

Effect of surface capacitance on the dielectric behavior of triglycine selenate near the transition temperature

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The dielectric constant of triglycine selenate (TGSe) has been measured at 1 kHz, for different crystal thicknesses (in the range 3–0.3 mm) over a wide temperature range to cover both ferroelectric and paraelectric regions. Measurements have been made on different samples using silver-conducting paint and evaporated gold as electrodes. The peak value of the dielectric constant near the transition temperature first decreases slowly and then rapidly with decreasing thickness of the crystal. The results can be explained by assuming a single surface layer of low dielectric constant (~ 4.5) and a few hundred angstroms (≈ 400 Å) thick. These parameters are independent of temperature. The surface-layer thickness shows little dependence on the electrode material, but even when the preparation conditions and electrode material are kept the same, the numerical values show a wide variation (more than a factor of 2) for samples from different batches.

INTRODUCTION

The decrease of the peak value of the dielectric constant at the transition temperature in barium titanate¹ and triglycine sulphate²⁻⁴ (TGS) with decreasing thickness of the sample is considered to be due to the existence of surface layers. There seems to be little agreement on the numerical values of the surface-layer parameters reported by different workers. Very little has been reported on the effect of surface layers with other ferroelectrics and the variation of surface-layer parameters with temperature. Recently, Shaulov and Simhony⁵ have tried to explain the lowering and widening of the peak of the dielectric constant in TGS by assuming the existence of an internal bias field.

We have measured the dielectric constant of triglycine selenate (TGSe) as a function of sample thickness over a wide temperature range that covers both ferro- and paraelectric phases to investigate whether the lowering of the dielectric constant with sample thickness is due to surface layers or an internal biasing field. To investigate the variability of the effect with sample source, measurements were made on specimens from different batches. To determine the effect of electrodes, evaporated gold and silver conducting paint were applied alternately to the same sample. The results indicate that the decrease of the dielectric constant with decreasing crystal thickness in TGSe can be adequately explained by assuming a single surface layer of low dielectric constant and thickness.

The measured dielectric constant at temperatures higher than the transition temperature enables one to determine⁶ the generalized Lorentz

coefficient β and the contribution of the combined electronic and ionic polarization γ . Values for these parameters in TGSe are also reported.

EXPERIMENTAL

Crystals of TGSe (about $3 \times 2 \times 1$ cm) were grown from a saturated solution of glycine (99.9% pure) and selenic acid (99.9% pure) mixed in the stoichiometric ratio. The solution was kept in a dark place and the temperature was maintained at 30 °C for about 20 days. Crystals transparent and free from any visible defects were cleaved to obtain crystal plates with faces perpendicular to the ferroelectric axis and were cut to a rectangular shape with a wet thread (string saw). The surfaces were lapped with 800-grit emery paper and the specimens then polished on a wet cloth to produce perfect rectangular faces. Finally, the samples were cleaned by etching with acetone before applying the electrodes. After making the electrical measurements at one thickness, the electrodes were removed by rubbing on wet cloth and the sample thinned down by rubbing on 800-grit emery paper. Care was taken not to change the crystal orientation while reducing its thickness. Once the new desired thickness was obtained, the sample was polished with a wet cloth, cleaned with acetone, and fresh electrodes applied on both sides. The same procedure was adopted after measurements at each thickness. The thickness was varied from about 3 to 0.3 mm and the area ($\sim 5 \times 3$ mm) was kept essentially constant. The thicknesses were measured before the application of electrodes at different places to ensure uniform thickness. The maximum error for the smallest thickness measurements was within 5%.

The same sample was used for both gold and silver electrodes because measurements on four samples from different batches showed that the peak value of the dielectric constant could vary from batch to batch by over 30% for the same sample thickness, even when sample preparation conditions were kept identical. However, the overall behavior for all the samples was the same. Hence, the results for only two samples from different batches are reported.

