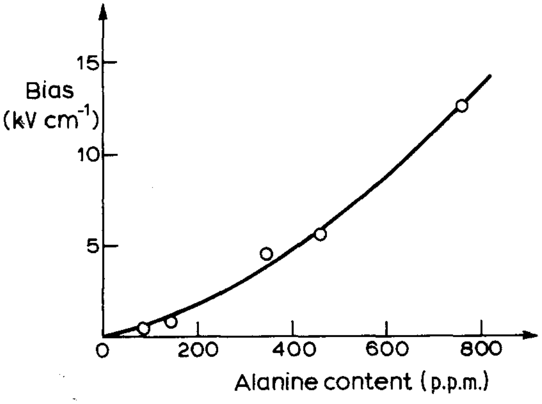

*Figure 1* Plot of alanine content versus internal bias.

A convenient method of growing crystals on seeds cut parallel to each of the major habit faces TGS, in order to identify the origin of material of different bias values was provided by the rotating disc growth technique [6]. In this technique a relatively thin crystal (1 to 1.5 cm) is grown onto a single large area seed mounted beneath a central shaft rotating at high speed in a relatively small volume of saturated solution. The smaller volume of solution used, and the ease of operation make this technique particularly suitable for sets of growth runs in which one parameter, e.g. the seed orientation, is changed between each run.

Seeds parallel to the major habit faces of TGS, shown in Fig. 2, were cut from large conventionally grown crystals using a wet string saw and were polished on wet tissue paper and mounted for rotating disc growth. Because of the difficulties associated with orienting the large crystals (~400 g) for cutting, only those faces which developed large areas on the available tall and short crystals were used. All growth was carried out in the same 18 mol % alanine solution (the alanine content was calculated as an excess over the glycine present). After each run the equivalent of the material removed by the growth of the crystals was replaced in the solution as glycine and sulphuric acid, and any water lost by evaporation was replaced so that each run started at the same saturation temperature. All the crystals grew well and maintained a large area of the original seed face, see for example Fig. 3. Although the relative

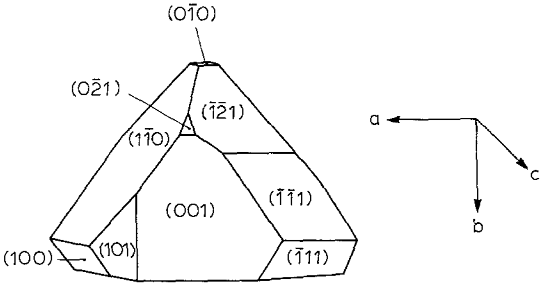

*Figure 2* Principal growth faces of TGS crystal labelled according to Wood and Holden axes $a = 9.162$ Å, $b = 12.643$ Å, $c = 5.735$ Å, $\beta = 105.55°$.

importance of the habit faces differed considerably from that normally encountered the faces were readily identified by comparison with a conventionally grown TGS crystal, and the cleavage plane located. A sample parallel to the $(0\,1\,0)$ plane was cleaved from each crystal and the internal bias measured at electrodes applied on a 5 mm grid pattern. The sample was taken from near the centre of each crystal to ensure that the measurement was made on material which had grown on the face chosen for the seed, rather than on one of the faces forming the sides of the crystal. The results of these measurements are given in Table I.

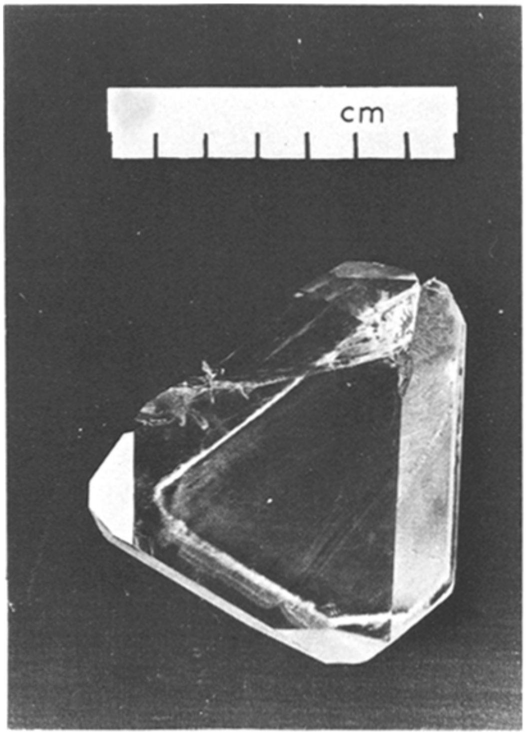

*Figure 3* "Tall" crystal grown on $(\bar{1}\,1\,1)$ face.

