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Electrical second harmonic generation by TGSe and TGS-Se in the autostabilized state

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Abstract. Second harmonic generation and TANDEL effect studies on ferroelectric triglycine selenate and triglycine sulphate-Selenate crystals near the Curie temperature indicate that the generated second harmonic is linear for low biasing fields with a zero off-set, while it decreases sharply at higher biasing fields. In the autostabilized state, the TANDEL elements adjust their impedance against the variation of a.c. field. The experiments on annealed crystals establish that the zero offset is due to the internal bias that owes its origin to the defect structure.

Keywords. Second harmonic generation; ferroelectrics; thermoautostabilized state; (TANDEL); internal bias; defect structure.

1. Introduction

Glanc *et al* (1963, 1964a, b) and Fousek (1965) reported the use of triglycine sulphate as a thermo-autostabilized nonlinear dielectric element (TANDEL). Abe *et al* (1971) studied the second harmonic generation in TGS employing an elaborate external temperature control system and suggested its use in electrometer circuits. Second harmonic generation in the state of temperature autostabilization has been studied, for TGS by Malek *et al* (1964). Similar effect is observed for $BaTiO_3$ and KH_2PO_4 by Miller (1964).

A zero off-set in the second harmonic versus d.c. bias plots for TGS i.e. the generation of second harmonic without any external bias has been observed by Abe *et al* (1971) and Mansingh and Prasad (1977). TGSe and TGS-Se are also expected to show temperature autostabilization with an advantage of being useful in electrometer circuits requiring additional parameters. Mansingh and Prasad (1977) studied the proportionality of the electrical second harmonic generation in the autostabilized state of ferroelectric TGS. The origin of this off-set is not clearly understood. Mansingh and Prasad (1977) suggested that it might be due to the presence of defects giving rise to internal bias.

In this present paper, we report our studies on TGSe and TGS-Se TANDELS and the results of the experiments on as-grown and annealed crystals.

2. Experimental

Large crystals of TGSe and TGS-Se were grown from solutions prepared by reacting an aqueous glycine solution with proper amount of the corresponding (sulphuric/

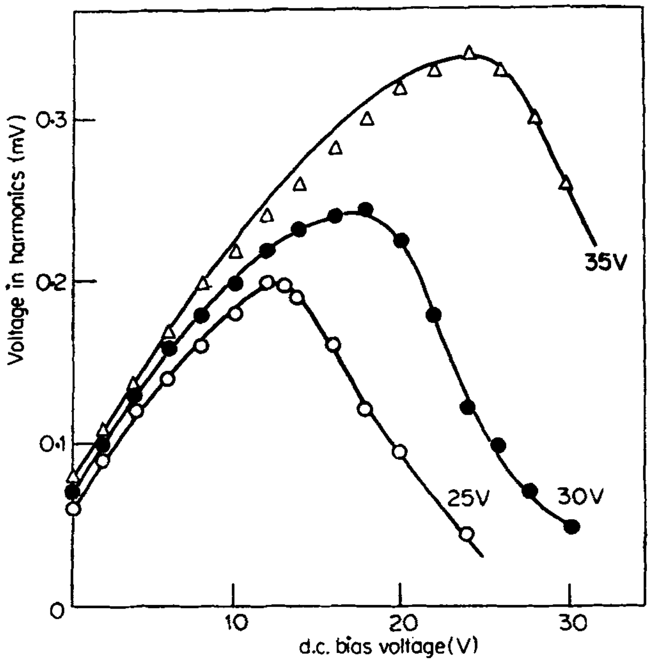

Figure 1. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak).
35 V, 30 V, 25 V for TGSe