Silver conducting paint was used to form full face electrodes on the first sample (sample No. 1) at all different thicknesses. For the second sample, gold (sample No. 2) and silver electrodes (sample No. 3) were applied alternately. It was noted that the gold electrodes peeled off during the electrical measurements unless the samples were annealed at 50 °C for 3 h after depositing the gold. Hence, for each thickness the sample was annealed after depositing the gold electrodes. Following the electrical measurements, the gold electrodes were removed and replaced by silver paint electrodes as discussed above. Dielectric measurements were again made and then the thickness changed as described earlier.

The dielectric measurements were made at 1 kHz using a GR 716CS bridge. The ac signal was adjusted to give a fixed field strength of 0.5 V/cm across the sample. Measurements were also made as a function of temperature while heating the sample at a rate of 0.05 °C/min. The measurements for each thickness and electrode material were repeated two or three times to improve the accuracy of the measurements. The values of the dielectric constant, even at the peak, were reproducible within 2%. The absolute temperatures were measured to an accuracy of ± 0.05 °C, while temperature differences could be measured with a greater accuracy. The details of the experimental setup and measuring technique have been described earlier.⁴

The measured dielectric constant showed a peak at 22.0 °C. There was no systematic shift in the transition temperature T_c with decreasing thickness, and the random scatter for both samples was within ± 0.05 °C. The temperature was normalized at the peak value of the dielectric constant for different thicknesses of the sample.

RESULTS

The measured values of the dielectric constant ϵ_m at the transition temperature T_c and at a temperature of -80 °C, far removed from the transition temperature, for sample No. 1 are given in Fig. 1 for different sample thicknesses d . The numerical values of ϵ_m close to T_c were higher for

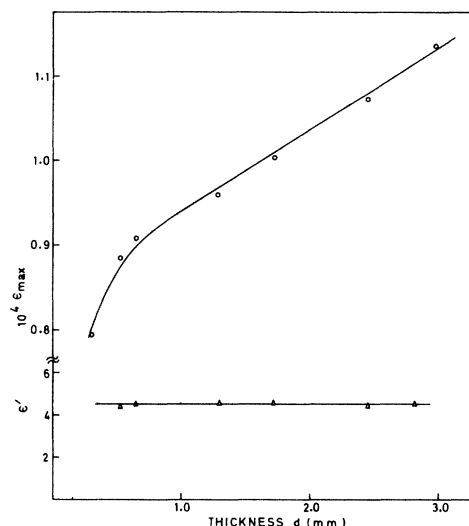


FIG. 1. Plot of measured dielectric constant against crystal thickness for sample No. 1. The upper plot, circular points, represent values at the transition temperature T_c . The lower plot triangular points are for -80 °C. Similar plots were obtained for the sample with gold and silver electrodes.

sample Nos. 2 and 3, but the overall behavior with thickness for sample Nos. 2 and 3 was similar to that shown for No. 1 in Fig. 1. It may be noted that at a temperature far removed from the transition temperature, the dielectric constant is independent of the thickness of the sample. At the transition temperature, the dielectric constant first decreases slowly and then rapidly with decreasing sample thickness. Sekido and Mitsui² found a linear variation of the dielectric constant with thickness in TGS. However, the results of Chincholkar and Unruh³ and Mansingh and Prasad⁴ for TGS are similar to the present results on TGSe.

Figure 2 gives the Curie-Weiss plot for one thickness of sample Nos. 1, 2, and 3. The slightly higher measured values of ϵ_m near T_c with gold electrodes (sample No. 2) may be due to the annealing; however, the difference in the values between samples with gold and silver (unannealed) electrodes is less than 5%. It may be observed that the Curie-Weiss law is obeyed in both the para and ferroelectric phases. The peaks became broadened at the transition temperature. Similar broadening has been reported⁷ in TGS. However, the extrapolated lines of the Curie-Weiss plots in ferroelectric and paraelectric phases do not meet at an infinite value of the dielectric constant as observed by Ganzalo⁷ with TGS. A finite value at the transition temperature in TGSe is indicated for both samples, and is consistent with the observations of Craig⁸ and Ishida⁹ on TGS.

