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### Abstract

Low frequency dielectric measurements in triglycine sulpho-phosphate (TGSP) and gamma-irradiated TGSP crystals were carried out around the ferroelectric to paraelectric phase transition. The dispersion found in the ferroelectric phase cannot be explained only by a Debye equation with a single relaxation time. The ratio of the Curie constants in the para- and ferroelectric phase ( $C_p/C_f$ ) for the irradiated TGSP samples show that the crystal is partially clamped. The deviations from the typical single relaxation behaviour are more pronounced in irradiated samples clearly indicating the contribution of defects in addition to the impurities to the dynamics of the system. © 2000 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Triglycine sulpho-phosphate (TGSP) finds wide application due to its interesting ferroelectric properties. It shows a typical second-order ferroelectric phase transition at the Curie temperature ( $T_c = 51^\circ\text{C}$ ) [1]. It belongs to the nonpolar point group  $2/m$  of the monoclinic system above the Curie temperature. Below  $T_c$ , the crystal splits into antiparallel domains. [2–4]. Microbial contamination with time was found to be delayed with partial substitution of sulphate with phosphate in TGS. The ferroelectric  $b$ -plane grew wider with increasing addition of phosphate in the solution [5].

The anomalous ferroelectric properties are closely related with the anomaly of the dielectric constant.

Hence, the investigation on the dielectric properties of TGSP is of great interest. Dispersion in ferroelectrics occurs due to the frequency response of the cumulative effects of the polarization of atoms or ions responsible for the ferroelectricity. Apart from these effects, in the ferroelectric phase, domain wall motion has a significant contribution to the dielectric properties. This leads to the well-known ferroelectric dispersion. Correlation between the domain structure and dielectric properties in pure TGS was reported by Strankowska [6]. The response of the domain walls to the imposing field is prominent in the low frequency region (200 Hz to 100 kHz). Dielectric dispersion with a single relaxation in this region for pure and doped TGS was reported by Batra et al. [7]. But Luther [8] investigated TGS in the microwave region and reported that the multiple relaxation below  $T_c$  is due to the domain wall and ferroelectric dispersion. The distributions of relaxation time were

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explained in terms of inhomogeneities such as surface layers or small spatial variations of the Curie point. Based on these observations, we carried out dielectric analysis on phosphate-doped TGS crystals. Phosphate substitutes partially in the pure TGS lattice and can be treated as an impurity. Decrease in the Curie point with increasing phosphate concentration in TGS was observed by Nakatani and Yoshio [9]. To analyse the effect of defects on the dielectric dispersion, gamma irradiation was carried out on TGSP. It is known that the microscopic defects created by irradiation severely affect the ferroelectric properties. Decrease in the dielectric permittivity, change in transition temperature and increase in the coercive field are macroscopic effects of irradiation. This analysis was carried out to shed more information on the contribution of defects and impurities to the domain wall motion.

## 2. Experiment

Phosphate-doped TGS crystals were grown in the ferroelectric phase by slow cooling method from aqueous solutions. The concentration of phosphate in the solution was 30 mol% and the phosphate content in the crystal lattice is roughly proportional to the solution concentration but it is very low in the crystal compared to the concentration in the solution [10]. Small b-cut plates of thickness 1–2 mm were prepared from the grown crystals by cleaving and polishing with fine grit alumina. Electrodes were made by electronic grade silver paint. Irradiation of the specimen with gamma rays was carried out for 18 h with  $^{60}\text{Co}$  radioactive source. Ferroelectric domains on the irradiated TGSP crystals were examined using a scanning electron microscope (Leica Cambridge) at low operating conditions (2 kV). Dielectric measurements were carried out using a thermal impedance analyser GenRad in the frequency range of 200 Hz to 100 kHz with a 1 V/cm ac field. Electrode specimen was loaded in the furnace, controlled by programmable thermal analyser coupled to a personal computer. Prior to the actual measurements, the samples were preheated through the phase transition to eliminate possible stray capacitance. The capacitance and dielectric losses were collected

at different frequencies against temperature by the computer.

