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# Domain pattern in ferroelectric triglycine sulphate using pyroelectric effect

V G BHIDE, M M PRADHAN and R K GARG
National Physical Laboratory, New Delhi 110012

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**Abstract.** A method to study domain structure in ferroelectrics, using pyroelectric effect is described. Variation of pyroelectric signal from the surface of a triglycine sulphate crystal plate has been studied by scanning the surface of the crystal with a low wattage He-Ne laser beam. The integrated pyroelectric signal is due to two components, namely, (1) the primary component arising out of the change in spontaneous polarization with temperature and (2) the delayed component arising out of the possible polarization reversal. The component of an electric field along the ferroelectric axis due to thermal hemisphere within the crystal plate formed by the laser beam has been calculated and shown to exceed coercive field, making polarization reversal possible. The delayed pyroelectric signal is a measure of polarization reversal within the patch illuminated and its observed variation over the surface yields information of the domain structure.

**Keywords.** Domain pattern; ferroelectric; pyroelectric signal.

## 1. Introduction

Ferroelectrics are characterised by electric field reversible spontaneous polarization. In a given ferroelectric crystal, the equivalent directions of the spontaneous polarization are determined by the crystal structure. Because of the depolarization energy and the dielectric crystalline anisotropy energy, a crystal of a ferroelectric substance is usually split into domains separated by domain walls. Unlike in ferromagnetics, in ferro-electrics the domain walls are narrow and the domains could be larger. Both the ferroelectric and ferromagnetic domain structure and the domain wall configuration are determined by the crystal structure. Thus in tetragonal $BaTiO_3$ as also in $PbTiO_3$, there are both 180° and 90° domain walls. In contrast, in orthorhombic $BaTiO_3$ there are 180° and 60° domain walls. The dielectric behaviour, the switching characteristics and in general the behaviour of a ferroelectric crystal is determined by the domain wall configuration. Consequently, the study of domain pattern in ferroelectrics and its dynamics under external stimuli such as electric field, hydrostatic pressure, etc., has attracted considerable attention over the years.

The earliest method of studying domain pattern used a polarizing microscope (Merz 1952, 1954; Little 1955) and exploits the birefringent properties of the crystal.

**Figure 1.** Domain pattern in triglycine sulphate crystal plate by etching technique.

The other one is due to Bhide and co-workers (Bhide *et al* 1961, 1963, 1965) who used multiple beam interference technique to study surface deformation caused by domain walls. This method is ideally suited to the study of 90° domain walls in tetragonal pervoskites and 60° domain walls in orthorhombic ferroelectric pervoskites. Chemical etching (Hooten and Merz 1955, Pearson and Feldmann 1959) has also been used to delineate the 180° domain walls. Colloidal suspensions (Pearson and Feldmann 1959) in insulating organic liquids have also been used to observe antiparallel domains. All these methods have their own advantages and limitations.

Chynoweth (1956) first showed that when a light beam falls on the surface of a ferroelectric crystal, one can observe pyroelectric signal. This is essentially because of the change in spontaneous polarization associated with temperature rise caused by irradiation. Using this method, Chynoweth studied the variation of spontaneous polarization with temperature. This observation also provided a clue to the development of currently commercially available pyroelectric infrared detectors. Hadni *et al* (Hadni *et al* 1970, 1971, 1973 *b*) showed that in addition to the pyroelectric signal, one observes a delayed signal when the crystal is irradiated with a He–Ne laser beam. This delayed signal was shown to be due to the polarisational reversal. Hadni *et al* (1972, 1973 *a*, 1974, 1975) have further utilised this method for obtaining pyroelectric map of the crystal. In this paper, we describe a method of delineating domain pattern in TGS using integrated pyroelectric signal.

## 2. Domain pattern in ferroelectric triglycine sulphate

Triglycine sulphate crystallises in the monoclinic structure and the ferroelectric axis corresponds to the *b* axis of the crystals (Hoshino *et al* 1959). In this crystal. one observes only 180° domain walls separating antiparallel domains. Using etching and powder techniques, Chynoweth and Feldmann (1960) observed domain pattern in TGS under normal and thermal shock conditions. Normally, the crystal surface is found to compose of small and large lentiles which represent domains. These are long in the direction of the ferroelectric axis and narrow in the direction right angles to it. These domains extend up to 1 mm in the crystal. Domain walls do not necessarily lie parallel to the ferroelectric axis. In most cases, large domains are surrounded by an almost regular array of small lentiles. Their major axis is parallel to the major axis of the large lentile. These represent the ends of a long, thin and spike shaped domains. Sometimes, these small lentiles do not have a distinct lenticular shape but appear as small multi-wrinkled areas. A typical domain pattern of our TGS crystal plate taken by etching method is shown in figure 1.

