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Homogeneity of triglycine sulphate crystals

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Powder suspensions in silicone oil have been used for decorating slices of TGS grown from aqueous solutions by conventional means, and by a spinning disc technique. The method provides a quick means of assessment of crystal quality and uniformity and has helped in the interpretation of some of the phenomena observed in electrical measurements on both undoped and doped TGS crystals. Sections of crystals grown with alanine as dopant – which gives the crystals an internal polarization bias – show a markedly non-uniform decoration pattern, indicative of a variation of polarization in different growth sectors. Much improved uniformity is demonstrated in crystals grown on a single surface under controlled conditions of solution flow.

1. Introduction

The use of fine particles suspended in a suitable non-polar liquid for "decoration" of domains in ferroelectric crystals has been known for some years [1], but little or no use has been made of it for serious investigations of crystal perfection or homogeneity. Indeed, it seems to have been dismissed as one of several methods of domain decoration, for example by etching [2], or vacuum evaporation [3]. More recently, a nematic liquid crystal material has been used which is effective in delineating domain walls but which appears to be inconvenient to apply in the laboratory [4].

The original powder technique has been adapted and developed to the point where well-defined decoration patterns can be obtained in a few minutes from materials which are commonly available. The results of these experiments are recorded here; their application to the investigation of the homogeneity of various forms of doped and undoped TGS grown from solution by two technqiues is described.

2. Experimental procedure

The decorating materials are applied to sawn, lapped or cleaved (0 1 0) surfaces of the TGS crystals. If cleavage steps are present these may be removed by water polishing on a wet filter paper covered with fine-mesh nylon gauze to give a smooth, but not necessarily flat, surface. Generally, surface topological features do not affect the decoration patterns provided that large, sharply defined steps are absent.

Decoration can be achieved in two ways:

(i) The slice is placed in a shallow dish and covered with a liquid suspension of a suitable powder. The crystal is covered to a depth of about 5 mm. The "thickness" of the suspension should be such that the crystal is just visible when first covered. The compositions of liquids and the powders are discussed below.

(ii) A thick suspension of the powder is brushed onto the crystal surface with a paint brush. This technique has the advantage of simplicity and speed and allows the specimen to be moved readily for photographic purposes without disturbance of the decoration pattern.

2.1. Choice of liquid

In the original technique, hexane was used as the suspension medium. However, it was not used for the present work because it usually led to severe cooling of the specimens by evaporation, which resulted in the crystals cracking.

Silicone oil was found to be very effective and, provided that it was at ambient temperatures, caused no thermal shock. The oil should preferably have a viscosity in the range 20 to 200 cP. Oils of higher viscosity were found to be less effective in developing satisfactory patterns.

2.2. Choice of powder

Many different types of powders were tried for decoration, but only a few were found to be effective. These included metals, semi-conductors and insulators. A complete analysis of all of the factors which are involved in decoration has not been undertaken, but certain desirable features have been determined:

(i) the particles should not be too fine ($\leqslant 1\ \mu m$) or settling times are very long and definition is lost (probably due to small temperature changes and hence polarization changes during the settling period);

(ii) the particles should not be so large that definition is lost, nor so heavy that little lateral motion under the influence of the local fields is possible. A uniform particle size of 2 to 5 μm is regarded as optimum;

(iii) in the settling technique, if the suspension is too concentrated it will deposit too quickly and heavily, masking much of the detail that is obtainable;

(iv) as stated in the original paper [1] materials can be found which are attracted to negative or to positive domain terminations. Yet other materials delineate only domain walls. A summary of the materials used and their particular decoration behaviour is given in Table I.

Pairs of powders of contrasting colours are particularly useful and the best results have been achieved with the settling technique using the following combinations:

(1) rare earth oxysulphides (white) with lead dioxide (dark brown);

(2) praesiodymium oxide (black) with mercuric iodide (red).

All these powders are obtainable commercially with suitable particle sizes (gadolinium oxysulphide from Syncryst Ltd; praesiodymium oxide from Rare Earth Products Ltd; lead dioxide and mercuric iodide from Hopkin and Williams Ltd).

