A simple technique for decorating ferroelectric domains in gadolinium molybdate

A number of different techniques have been developed for revealing the domain structure in the ferroelectric single crystals: (a) microscope techniques; optical [1], scanning electron microscope [2], mirror electron microscope [3] and transmission electron microscope [4]; (b) etching technique [5]; (c) decoration techniques: dew method [6], powder pattern [7], liquid crystal [8] and (d) X-ray topographic studies [9]. In this note we describe a new technique to decorate the ferroelectric domains in gadolinium molybdate. The technique is unusual in that it gives a permanent record of the domain configuration, but may be 'overprinted' to record changes in the structure.

Single crystals of gadolinium molybdate (GMO) for domain studies are cut and polished to have large area plane '*c*' faces. After cleaning, the sample is dipped into dilute hydrofluoric acid (HF ~ 1% water solution) for a few seconds. Crystals are taken out and washed with freon, dried and are now ready for study.

When the dip times are suitably chosen, the domain pattern is revealed in reflected unpolarized light in clear contrasting colours (Fig. 1). It appears that the uniform colour in each domain region is produced by interference between front and back surfaces of a film of uniform thickness deposited over the domain, and that the colour contrast is associated with a change in this thickness. It would appear also that the length of time taken in the HF solution has a controlling influence on the film thickness and thus on the colour. Shorter times lead to the vivid colours of the lower order Newtonian spectrum (Fig. 2) and longer times to the "washed out" greens and pinks of the higher orders in the subtraction spectrum (Fig. 3).

When the same decoration technique is applied to the (1 0 0), (0 1 0), (1 1 0) or any other face but normal to the polar axis, uniform colours were not observed and the films have a patchy appearance.

After drying the deposited film on the crystal surface is quite robust and will stand rough physical handling and temperatures up to more than 200° C without visible degradation.

This decoration technique can be used repeatedly on the same surface, and if between decorations a domain feature has been moved the composite pattern will record both the original and the new location of the domain wall (Fig. 4).

For this method applied to GMO we would list the following advantages and special features: (1) polarized light is not needed to see the domains and larger features are clearly visible to the naked eye, (2) the deposited film is very robust, and gives a good permanent record, (3) since decoration can be repeated, wall motion can be studied, (4) since the decoration is influenced by the polarization at the surface, three dimensional structures can be easily sorted out by comparing reflected and polarized transmitted light microscopic pictures (Fig. 5), (5) The decoration patterns have very high resolution (less than one micron) and provide a very simple way to illustrate the large departures

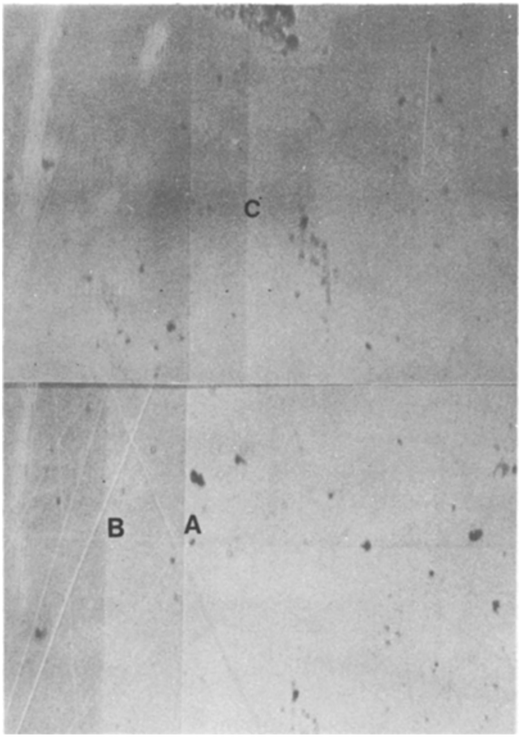

Figure 4 Repeated decorations on GMO sample. 'A' showed the original wall position in the sample; after first decoration the wall was moved by the application of elastic stress. B and C are the positions of the displaced walls in the second and the third decoration of the same sample. × 200.

from preferred wall orientations resulting from the incompatible shear systems associated with orthorgonal domain families (Fig. 6).