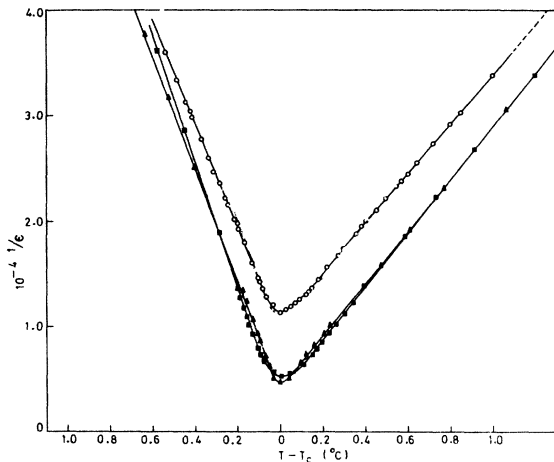


FIG. 2. Curie-Weiss plot for two samples of TgSe from two different batches. Circular points represent sample No. 1, while the triangular and square points are for sample No. 2 (gold electrodes) and sample No. 3 (silver electrodes), respectively.

Measurements at temperatures higher than T_c enable the determination of the generalized Lorentz coefficient β which is given by⁶

$$\beta = 4\pi T_c / C \quad \text{for } T \gg T_c. \quad (1)$$

The combined electronic and ionic polarization per unit volume can be expressed⁶ as

$$\gamma = (\epsilon_0 - 1) / [4\pi + \beta(\epsilon_0 - 1)], \quad (2)$$

where ϵ_0 is obtained by fitting the Curie-Weiss law

$$\epsilon_m = \epsilon_0 + C / (T - T_c) \quad (3)$$

at temperatures in the paraelectric phase far removed from the transition temperature. The Curie constant C and the value of ϵ_0 obtained by fitting the experimental points of ϵ_m in Eq. (3) for temperatures above $T_c + 2^\circ\text{C}$ are given in Table I. The calculated values of β and γ are also listed in Table I. It may be noted that different samples show much smaller variation in these parameters as compared to variation in ϵ_m near T_c , i.e., a factor of 2. The ratio of the Curie constants C_p (in the paraelectric phase) and C_f (in ferroelectric phase) and the values of β and γ for TGSe are in good agreement with the reported⁶ values for TGS and TGFB. These parameters are obtained by fitting the data at temperatures far removed from the transition temperature where the dielectric constant does not show much thickness dependence and thus their value independent of the sample thickness.

DISCUSSION

The presence of an internal electric bias due to defects in the crystal can cause the broadening of

the peak and lowering of the peak value of the dielectric constant.⁵ The biasing field is principally due to microeffects and in the absence of a surface layer it should be independent of sample thickness. Hence, the dielectric constant should also be independent of sample thickness d . The present measurements show a decrease in the measured dielectric constant ϵ_m with decreasing sample thickness near the transition temperature. A straight line is obtained by plotting d/ϵ_m against d as shown in Figs. 3 and 4 for sample Nos. 1, 2, and 3 respectively. This indicates that the lowering of the dielectric constant with sample thickness can not be accounted for by assuming the presence of an internal bias.

Sekido and Mitsui² observed a linear dependence of the measured dielectric constant on the thickness at the transition temperature in TGS and concluded that bulk value of the dielectric constant ϵ_b at the transition temperature is infinite. Chincholkar and Unruh³ who observed a nonlinear dependence of ϵ_m on d at the transition temperature in TGS explained their results by plotting $1/\epsilon_m$ vs $1/d$. They observed two different slopes which they considered as evidence of the existence of two surface layers in TGS. However, the surface capacitance is more important in affecting the measured values