More colourful effects can be obtained with combinations of these powders and chromia (green) or lead iodide (yellow), but these were not easily attainable in convenient particle sizes. The chromia, in particular, contained a high proportion of fine particles which required a long settling time.

For decoration by brushing, a suspension of various commercial dyes were found to give good results. Typical dyes were: thioindigo violet and pigment red 1 (obtainable from Edward Gurr Ltd). More conveniently a suspension of "Xerox toner" powder applied with a flat, fine textured paint brush gave excellent results.

TABLE I Powders effective in decorating TGS crystals

Positive terminations	Domain boundaries	Negative terminations
Bi_2O_3 – white HgI_2 – red PbI_2 – yellow PbO_2 – dark brown	CdS – yellow CdSe – dark red	CuO – red Pr_2O_4 – black Gd_2O_2S – white Cr_2O_3 – green Tb_2O_3 – dark brown ZnO – white "thioindigo violet" "pigment red 1" "Xerox toner" powder – black

Other materials showing slight effect: $BaTiO_3$, TGS, S, AL_2O_3, SiO_2, V_2O_5, Ta_2O_5, Nb_2O_5, In_2O_3, C, Fe_2O_3, MnO_2, $BaCO_3$, BaF_2, Fe. The list should not be regarded as exhaustive.

2.3. Preparation of suspension

The suspensions were prepared by simple stirring. If many agglomerates were present the suspension was allowed to stand for several seconds before use to enable these large particles to settle. It was found to be important that the suspension did not differ appreciably in temperature from the crystal slice, or complex changes in the patterns occurred, accompanied by loss in definition. The specimens and materials were preferably allowed to stand in the same locality for about 30 min before use.

Care should be taken not to handle the slices directly, immediately prior to decoration, particularly if thin slices are used. Local heating from fingers is sufficient to disturb the charge distribution and hence the decoration pattern.

2.4. Observation of patterns

The rate of development of the patterns was found to be related to the type of crystal specimen used. Undoped crystals typically took some minutes for decoration features to appear, while alanine-doped (biased) crystals showed features within a few seconds.

The development of the patterns was assisted in all cases by standing them on a "cold-light" viewing box of the type used for examining X-ray photographs. This permitted sufficient gentle heating for the enhancement of surface charge production. (Prolonged standing on a viewing box often caused very high voltages to be developed. Caution should be exercised to avoid unexpected shocks on handling thick specimens.)

3. Results

The patterns obtained on slices taken from undoped TGS crystals grown in conventional types of rotary crystalliser showed characteristics representative of the growth sectors intersected by the cleavage plane. These differences in decoration within the various growth sectors were apparent in the "texture" of the domains present, i.e. in the shape, size and distribution of the domain terminations (Fig. 1). This suggests either that some variation exists in the defect concentrations associated with different growth sectors which may determine the domain texture by local strains, or that the domain arrangement is influenced in some manner by the growth kinetics, which differ for specific crystallographic faces.

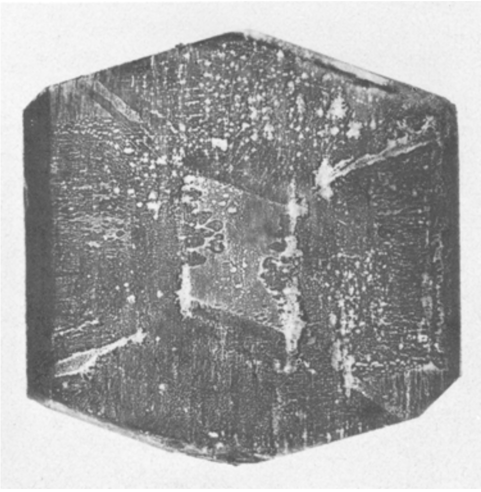

Figure 1 Undoped TGS crystal decorated with PbO_2 and Gd_2O_2S by immersion.