## 3. Results and discussion

The cleaved surface observed under a scanning electron microscope immediately after cleaving shows the presence of typical lenticular domains (Fig. 1a). After  $\gamma$ -irradiation for 18 h, the modified surface when viewed under scanning electron microscope is shown in Fig. 1b. The domain structures observed on the cleaved surface were found to be

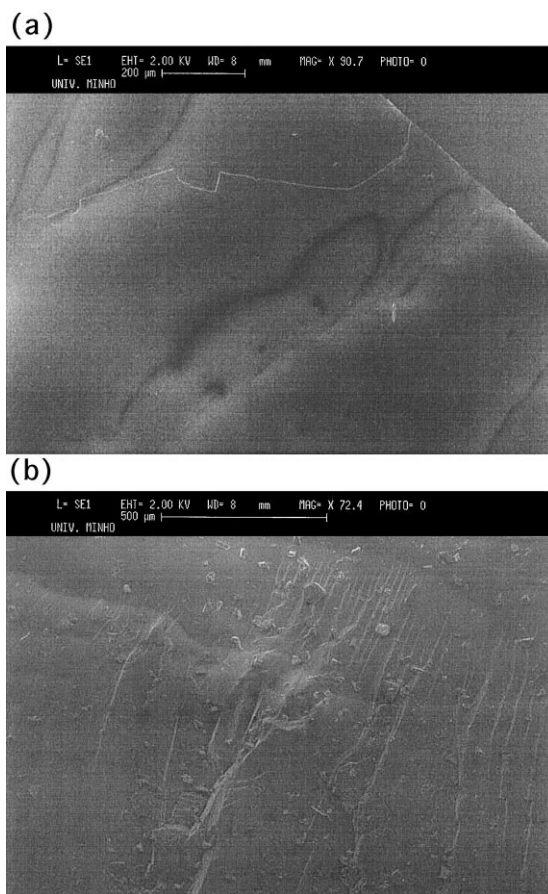


Fig. 1. (a) Secondary electron image of the cleaved TGSP surface showing the domains in the presence of cleavage layers. (b) Secondary electron image of the TGSP surface after  $\gamma$ -irradiation, the rough morphology is due to surface modification that occurs after irradiation.

destroyed due to irradiation. The temperature dependence of real and imaginary part of the dielectric constants of TGSP and irradiated TGSP crystals are shown in Fig. 2(a,b). Dispersion due to the domains in the ferroelectric phase with frequency is observed. The dielectric constant at the transition temperature shows a finite value and a similar result was observed on TGS [11]. Close to the transition temperature, peak rounding was observed in irradiated samples. The broadening effect in TGS was explained taking into effect the existence of surface layers [11]. Application of external dc bias field also results in the broadening of the peak. Same effect was also observed on crystals with intrinsic bias field. The origin of the bias field was ascribed to the presence of defects and impurities [12]. Since irradiation causes defects in the crystal, peak rounding can be related to these defects. The ratio of the Curie constants calculated in the para- and ferroelectric phases for the pure and irradiated samples show an increase in the ratio with irradiation.

$$C_p/C_f = 1.08 \text{ (TGSP)}$$

and

$$C_p/C_f = 1.84 \text{ (irradiated TGSP)}$$

This is due to the clamping of the crystals. Such a clamping effect of a domain occurs near the defect site. The broadening of peak is not prominent in non-irradiated TGSP, where phosphate is treated as an impurity. This clearly shows that defects have a major contribution in the peak broadening compared to impurities.

The experimental data were fitted with the Cole–Cole expression for single relaxation time.

$$\omega \varepsilon''(\omega) = [\varepsilon_0 - \varepsilon'(\omega)]/\tau$$

$$\varepsilon''(\omega)/\omega = [\varepsilon'(\omega) - \varepsilon_\infty]\tau$$

where  $\tau$  is the relaxation time,  $\varepsilon''$  and  $\varepsilon'$  are the imaginary and real part of the dielectric constant,  $\varepsilon_0$  and  $\varepsilon_\infty$  are the static and infinite dielectric constants. A fit of the experimental data yields straight lines for both the equations if it is a single relaxation; how-