Regarding the mechanism responsible for generating the optical contrast, we believe that the electric fields associated with the emergent spontaneous polarization must play an important role in modulating the thickness of the deposited solid film. We believe that during the etching process, which proceeds at different rates on the differently charged domain surfaces, a thin coherent insoluble film of GdF_3 is built up. It appears to be this lower index film which is responsible for the interference colours. Ion scattering spectroscopy gives clear indication of gadolinium and fluorine in the coloured surface, with no evidence of oxygen or molybdenum. These peaks, however, do become apparent after ion-milling off the modified surface region.

GdF_3 is inferred as the most probable film material since it is almost insoluble in weak HF. The very large index difference between the fluoride and the molybdate appear to be responsible for the bright surface colours. Interesting dielectric and elastic effects occur in the coated crystals, these and a more detailed physical and chemical description of the films will be published shortly.

In conclusion, this technique is fast, very simple, has high resolution and can be repeated many times on the same surface. So far it has only been used with GMO, but may have applications in other non-water soluble ferroelectrics.

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The fabrication of the translucent ZnO by sintering

Zinc oxide is a structure-sensitive material with a wurtzite structure. It is not sintered without introducing colour centres; specimens treated at high temperature are yellow. Small amounts of additives such as Li^{+1} and Al^{+3} ions result in red and green colourations, respectively [1]. Sintering at temperatures higher than 1300° C is not possible because of the high vapour pressure [2]. The fabrication of high-density zinc oxide without colour centres has not been previously reported. This short communication discusses the sintering of zinc oxide treated by H_3PO_4, which produces white translucent compacts.

Reagent grade basic zinc carbonate was decomposed *in vacu.* at 300° C for 30h. The resultant zinc oxide was added to a solution of a known quantity of reagent grade H_3PO_4, and the suspension evaporated dry with a heater. The powder was lightly ground and fired at 500° C for 24h in air. Additives amounted to 1.0 at.%. Electron micrographs showed that the particle size of the powder was less than 0.2 μm. The density of compacts before sintering was about 55% of the theoretical. All the sintering runs were carried out in air at 1000 to 1250° C. The zinc oxides sintered at 1000 to 1200° C were white, while that at 1250° C was slight greenish yellow.

Photomicrographs of sintered sample, Fig. 1, indicate that rapid grain growth occurred in the