The patterns obtained by the technique are quite consistent and reproducible. If the slice is reversed a similar pattern is obtained (see Fig. 2), but the corresponding regions are reversed for two-colour decoration. Similar patterns, with reversal, are also obtained from the surfaces on either side of the cleavage (Fig. 3). Successive slices from one crystal show an overall pattern which persists throughout, although minor variations occur on individual slices.

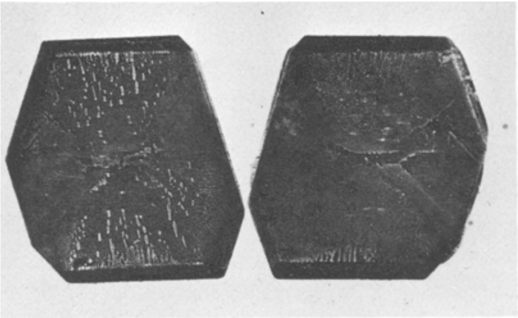

Figure 2 Opposite sides of an undoped TGS single cleavage decorated with pigment red by brushing.

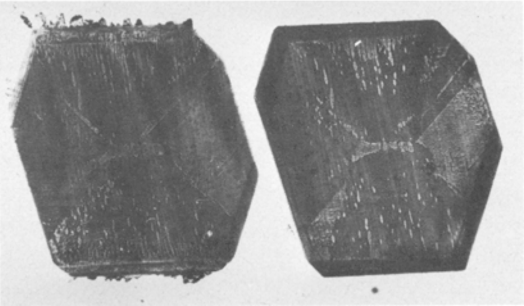

Figure 3 Successive slices of an undoped TGS crystal decorated with pigment red by brushing.

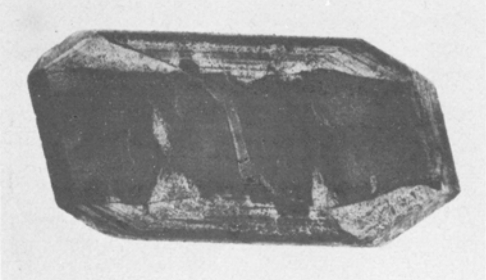

Figure 4 LATGS crystal decorated with "Xerox toner" by brushing.

Several differences from undoped TGS were observed in slices of L-alanine doped crystals (LATGS) [5]. Generally, the borders between sectors were less well defined, but in all cases a central region was present associated with the growth sector of the 0 1 0 face. Distinct banding was apparent in the other growth sectors (Fig. 4). The greater activity shown by LATGS crystals was well demonstrated by directing a quartz–halogen lamp on to a specimen during decoration. Intense activity occurred at localized regions which caused the powders to be rejected from the slice and ejected some distance from the crystal. This effect was most pronounced in the regions associated with the $(\bar{1}\,2\,1)$ growth sector.

By taking care to equilibrate temperatures and by using thin slices of LATGS crystals, very considerable detail in the decoration patterns was obtainable. Generally these indicated that the doping was far from homogeneous and, as might be expected, varied in the different growth sectors, since the amount of alanine included in the crystal is different for each habit face. Well defined striations were also observable, suggesting that the uptake of alanine is by no means uniform during growth by conventional means.

The need for crystals of uniform properties and homogeneous doping has been discussed by White *et al.* [6], who overcame the problem by growing principally on a single habit face, and by employing a spinning disc growth technique. The improved uniformity of decoration shown by the crystal products from this technique can be seen from Fig. 5.

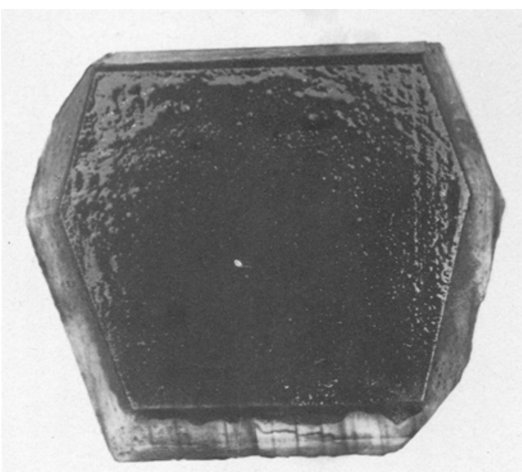

Figure 5 LATGS crystal grown by spinning disc method, decorated with pigment red by brushing.