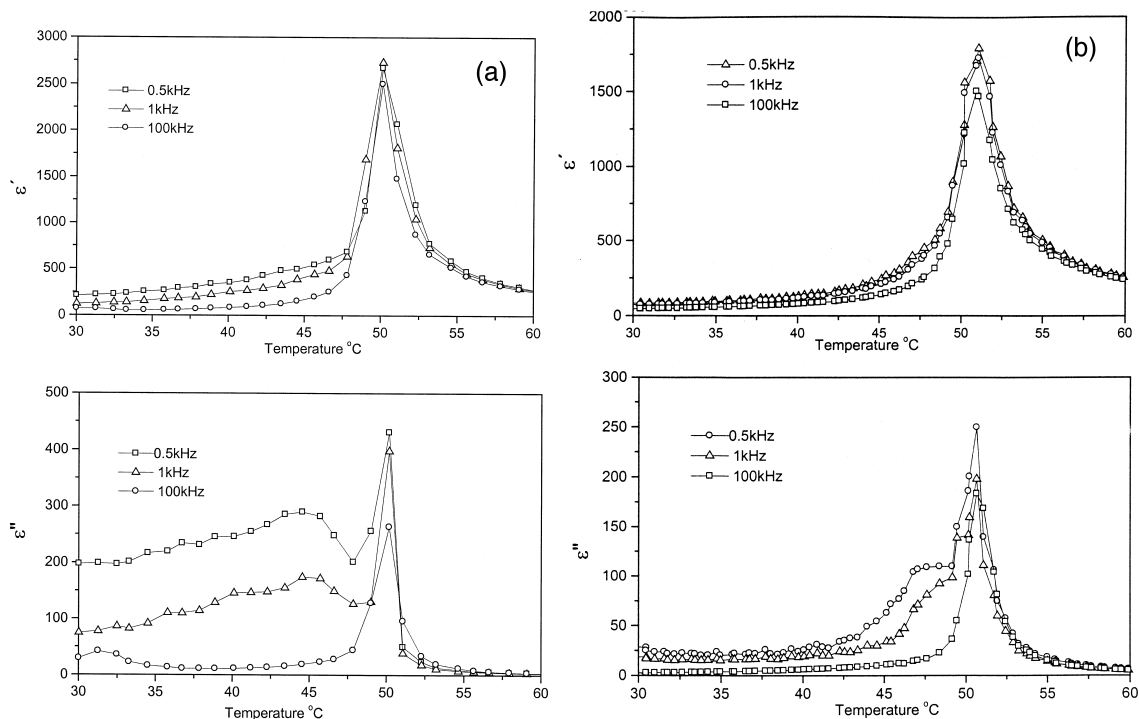


Fig. 2. (a)  $\varepsilon'$  and  $\varepsilon''$  of TGSP vs. temperature. (b)  $\varepsilon'$  and  $\varepsilon''$  of  $\gamma$ -irradiated TGSP vs. temperature.

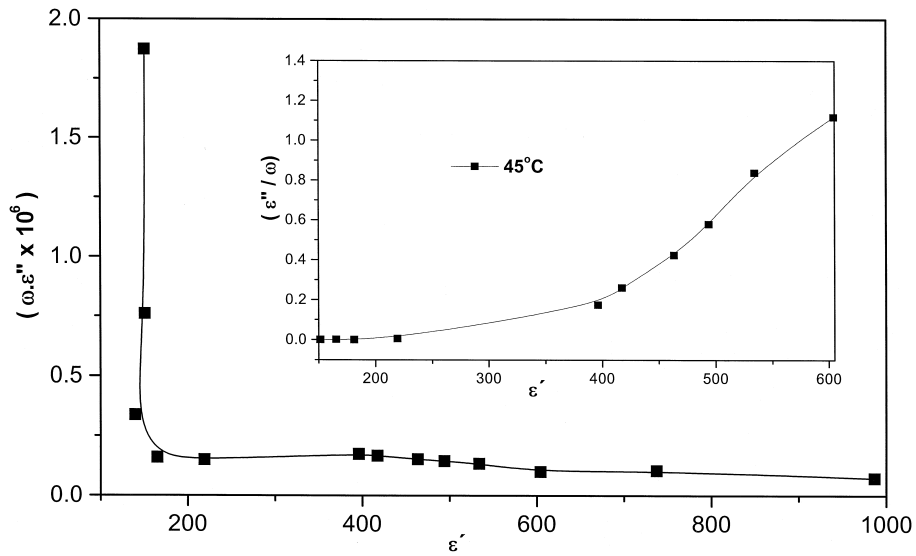


Fig. 3. Cole–Cole plot of TGSP at 45°C.