## 3. Experimental

Single crystals of triglycine sulphate were grown from the solution following the method described elsewhere (Garg and Pradhan 1975). These crystals were cut perpendicular to the ferrolelectric axis and in the present investigation 150 micron thick crystal plates were used. One surface of the crystal plate perpendicular to

the ferroelectric axis was coated with a thin transparent coating (about 200 A.U.) of gold. The crystal was fixed on the opposite surface to a metal block with the help of conducting cement. These two surfaces formed the electrodes. Radiation from 2 mW He–Ne laser was used for the study of pyroelectric signal. Intensity of the laser beam could be reduced to a desired value with the help of a neutral density filter. The laser light was focussed on the crystal surface coated with gold to a spot of 40 $\mu$m diameter with a lens. The radiation from the laser was modulated by a fixed frequency mechanical chopper. The crystal surface was scanned by giving displacement along the $x$ and the $y$ axes of the crystal surface; the $z$ axis being along the laser beam. The line section of the crystal was scanned by giving a displacement of 20 $\mu$m to the crystal along the $x$ axis relative to the focal spot. After a given section was scanned, the crystal was displaced for another line scan along the $y$ axis by a distance of 20 $\mu$m. This way the whole crystal surface was scanned.

One megohm resistance was connected across the two electrodes. The signal across this resistance was fed to a FET preamplifier and PNP transistor. The output of a preamplifier was fed to a tuned amplifier which was set to the chopping frequency. The experimental set up is shown in figure 2.

## 4. Results and discussion

Figure 3 shows the variation of pyroelectric signal when different line sections were scanned by the laser beam. Eight such measurements are shown in a three-dimensional pattern in figure 4. It is seen that the pyroelectric signal varies over the section and there are certain regions over which pyroelectric signal is more than the average. From the three dimensional representation of the pyroelectric response of the crystal, we have determined the areas on the crystal