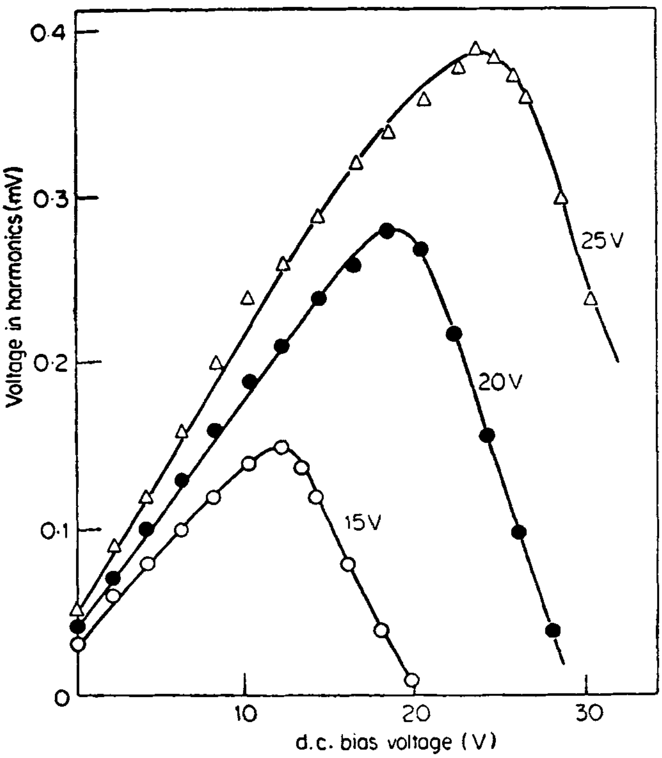

Figure 2. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak)
25 V, 20 V, 15 V for TGSe after annealing at 70°C.

selenic) acid. The growth can be achieved by slowly lowering the temperature at constant supersaturation. The crystal of TGSe and TGS-Se could be cleaved on (010) very easily.

The TANDEL elements were made using TGSe and TGS-Se single crystal plates with faces perpendicular to ferroelectric axis. In the present study we have investigated the voltage response of TGSe and TGS-Se TANDELS, which were connected with a resistor of 10 ohms in series in the experimental set-up, which is similar to that used by Mansingh and Prasad (1977) with the addition of a.c. voltmeter. The plates used were 0·065 cm (TGSe) and 0·079 cm (TGS-Se) in thickness. Silver paint was used for electrodes. A frequency of 10 kHz was used and the single tuned amplifier was adjusted at 10 kHz. The crystal holder was fabricated in the laboratory. The TANDEL experiments were carried out on TGSe and TGS-Se at temperatures 21°C and 33·5°C respectively. The experiments on annealed crystals were also carried out at the same temperatures. The second harmonic voltage response of TGSe-TANDELS using as-grown and annealed crystals of TGSe are shown in figures 1 and 2 respectively. Similar results are presented in figures 3 and 4 for the as-grown and annealed mixed crystals of TGS-Se respectively.

3. Results and discussion

The figures show that the generated second harmonics are linear with the applied d.c. voltage for low biasing fields in accordance with the equation given by Mansingh and Prasad (1977)

$$V_{2h} = W\ C\ Rd\ BP_0\ P_w^2 \cos 2wt, \tag{1}$$

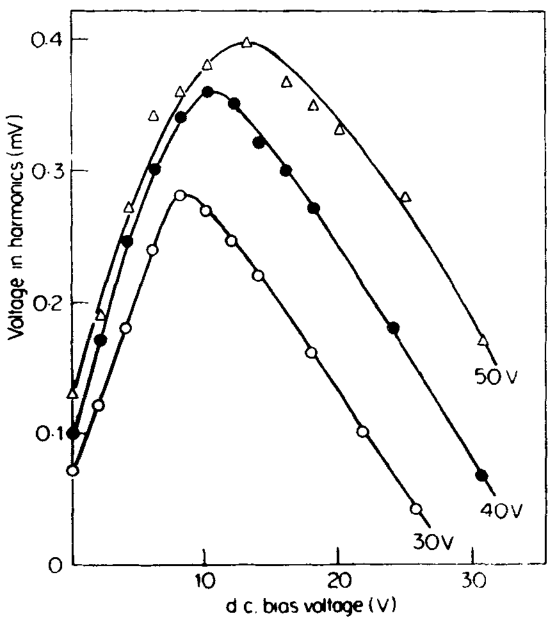

Figure 3. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak)
50 V, 40 V, 30 V for TGS-TGSe mixed crystals.

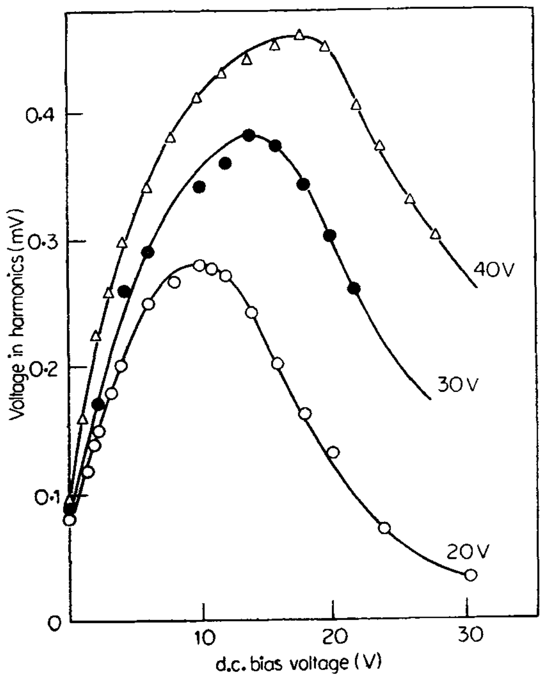

Figure 4. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak)
40 V, 30 V, 20 V, for TGS-TGSe mixed crystals after annealing at 70°C.