ever, in this case, the fit does not follow a straight line (Figs. 3 and 4). This deviation appears as poly-dispersive immediately below  $T_c$  and was observed in TGS in the microwave region [8]. It was explained that the critical slowing down occurs immediately below  $T_c$  in the frequency region of the domain wall

dispersion [13,14]. In the present investigation, deviation was clearly observed in irradiated TGSP crystal, which leads to the conclusion that the deviation is due to the defects created in the lattice. On the irradiated samples, the domain wall motion is hindered by the defects leading to polydispersion. Less

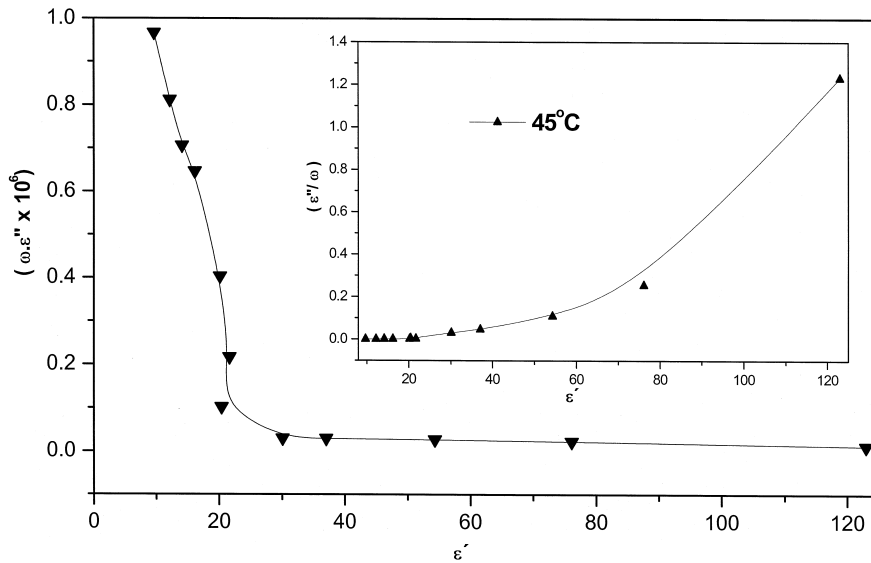


Fig. 4. Cole–Cole plot of  $\gamma$ -irradiated TGSP at 45°C.

deviations in pure TGSP can be correlated to the surface layer effect or to the impurities. The relaxation time and activation energy calculated are  $\tau = 4.65 \times 10^{-3}$  s,  $E_a = 0.85$  eV for TGSP and  $\tau = 1.3 \times 10^{-3}$  s,  $E_a = 1.15$  eV for irradiated TGSP. This reinforces the fact that irradiation hinders the dynamics of the system.

The relation between shift in  $\Delta T_c$  and defect density  $N$  is given as

$$\Delta T_c = NCDd$$

where  $D$  is the correlation–energy coefficient, and  $d$  is the radius of defect core.  $C$  is the Curie constant [15,16]. For a numerical approximation, for  $D = 5 \times 10^{-15}$  cm<sup>2</sup>,  $d = 7 \times 10^{-8}$  cm,  $\Delta T_c = 1.1^\circ\text{C}$  and  $C = 2670$  K, the calculated defect density is  $N = 1.2 \times 10^{18}$  cm<sup>3</sup>

#### 4. Conclusion

Dielectric dispersion in TGSP is similar to the ferroelectric dispersion in TGS, where the low frequency dispersion is dominated by the domain wall motion. Defects and impurities affect the domain wall motion and is clearly evident in TGSP and

irradiated TGSP crystals. It is also clear from this investigation that the deviations from the single relaxation are prominent in irradiated samples due to the pinning of domain wall motion by defects.

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