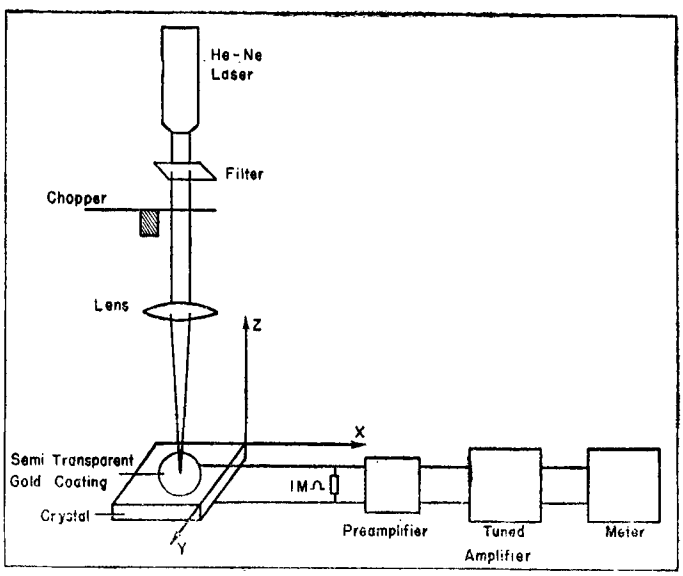


**Figure 2.** Schematic diagram of experimental set-up.

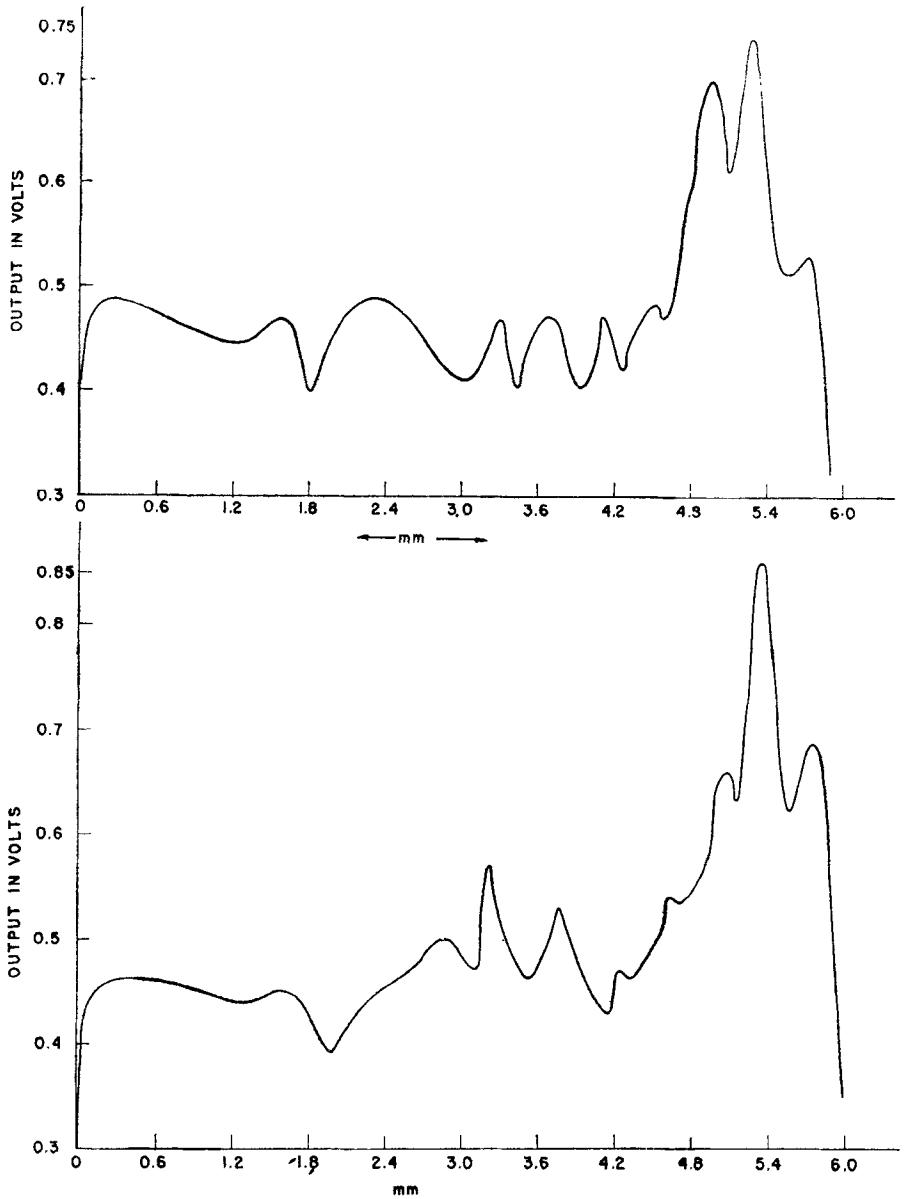


**Figure 3.** Variation of pyroelectric signal along $x$-axis. The two curves have been taken at an interval of 20 microns along $y$-axis.

surface which give higher pyroelectric signal. These areas are shown in figure 5. It is tempting in view of the similarity between this pattern and the typical domain pattern on a ferroelectric TGS to conclude that these areas represent the lenticular domains. However, before we do this, we may first discuss as to what happens when the laser beam irradiates the crystals and what does the pyroelectric signal represent.

When a laser beam is incident on the surface, the temperature of the crystal over which radiation falls, increases. It can be safely assumed that the heat wave