where d is the thickness of the crystal, B is material specific constant, w is sinusoidal current frequency, R is resistance, C is capacitance, P_0 is polarization due to d.c. bias and P_w is polarization due to a.c. voltage. Similar results were reported by Malek *et al* (1964) and Mansingh and Prasad (1977) for TGS but at higher biasing voltages, there are deviations from linear behaviour and a sharp decrease in the amplitude of second harmonic is observed. The region over which the second harmonic is linear with the applied d.c. bias is extended by increasing the heating a.c. voltages. This is due to the fact that at low biasing fields the P_w polarization is counteracted by d.c. bias field so that the second harmonic is generated. At high biasing fields the polarization is counteracted till the crystal does not fall out of the state of autostabilization. As the a.c. voltage is increased, higher bias would be required to drive the crystal out of the state of autostabilization. This has been explained from the impedance voltage hysteresis behaviour by Malek *et al* (1964).

It can be observed from equation (1) that the generated second harmonic should be proportional to the square of the applied a.c. voltage. But in the present investigations and also in the work of Mansingh and Prasad (1977), such variations have not been observed perhaps due to the basic TANDEL behaviour. The TANDEL element adjusts its impedance against variations of applied a.c. voltage, so that product CP_w^2 in equation (1) remains constant and this agrees with the TANDEL theory outlined by Dvorak *et al* (1964). It can be seen from the figures that when the d.c. bias voltage is zero, there is still some second harmonic output. This agrees with the result of Abe *et al* (1971) and Mansingh and Prasad (1977), but contrary to those

Table 1.

Crystal	Treatment	Threshold peak voltage for autostabilization (volts)	Peak a.c. voltages (volts)	Magnitude of second harmonic at zero bias in (mili volts)	Magnitude of d.c. bias for going out of autostabilization (volts)
TGSe	As-grown	16	25	0·06	12·6
			30	0·07	19
			35	0·08	24·2
	Annealed	10	1	0·03	13
			20	0·04	19·4
			25	0·05	24·6
TGS-Se	As-grown	25	30	0·07	8
			40	0·10	11·4
			50	0·13	14
	Annealed	15	20	0·08	9
			30	0·09	14
			40	0·095	19

observed by Malek *et al* (1964). Mansingh and Prasad (1977) attributed this off-set to the presence of defects, giving rise to an internal bias which in turn generates a second harmonic. Our experiments on annealed crystal plates confirm the role of the defects in crystals in giving rise to the internal bias. Table 1 summarises our observations on the threshold voltages for transition to autostabilized state, amplitude of a.c. signal used in different experiments, magnitude of second harmonic at zero bias and magnitude of d.c. bias at which samples go out of the autostabilized state. The following observations could be noted

(i) Zero off-set decreases considerably after annealing.

(ii) The minimum peak voltage required for autostabilization is also less for the annealed crystals.

(iii) The d.c. bias voltage that drives the TANDEL out of autostabilization also increases for annealed crystals.

All these observations are consistent with each other in view of the explanation of the TANDEL behaviour. The defects and dislocations in the crystals give rise to the internal bias; because after annealing some of the non-equilibrium defects are annealed out thereby, decreasing the internal bias.

Our results establish that TGSe and TGS-Se can also be used as TANDEL elements with an additional advantage of providing the autostabilization state in the temperature range 22° to 49°C.

References

Abe Z, Koto Y and Furuhata Y 1971 *Rev. Sci. Instrum.* **42** 805
Dvorak V, Malek Z, Mastner J, Janovec V and Glanc A 1964 *J. Appl. Phys.* **35** 1875
Fousek J 1965 *J. Appl. Phys.* **36** 588
Glanc A, Dvorak V, Janovec V, Rechziegel E and Janousek V 1963 *Phys. Lett.* **7** 106
Glanc A, Malek Z, Mastner J, Novak M and Strajblova J 1964a *J. Appl. Phys.* **35** 1870
Glanc A, Malek Z, Mastner J, Novak M and Strajblova J 1964b *J. Appl. Phys.* **35** 1870
Malek Z, Mastner J, Hridicka J and Janta J 1964 *Solid State Electron.* **7** 655
Mansingh A and Eswar Prasad S R J 1977 *J. Phys. Chem. Solids* **38** 1207
Miller R C 1964 *Phys. Rev.* **A134** 1313