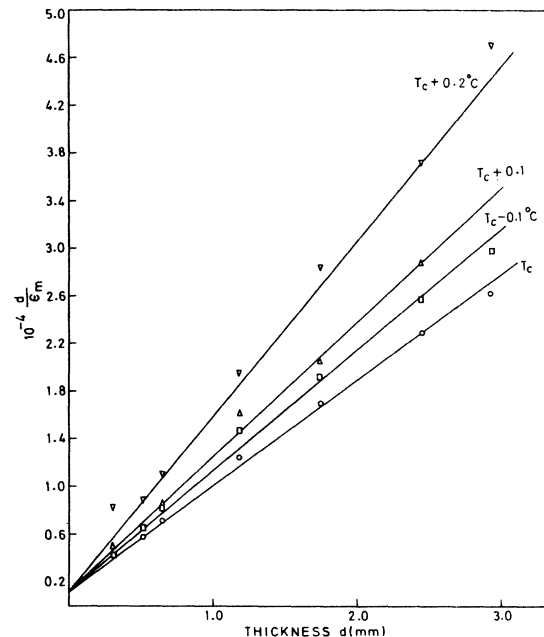


FIG. 3. Plots of d/ϵ_m against crystal thickness d for sample No. 1. Circles indicate the measured values at the transition temperature T_c , rectangles at $T_c - 0.1^\circ\text{C}$, triangles at $T_c + 0.1^\circ\text{C}$, and inverted triangles at $T_c + 0.2^\circ\text{C}$. The straight lines of different slopes and constant intercept indicate a temperature-independent surface capacitance.

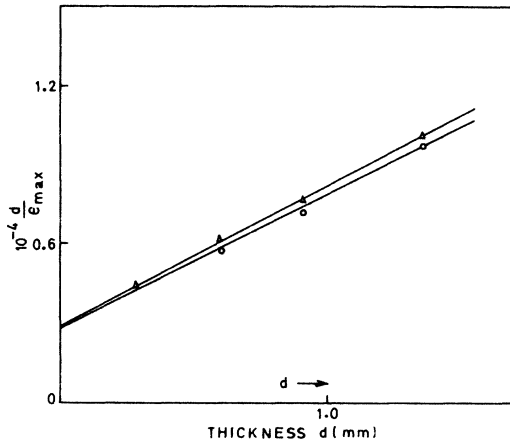


FIG. 4. Plots of d/ϵ_m against crystal thickness d at the transition temperature T_c for sample Nos. 2 and 3. The circular points represent sample No. 2 while the triangles represent sample No. 3. The gold and silver electrodes were applied on the same sample alternately.

than the surface layer dielectric constant is. If we assume that a single surface layer of dielectric constant ϵ_s and thickness d_s (combined thickness of the two surfaces) is formed, then the crystal can be represented by a series combination of the bulk and layer capacitances. The measured dielectric constant ϵ_m for a sample of thickness d and bulk dielectric constant ϵ_b can be given by the relation

$$d/\epsilon_m = d/\epsilon_b + d_s(1/\epsilon_s - 1/\epsilon_b). \quad (4)$$

It is evident from Eq. (4) that a plot of d/ϵ_m vs d should yield a straight line if a single surface layer is responsible for lowering the dielectric constant of the sample with thickness d . Plots of d/ϵ_m vs d at the transition temperature T_c and two temperatures above and one below T_c are shown in Fig. 3 for sample No. 1 and in Fig. 4 for samples No. 2 and No. 3 at T_c . It may be observed that straight-line plots are obtained. This shows that reproducible surface layer parameters are obtained under identical preparation conditions in the same sam-