The results shown in Table I confirm that the internal bias of *l*-alanine doped TGS varies according to the growth pyramid in which the material was deposited, but also show that, for the major habit faces, the variation is rather small except in the case of the $(0\,\bar{1}\,0)$ face, perpendicular to the ferroelectric axis, and the $(\bar{1}\,\bar{1}\,1)$ face. Material grown on the $(\bar{1}\,\bar{1}\,1)$ face was identified as the source of the high bias measurement encountered in small regions of crystals grown on $(0\,\bar{1}\,0)$ seeds.

The high bias (and other properties associated with presence of alanine) developed by this material is unlikely to be useful in application requiring a large area of the material since the angle between growth plane and the ferroelectric axis would lead to a high proportion of waste in cutting from the large crystals which would have to be grown. The problem of striations due to irregularites in the growth rate would also have to be overcome; these are unimportant when the direction of growth is perpendicular to the cutting plane as is the case for $(0\,\bar{1}\,0)$ seeded crystals. The highly biased material produced by growth on the $(\bar{1}\,\bar{1}\,1)$ face could be useful for applications requiring only a small area however.

The results also show that alanine is incorporated to a greater extent by a short crystal not only for the $\{0\,1\,0\}$ faces, but also for the other pairs of faces examined. It should be noted that the investigation was carried out for the fixed composition containing 18% alanine in solution; while, on the basis of isolated measurements made on crystals grown from solutions of different compositions, alanine incorporation at all faces would be expected to decrease if the solution alanine concentration

TABLE I Internal bias ($E_B$) and alanine content of TGS grown on seeds of different orientations

| Growth face | | $E_B$(kV cm$^{-1}$) | Alanine content (p.p.m.) |
|---|---|---|---|
| $(1\,1\,0)$ | | 1.0 | 130 |
| $(\bar{1}\,1\,1)$ | tall | 0.6 | 95 |
| $(\bar{1}\,2\,1)$ | | 0.5 | 80 |
| $(\bar{1}\,\bar{1}\,1)$ | short | 8.0 | 570 |
| $(\bar{1}\,\bar{2}\,1)$ | | 0.8 | 115 |
| $(0\,1\,0)$ | | 0.1–0.2 | <20 |
| $(0\,\bar{1}\,0)$ | | 3.0–6.0 | 300–460 |

decreased, or vice versa, these changes do not necessarily occur at the same rate for all faces. The relative rates of incorporation at the different faces would then change as the solution composition changed.

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## *Development of mechanical strength in hot-pressed silicon nitride*

Alpha-silicon nitride, when hot-pressed with magnesia as an aid to densification, shows anomalous strength development behaviour in that its room temperature modulus of rupture (M O R) continues to increase with hot-pressing time after the completion of densification [1]. This increase is known to be linear with time up to a maximum of approximately $800\,\text{MNm}^{-2}$, after which continued hot-pressing leads to a reduction in strength.

Several explanations for the strength increase have been put forward, including the removal of large microstructural features during prolonged hot-pressing [1] or the removal of traces of closed porosity by a mechanism involving $\alpha$- to $\beta$-silicon nitride phase transformation [2]. Material prepared from a starting powder containing a high proportion of $\alpha$-silicon nitride has been shown [3] to have twice the strength and a fracture energy four times as great as material hot-pressed from powder with a high $\beta$-content. The greater fracture energy of the hot-pressed $\alpha$-silicon nitride has been attributed to the formation, during hot-pressing, of lath or fibre-like grains thus increasing the frictional interaction between grains during crack propagation. It is believed [4–6] that the high-temperature strength of hot-pressed $\alpha$-Si$_3$N$_4$ may also be enhanced by an increased grain pull-out contribution of fibre-like grains to the crack propagation stress.

The purpose of the present work is to investigate further, the post-densification development of strength of hot-pressed $\alpha$-silicon nitride containing magnesia. Accordingly, the room temperature M O R has been measured on a number of samples of $\alpha$-silicon nitride hot-pressed to theoretical density and then subjected to continued hot-pressing or to subsequent heat treatment without applied pressure.

Discs, 25 mm in diameter, were hot-pressed, as described elsewhere [7], from high purity silicon nitride* containing 94% of the $\alpha$-phase. Each disc was diamond machined into six bars of dimensions 2 mm × 2 mm × 22 mm. The longest faces of the bars were ground by hand with 1200 mesh silicon carbide powder on a flat glass plate to impart an even surface finish. The room temperature M O R was determined in three-point bending using fixed steel knife-edges of 19 mm span in an Instron model 1026 testing machine operating at a cross-head speed of $0.5\,\text{mm min}^{-1}$. $\alpha$- and $\beta$-silicon nitride contents were measured by X-ray diffractometry [8]. Thin foil specimens and fracture surfaces were examined respectively by high voltage transmission electron microscopy† and scanning

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