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Electrical second harmonic generation by $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$ in the autostabilized state

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Abstract. The temperature autostabilizing nonlinear dielectric element (TANDEL) effect and second harmonic generation have been studied in the ferroelectric solid solutions of $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$ near the Curie temperature used as TANDEL. The generated second harmonics are linear for low d.c. biasing fields with zero off-set while they decrease sharply at higher d.c. biasing fields. The results show that these solid solutions might be used as TANDEL elements.

Keywords. Ferroelectrics; second harmonic generation; thermo-autostabilized state; TANDEL; internal bias; defect structure.

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1. Introduction

Second harmonic generation (SHG) has earlier been studied in various ferroelectric materials. SHG effect was reported by Miller (1964) in barium titanate, Smith (1964) and Suvorov *et al* (1968) in triglycine sulphate and Van der Ziel *et al* (1964) in potassium dihydrogenphosphate. Glanc *et al* (1963, 1964) and Fousek (1965) reported the use of TGS as temperature autostabilizing nonlinear dielectric element (TANDEL). SHG study in TGS employing an elaborate external temperature control system was done by Abe *et al* (1971) who suggested its use in electrometer circuit. Mansingh and Prasad (1977) studied the electric second harmonic generation in the autostabilized state of ferroelectric triglycine sulphate. Similar TANDEL effect has been studied for TGS by Malek *et al* (1964). A zero off-set in second harmonic without any external bias was found by Abe *et al* (1971) and Mansingh and Prasad (1977) in TGS. Chavan and Patil (1980) studied the proportionality of the electric SHG in the autostabilized state of ferroelectric TGS, TGSe and TGS-Se and suggested the zero off-set due to internal bias that owes its origin to the defect structure.

In this paper we report SHG and TANDEL effects carried out on the ferroelectric solid solutions of $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$. Three different compositions for each type of solid solutions as mentioned in table 1 were studied. The other possible compositions were not studied because their Curie temperature is below room temperature.

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2. Experimental

Lead titanate ceramics was prepared from a mixture of lead carbonate and titanium dioxide with 1 : 1 molar proportions and heated in platinum crucible in global furnace up to 1200°C for 4 hr by the method reported by Sawada and Nomura (1950). Similarly $BaTiO_3$ and $SrTiO_3$ ceramics were prepared.

Solid solutions of $(Pb_x\text{-}Ba_{1-x})TiO_3$ were prepared by a mixture of $PbTiO_3$ and $BaTiO_3$ having different molar proportions and heated in globar furnace at 1200°C for 4 hr by using a platinum crucible. Similarly the solid solutions of $(Pb_x\text{-}Sr_{1-x})TiO_3$ were prepared.

The solid solutions prepared were scanned on X-ray diffractometer and it was confirmed that homogeneous solid solutions were formed. The pellets of these solid materials (thickness about 1 mm and diameter 1 cm) were prepared under a pressure of 5 tonnes using a hydraulic press machine. The test samples were made by sintering these pellets at 750°C. The two end faces of the test sample were made conductive by applying silver paint and placed in a sample holder fabricated in our laboratory.

The voltage response of the solid solutions of $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$ which were connected in series with 10 ohms employing the same experimental set-up as described by Mansingh and Prasad (1977) and Chavan and Patil (1980) is investigated. The single tuned amplifier was adjusted to a frequency of 10 kHz. The sample temperature was maintained in the neighbourhood of Curie temperature using adequate temperature controller. The Curie temperatures of the solid solutions of $(Pb_{0.8}\text{-}Ba_{0.2})TiO_3$, $(Pb_{0.6}\text{-}Ba_{0.4})TiO_3$ and $(Pb_{0.5}\text{-}Ba_{0.5})TiO_3$ were obtained at 440, 380 and 350°C respectively using modified form of Sawyer and Tower (1930) circuit by hysteresis loop method. Similarly the Curie temperatures of the solid solutions of $(Pb_{0.8}\text{-}Sr_{0.2})TiO_3$, $(Pb_{0.6}\text{-}Sr_{0.4})TiO_3$ and $(Pb_{0.5}\text{-}Sr_{0.5})TiO_3$ were obtained at 340, 200 and 125°C respectively. Therefore, electric second harmonic generation and TANDEL experiments were carried out in the neighbourhood of the above mentioned Curie temperatures for different compositions of $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$.

Preliminary investigation showed that the minimum peak voltage was 20 V for $(Pb_x\text{-}Ba_{1-x})TiO_3$ TANDEL for autostabilization state. Hence three amplitude levels viz 25, 30 and 35 V peak were selected for present investigations. The minimum peak voltage for $(Pb_x\text{-}Sr_{1-x})TiO_3$ TANDEL in autostabilization state was found to be 15 V, therefore, the amplitude levels 20, 25 and 30 V peak were selected.