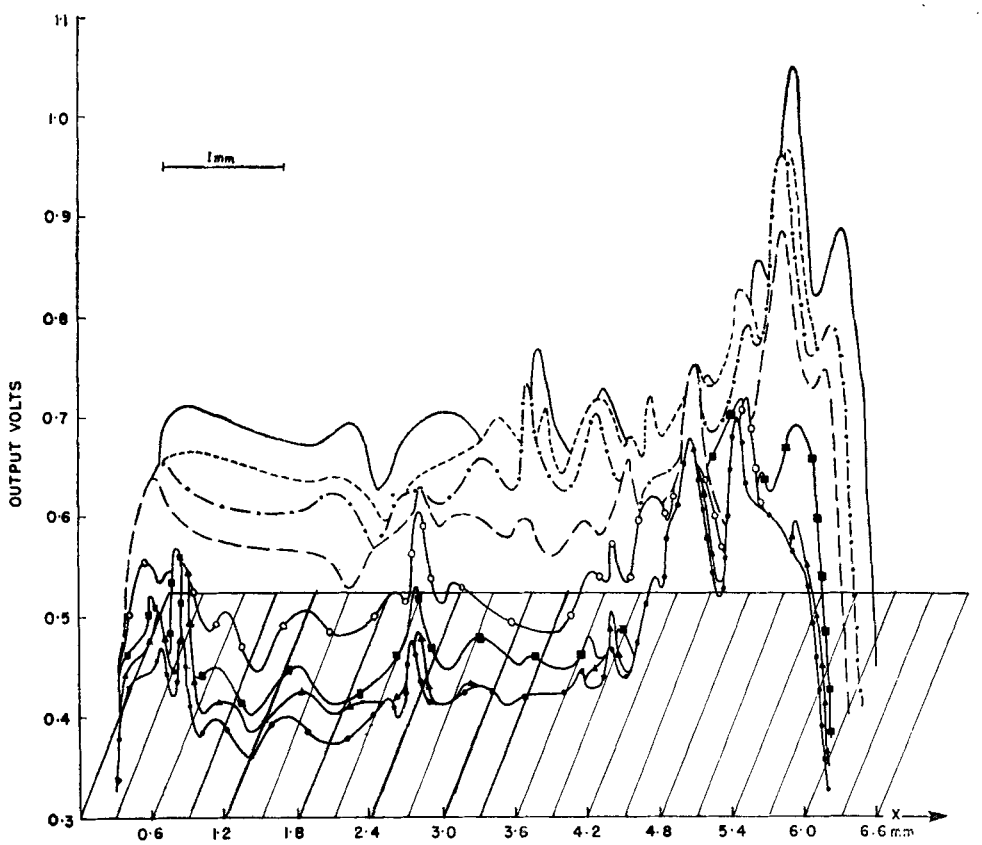


**Figure 4.** Three dimensional representation of pyroelectric signal for eight different measurements which were taken at an interval of 20 microns along $y$ axis.

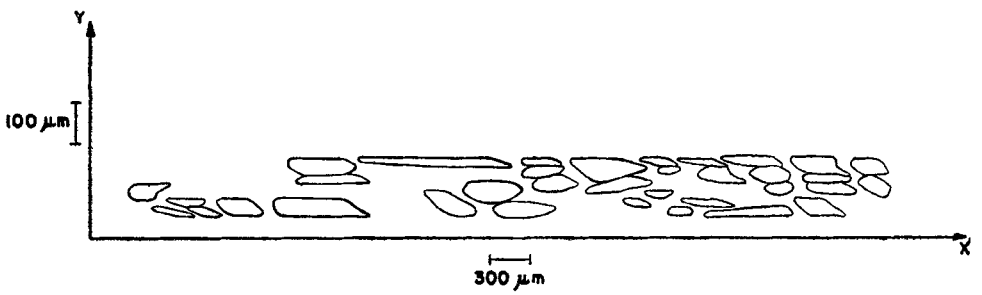


**Figure 5.** Domain pattern as revealed by pyroelectric signal in figure 4.

front is hemispherical with higher temperature inside the hemisphere. Let $Ps$ be the spontaneous polarization of the crystal at a temperature $T$ and $Ps + \triangle Ps$ be the spontaneous polarization at a temperature $T + \triangle T$; $\triangle T$ being the temperature rise of the crystal within the hemisphere. Because of this change in the polarization, a surface charge $A \cdot \triangle Ps$ is created on the surface of the crystal where $A$ is the electrode area. This gives rise to a voltage signal of $(A \,.\, \triangle Ps)/c = (A/C) \,.\, (dPs/dT) \,.\, \triangle T = (A/C) \,.\, \lambda \,.\, \triangle T$ where $\lambda$ is the pyroelectric coefficient and $c$ is the capacity of the crystal. It will be thus seen that the pyroelectric

signal will rise and when the temperature stabilizes, the signals will become zero. This signal is the primary pyroelectric signal. In addition to this signal, there is another delayed signal which Hadni *et al* (1973 *b*) have shown to arise because of polarization reversal.