4. Discussion

The decoration effects observed are not readily explainable. Pearson and Feldman [1] pointed out that if the particles in suspension are electrically neutral, yet polarizable, they would be expected to move to positions of the highest field gradient; this is to domain boundaries. This is observed in some instances, for example with suspension of CdS. Generally, however, most materials were either ineffective and settled uniformly, or decorated the negative ends of domains. Very few materials were found which decorated the positive ends; these included the lead and mercury compounds referred to in Table I. The implication is that compounds that are effective in decoration possess a charge on the individual particles when in silicone oil suspension. This charge is unlikely to arise through interaction with silicone oil, which is chemically inert, or from abrasion during addition of the powders to the liquid. It seems more probable that it arises from the weakly basic or acidic nature of most materials in conjunction with the presence of traces of moisture present either in the powders or in the silicone oil. This would fit the observations of Pearson and Feldman [1] with respect to the presence of a charged double layer.

A further complexity arises when the decoration of LATGS crystals is considered. The effect of alanine doping is to convert a TGS crystal into a single domain crystal in which reverse domains can only be generated by high electric fields. The fact that such crystals show decoration patterns with two-powder suspensions not only indicates that the incorporation of alanine is non-uniform, but that the powders of one type decorate the regions that are highly charged, and the powders with opposite charge decorate the regions that are less charged. This accounts for the fact that decoration patterns for thick LATGS crystals are usually less well defined than those for undoped TGS, and are also more readily perturbed by temperature changes.

In LATGS crystals grown by the spinning-disc method the uniformity of decoration is better than for normal crystals, but it is still not perfect. A further improvement is achieved by growing the crystals above the Curie temperature [6]. The best decoration patterns achieved show overall good uniformity of decoration with some randomly distributed variations. It is thought that these may be associated with crystallographic defects present

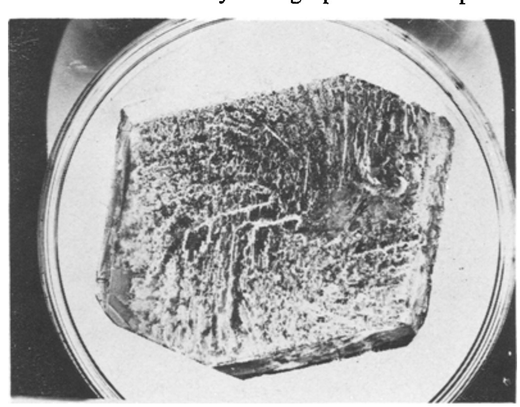

Figure 6 LATGS crystal grown by spinning disc method, showing spiral decoration pattern by inversion using PbO_2 and Gd_2O_2S.

in the original seed crystal.

The above results with LATGS crystals suggest the uptake of alanine in the crystal is modified, to some extent, by the concentration of alanine already present in the crystal – or, in other words, by the changes present on the surface during growth. It is highly significant that decoration of a crystal grown by spinning showed a spiral pattern which corresponds closely to a spiral etch pattern of inclusions formed at the seed-crystal interface approximately 10 mm below the final, decorated growth surface (see Fig. 6). No visible defects were present in the intervening space. The inferences to be drawn from these results should throw some light on the mechanisms of alanine incorporation, at least on a molecular level.

5. Conclusions

The use of powder decoration for domain structures in TGS provides a simple and effective method for quickly evaluating the crystal uniformity of specimens for device fabrication. It has further demonstrated the inhomogeneous nature of crystals grown by conventional techniques, due to segregation differences at various habit faces during growth. The advantages to be gained by the use of large-area seed growth above the Curie temperature are apparent in the uniformity of decoration achieved.

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