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Induced growth anisotropy in TGS crystals

Crystals of ferroelectric triglycine sulphate (TGS) are currently of interest for use in infrared imaging and detection devices, and the controlled growth of large crystals has received considerable attention.

The pure material usually grows with antiparallel arrays of ferroelectric domains which can be displayed by various techniques, including decoration by vacuum evaporation of tellurium on to freshly cleaved surfaces [1]. Single domain specimens can readily be formed by polarizing fabricated crystal specimens by the application of relatively low fields, of the order of 200 V cm^{-1} The material is, however, subject to depolarization by thermal, mechanical or electrical means and great interest has resulted from the discovery that crystals doped with small concentrations ($\sim 1\%$) of L-alanine result in a built-in bias which can only be reversed by application of a large field.

In the controlled programmed growth of the doped (LATGS) crystals from aqueous solution, a curious phenomenon was noted. The growth technique used involves placing seed crystals, prepared from cleaved slices, on a perspex shelf in such a manner that only one "half" of a crystal develops. Starting with undoped TGS seeds in L-analine doped solution, it was noted that all crystals grew in an elongated manner along the *c*-axis, as reported by Lock [2], but some were also elongated along the *b*-axis, while others grew in a truncated form. Subsequent experiments with doped seeds confirmed that the difference in form was related to the orientation of the seed and depended on whether the 0 1 0 or $0\bar{1}0$ plane was exposed to the solution. Crystals grown along the two directions are shown in fig. 1, the lower crystal (inverted for the photograph) corresponding to growth on the $0\bar{1}0$ plane. This confirms that the alanine molecules are stereo-specifically adsorbed on to the crystal surface and are incorporated into the crystal in a precise orientation and indicates that the built-in bias occurs without the necessity of using single-domain seed crystals.

One other difference noted between the two forms of crystal was that truncated crystals were badly strained and tended to shatter either during growth or on cooling to room temperature at the termination of the run. This occurred when both forms of crystal were grown in the same tank under identical conditions of supersaturation. The tall-form crystals were unstrained and showed no unusual defects even though the linear growth rate was approximatly 1.5 × that

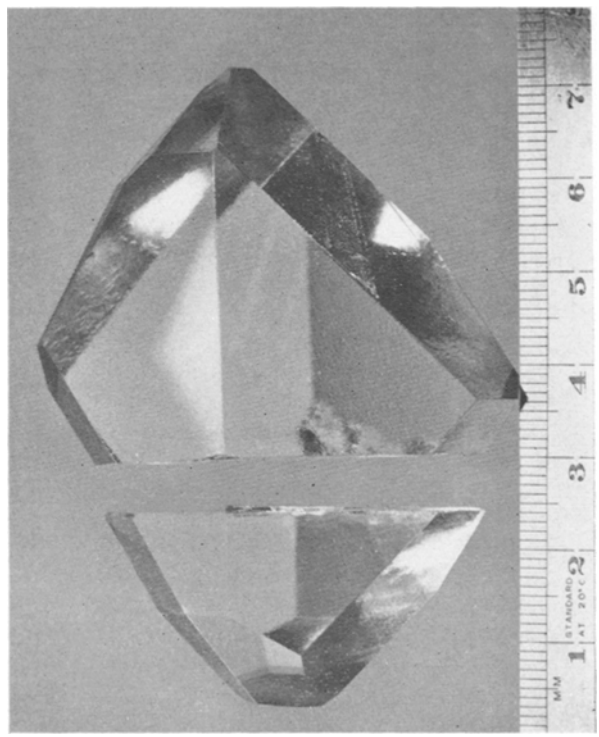

Figure 1 Tall and short habit crystals of LATGS.

of the short form. The average weight of tall-form crystals was 120 g, while that of the short form was 25 g.

Attempts to display domain configuration on both types of crystals by tellurium evaporation showed that the lenticular domains normally observed in TGS slices were absent. Qualitatively this effect was confirmed by the difficulty experienced in separating cleaved slices from a crystal specimen. The absence of reversely polarized domains would lead to a greater electrostatic attraction due to the enhancement of the surface charges developed on the opposing surfaces of the cleavage.

A Sawyer-Tower hysteresis loop circuit was used to observe any differences between doped and normal TGS crystals. "y"-axis cleavage plates approximately 0.25 mm thick were prepared and gold electrodes of 3 mm diameter were vacuum deposited onto the faces. Comparison with undoped TGS showed no significant difference in the value of spontaneous polarization P_S, but large intrinsic bias was observed in hysteresis loops from both tall and short habit crystals. In addition, about one third of the specimens investigated showed gross deformation of the P/E loops, i.e. pronounced double or triple loops, while one in ten showed slight deformation of the loop.

It is concluded that the addition of alanine induces a growth asymmetry which is not observed in "pure" TGS growth. This observation tends to confirm the work reported on locked-in polarization of alanine doped TGS crystals.

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Longitudinal crazing in isotropic polymers

Crazing in isotropic amorphous polymers has been extensively studied and several criteria have been proposed for craze appearance and the orientation of craze growth with respect to the applied-stress field [1-5]. In total, the observation of Sternstein *et al* [2] that "craze growth occurs along a path such that the major principal (tensile) stress always acts perpendicularly to the craze plane" provides an adequate description of the areal development of crazes in unidirectional deformation. We wish to report some unusual, new observations on craze growth in cyclic deformation; these observations indicate that factors other than the applied-stress field can significantly alter criteria for craze formation and growth in nominally isotropic glassy polymers.

Samples of poly(methyl methacrylate) (PMMA), and polycarbonate (PC), were cycled at constant strain-rate between equal strain limits in tension and compression at 77 K; the experimental technique has been discussed elsewhere [6]. Fig. 1 shows a typical low-cycle fatigue fracture surface in PC; two important fracture characteristics are noteworthy. First, the fracture face is smooth and planar, and shows the high reflectivity typical of a surface created by crack propagation through a well-developed pre-existing craze [4]. In other words, prior to crack propagation, crazes grew normal to the stress axis, i.e., in the conventional craze mode, completely across the specimen cross-section. Second, as shown in greater detail in Fig. 1b, a series of concentric ring-shaped markings cover the fracture surface. Fractured samples were sectioned longitudinally (by a technique described in [7]); Fig. 2 shows such a section, and detailed examination established unequivocally that the shorter longitudinal markings (parallel to the stress axis) are, in fact, crazes. The transverse markings are the traces of conventional crazes formed perpendicular to the stress axis. The concentric rings in Fig. 1 mark the