3. Results and discussion

The second harmonic voltage response of the ferroelectric solid solutions of $(Pb_x\text{-}Ba_{1-x})TiO_3$, TANDEL elements is shown in figure 1 and for TANDEL elements, $(Pb_x\text{-}Sr_{1-x})TiO_3$ is shown in figure 2. These figures show that for low biasing fields, the generated second harmonics are linear with the applied d.c. voltage, which is in agreement with the equation given by Mansingh and Prasad (1977) and Chavan and Patil (1980).

$$V_{2h} = 6\omega CRdBP_0P_w^2 \cos 2\omega t \tag{1}$$

where, ω is sinusoidal current frequency, C the capacitance, R the resistance, d the

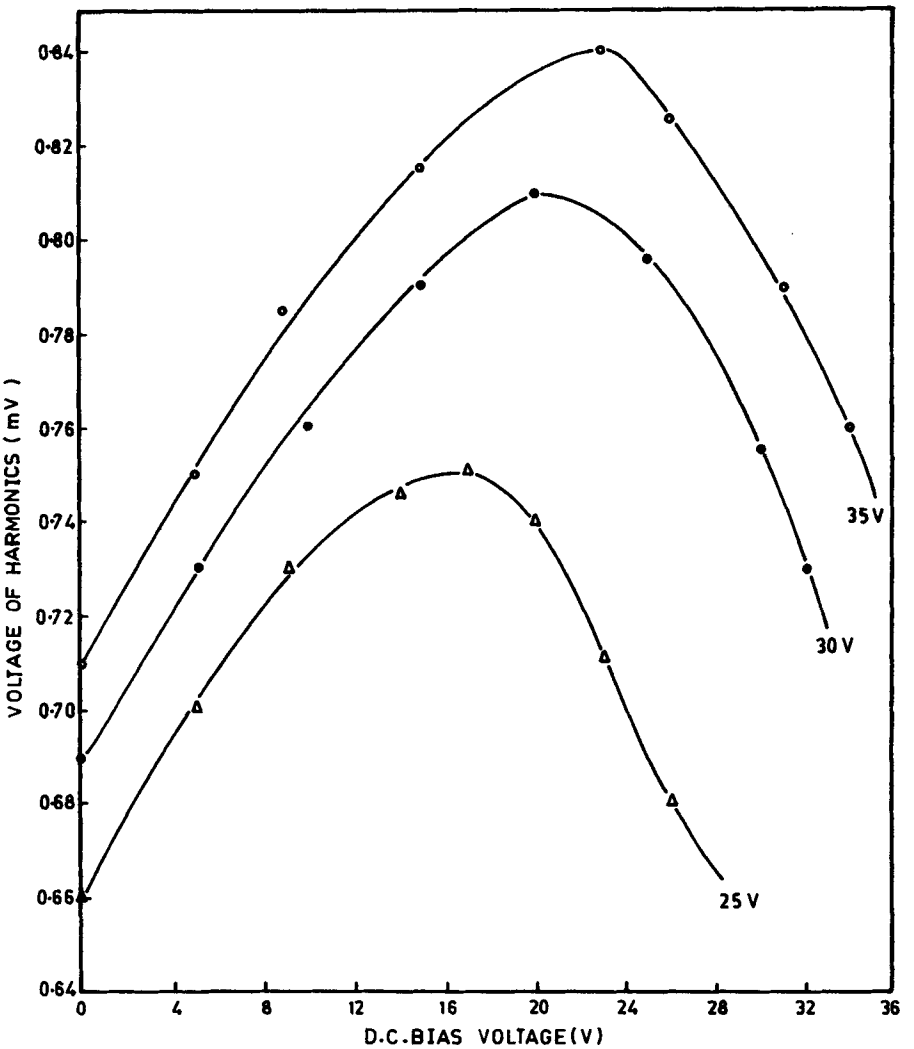

Figure 1. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak) Δ25 V, ● 30 V, ○ 35 V for $(Pb_{0.8}-Ba_{0.2})\ TiO_3$.

thickness of the sample pellet, B the material specific constant, P_0 the polarization due to d.c. bias and P_w the polarization due to a.c. voltage. Similar results were reported by Malek *et al* (1964) and Mansingh and Prasad (1977) for TGS and Chavan and Patil (1980) for TGSe and TGS-Se crystals. However, the deviations from linear behaviour and sharp decrease in the amplitude of second harmonic is observed at higher bias voltage. 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 fields so that second harmonic is generated. At high biasing fields the polarization is counteracted till the material does not fall out of the state of autostabilization. It is observed that as the a.c. voltage is increased, higher bias would be required to drive the material out of the state of autostabilization. This explanation was given by Malek *et al* (1964) on the impedance voltage hysteresis behaviour.