As we have seen earlier, the temperature within the hemisphere is higher $T+\triangle T$ whereas outside it is lower $T$. Because of the variation of spontaneous polarisation with temperature, there will be a polarisation discontinuity at the boundary of the hemisphere. Polarisation discontinuities will give rise to charges at the boundary which in turn will create an electric field. In cartesian coordinates, the front electrode may be considered as $xy$ plane and $z$ axis lies perpendicular to the crystal face, *i.e.*, along the ferroelectric axis in the present case. The $z$ component of electric field can be calculated from the expression given by Hadni *et al* (1973 *b*).

$$E_z = \frac{\lambda}{4\pi\epsilon_0\epsilon_R} \cdot \triangle T \cdot r^2 \int_{\alpha=0}^{2\pi} \int_{\theta=0}^{\pi/2} \frac{(z - r\cos\theta)\sin\theta\cos\theta\, d\theta\, d\alpha}{(z^2 + r^2 - 2rz\cos\theta)^{3/2}}$$

where $\lambda$ is the pyroelectric coefficient. $\epsilon_0$ and $\epsilon_R$ are the dielectric constants in vacuum and the relative dielectric constant along $z$ axis respectively. $(r, \theta, \alpha)$ are the polar coordinates of any point say $F$ at the boundary of the hemisphere. We have calculated the values of the field at different values of $r$ for various values of $\triangle T$. In a typical case of $\triangle T = 7°$ C; ($T = 23°$ C and $T+\triangle T = 30°$ C), $E_z$ as a function of $r$ is shown in figure 6. The maximum value of $E_z$ ($E_z$(max)) for different values of $r$ is given in the table given below.

It may be noticed that the values of $E_z$ are greater than the coercive field (Chynoweth 1959) of the crystal. It is because of this electric field that the region where polarization is against the $z$ axis will switch over. This polarization reversal would give rise to an additional signal which will be delayed with reference to the primary pyroelectric signal.

It is thus clearly seen that the integrated pyroelectric signal is in general made up of two components, namely, (1) primary pyroelectric signal arising out of the variation of spontaneous polarization with temperature (2) the delayed signal arising out of the polarization reversal. In TGS particularly there are only 180° domain walls and antiparallel domains and hence the primary signal is expected to be the same all through the crystal. However, the delayed signal

**Table 1.** Maximum values of $E_z$ as a function of $r$

| $r$ | $E_z$ (max) |
|---|---|
| $\mu$m | $\times 10^4$ volts/metre |
| 5 | 3·727 |
| 10 | 3·957 |
| 20 | 3·909 |
| 30 | 4·045 |

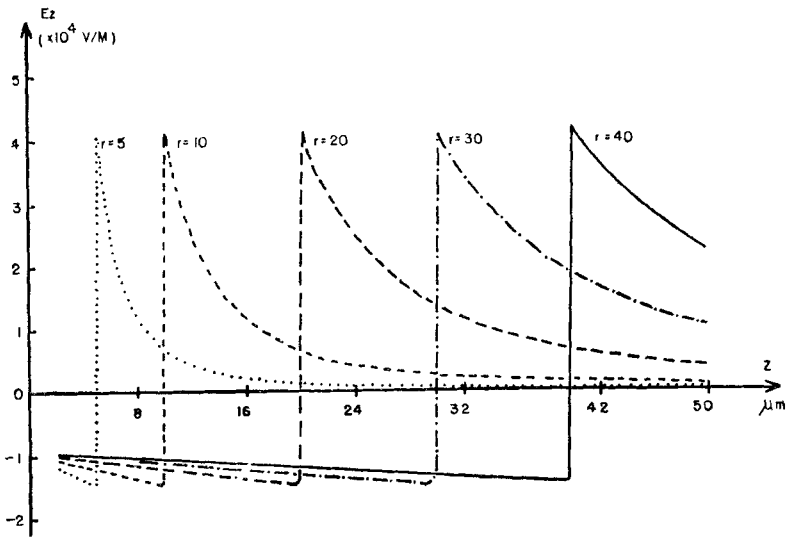


**Figure 6.** Variation of electric field along $z$ axis for different values of $r$.

will vary from region to region. Those areas in which polarisation is already along the $z$ axis, there will be no reversal of polarisation and hence will have negligible delayed signal. However, regions in which polarisation is along direction opposite to the $z$ axis, the electric field created by the thermal hemisphere will give rise to polarisation reversal. It is thus seen that delayed signal will vary tover the parallel and antiparallel domains. In the case of pervoskite $BaTiO_3$ in the tetragonal phase, the primary signal will itself vary 90° domain walls in addition to the change in the delayed signal across the 180° domain wall. In view of the above similarity between figure 1 and the typical domain pattern is not fortituous but the method has delineated the 180° domains as shown in figure 5.

This method is nondestructive and can be used for studying domain structure in a variety of ferroelectrics. However, there is a limit to the resolution of small domains and this is determined by the size of the laser beam.

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