ple. It may be noted in Fig. 3 that the slope which gives ϵ_b varies with temperature, as expected, and the intercept is independent of temperature, indicating that the second term in the right-hand side of Eq. (4) is independent of temperature. Since ϵ_b is a function of temperature, the temperature-independent intercept implies that near T_c , ϵ_b is very much greater than ϵ_s and d_s/ϵ_s is independent of temperature. The thickness d_s of the surface layer is not likely to change with temperature and so ϵ_s can also be considered to be independent of temperature. The fact that ϵ_m at -80°C is independent of d implies that the second term on the right-hand side of Eq. (4) is zero and so at this temperature ϵ_s can be taken equal to ϵ_b . Hence, the measured values of the dielectric constant at -80°C can be taken as the surface-layer dielectric constant and thus the surface-layer thickness can be estimated, assuming ϵ_s to be independent of temperature. The numerical values of d_s , ϵ_b , and d_s/ϵ_s estimated from Figs. 3 and 4 at the transition temperature for sample Nos. 1, 2, and 3 are given in Table I.

The surface-layer parameters are expected to be very sensitive to the sample preparation conditions, quality of sample, and the nature of the electrodes. This may be the reason for the disagreement in the reported²⁻⁴ values of surface-layer parameters of TGS. The values of ϵ_b and d_s/ϵ_s in Table I show negligible difference between gold and silver electrodes. However, under the same sample thinning and preparation conditions, samples from two different batches with the same electrodes (silver conducting paint) exhibit wide variations in the numerical values of ϵ_b and d_s/ϵ_s , as shown in Table I. The spread in these parameters with samples from other batches were found to be within this same range. The approximate average values of ϵ_b at the peak was $(1.5 \pm 0.5) \times 10^4$ and d_s was approximately $400 \pm 200 \text{ \AA}$. Samples from different batches showed only about $\pm 30\%$ of variation in the estimated value of ϵ_b , but the surface-layer thickness varied by more than a fac-

TABLE I. Calculated values of the surface layer parameters at the transition temperature and that of generalized coefficients in the paraelectric phase.

Sample	C (°K)	$\frac{C_p}{C_f}$	β (cgs units)	γ (cgs units)	ϵ_0	$10^4 \epsilon_b$	$\frac{d_s}{\epsilon_s}$ (Å)	ϵ_s	$\frac{d_s}{2}$ (Å)
No. 1 ^a	4080	2.40	1.015	0.885	112	1.12	100	4.5	225
No. 2 ^b	4012	2.26	0.949	0.940	120	1.96	250	4.5	552
No. 3 ^c	3928	2.34	0.974	0.926	120	1.91	280	4.5	610

^aSample No. 1 with silver electrodes.

^bSample No. 2 with gold electrodes.

^cSample No. 3 with silver electrodes on sample No. 2.

tor of 2. Hence, it may be said that the quality of the sample and preparation conditions have a more pronounced effect on the surface-layer parameters than the electrode material.

The present studies show that the surface layer in TGSe has a low dielectric constant 4.5 and the thickness of the order of 400 Å. These surface layers may be considered to be formed due to a space charge at surfaces. The field produced by these charges may be sufficient to create saturation and freeze the rotating dipoles at the surface,^{1,2} giving a low value of the dielectric constant, which is independent of temperature. The exact origin of these surface charges cannot be ascertained in the absence of dc-conductivity data. However, as has been suggested¹⁰ for TGS, the space charge may be due to the sudden disturbance of the periodic lattice at the surface,¹¹ rather than due to impurities and vacancies¹² in the bulk.

CONCLUSION

The thickness-dependent dielectric constant of TGSe near the transition temperature can be ade-

quately explained by assuming a single surface layer of low dielectric constant (4.5) and thickness ~400 Å (~200 Å on each side of the crystal). The surface-layer parameters are independent of temperature. The surface-layer thickness varies by as much as a factor of 2 between samples from different batches studied under similar conditions. However, there was little effect of the electrode material, gold and silver conducting paint, on the sample capacitance. The generalized Lorentz coefficient and the contribution of combined electronic and ionic polarization which were evaluated from the measured values of the dielectric constant above the transition temperature, where the surface capacitance has no pronounced effect, show good agreement in samples from different batches and also agree with the values reported for TGS and TGFB.

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