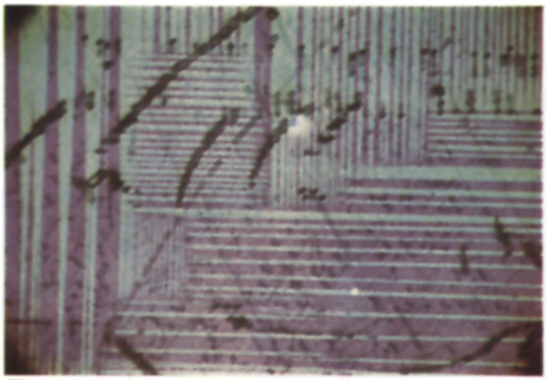

Figure 1

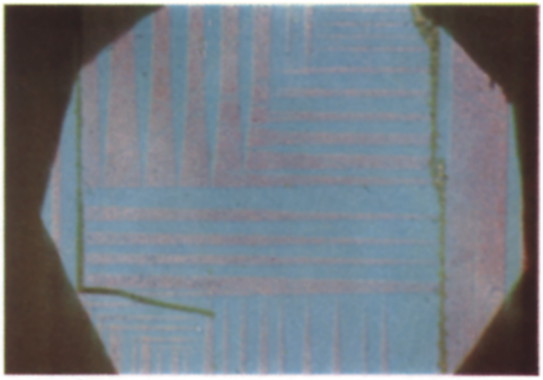

Figure 2

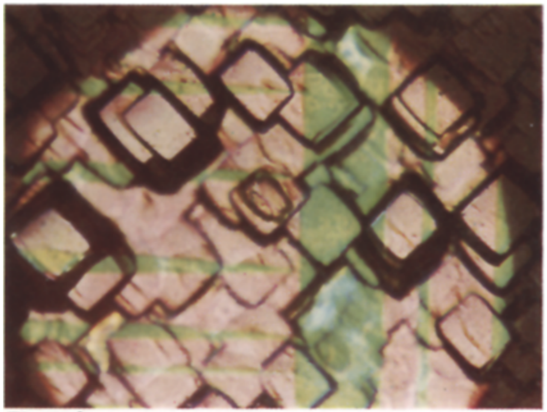

Figure 3

Figure 1 Domain pattern on a single crystal of GMO in unpolarized reflected light. × 120.

Figure 2 Decoration colours on GMO. Crystal was dipped in HF solution for about 1 min. × 300.

Figure 3 Decoration pattern on previously etched surface of GMO. Decoration time 3 to 4 min. × 600.

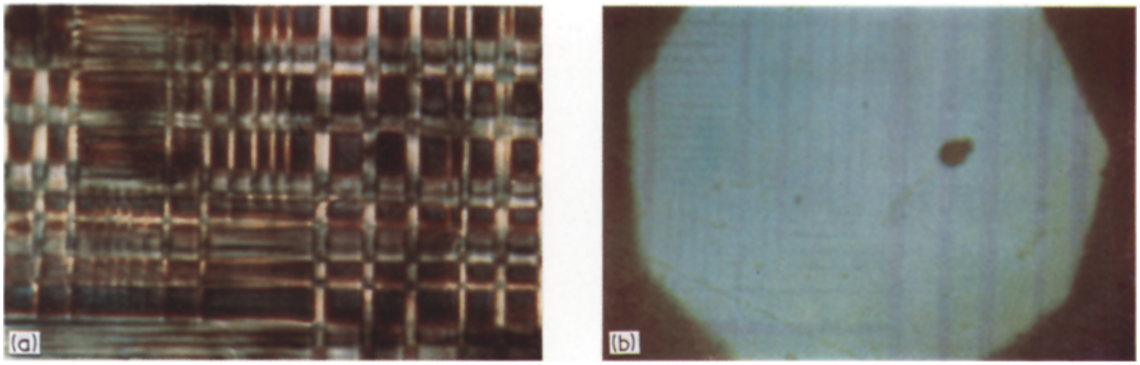

Figure 5 (a) Domain pattern on GMO in polarized, transmitted light. × 120. (b) Same area when decorated and observed in the reflected unpolarized light. × 120.

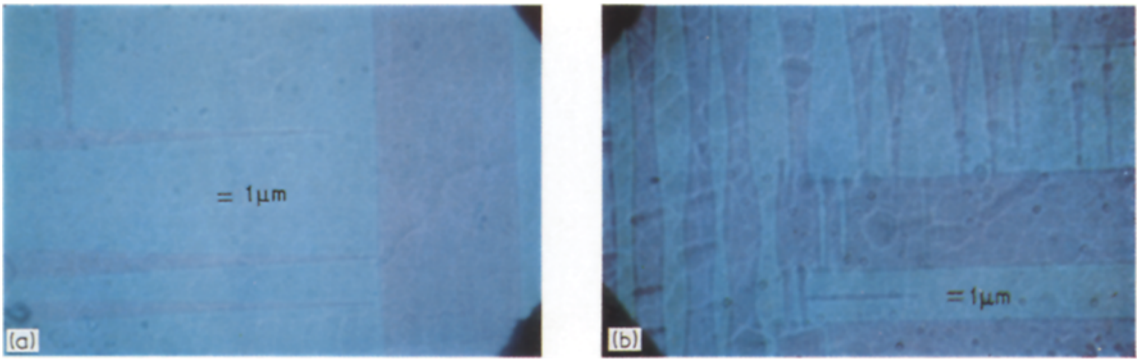

Figure 6 (a) Departures from the crystallographic orientation of the orthogonal walls resulted from the incompatible shear systems at the junction. (b) Scale marks indicate the resolution of the pattern at higher magnification.