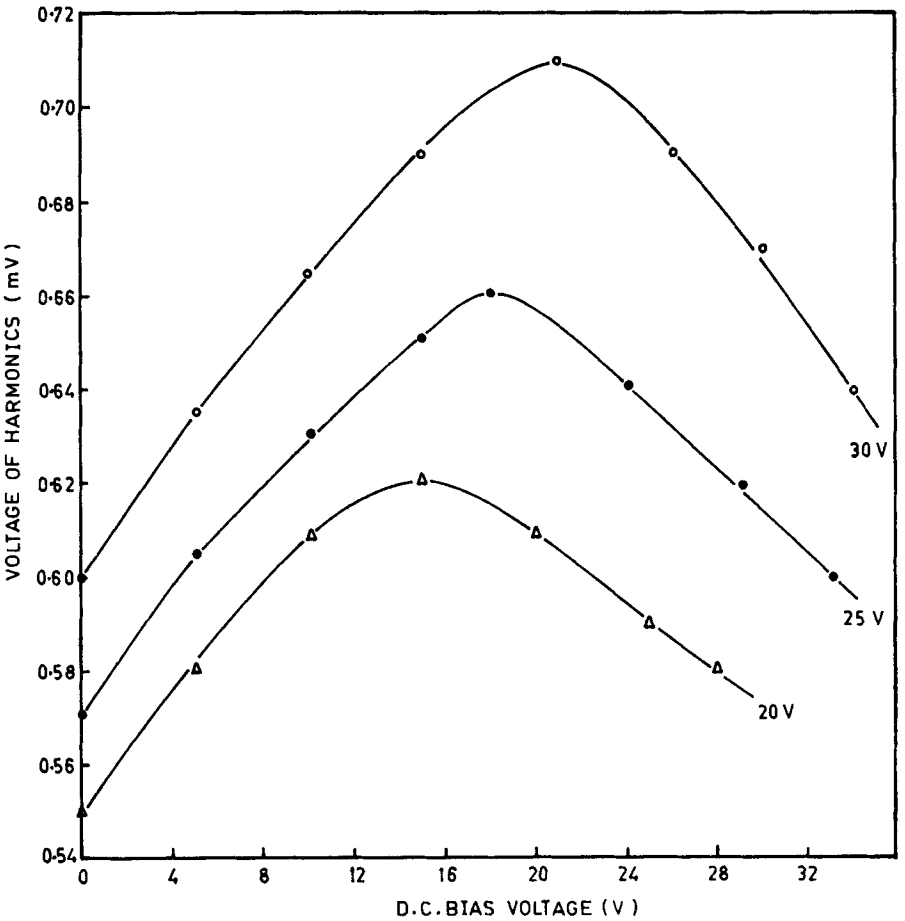

Figure 2. Variation of second harmonic voltage with d.c. bias for different a.c. voltages (volts peak) Δ20 V, ● 25 V, ○ 30 V for $(Pb_{0.8}-Sr_{0.2})\,TiO_3$.

From the table 1, it is seen that zero off-set go on increasing as the compositions of lead titanate increases in the solid solutions $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$. Also d.c. bias voltage which drives the TANDEL element out of autostabilization increases with increasing composition of lead titanate in $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$. It can be observed from (1) that the generated second harmonic should be proportional to the square of the a.c. voltage. But in our present investigations and also in the work of Mansingh and Prasad (1977) and Chavan and Patil (1980) no such variations have been observed. It might be due to the basic TANDEL behaviour. TANDEL element adjusts its impedance against the variations of applied a.c. voltage so that the product CP_w^2 in (1) remains constant and this is consistent with the TANDEL theory outlined by Dvorak *et al* (1964). It is also apparent from table 1 that when the d.c. bias voltage is zero, there is still some second harmonic output. This is consistent with the results of Abe *et al* (1971), Mansingh *et al* (1977) and Chavan *et al* (1980). This off-set is due to the presence of defects giving rise to an internal bias which, in turn generates a second harmonic. Zero off-set go on increasing as the applied a.c. voltage increases in the solid solutions $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$. This might be due to the increase in the internal bias with increase

Table 1. Values of various parameters for different $PbTiO_3$, $BaTiO_3$ and $SrTiO_3$ solid solutions.

Substance	Threshold peak voltage for auto-stabilization (v)	Peak a.c. voltage (v)	Magnitude of second harmonic at zero bias (mV)	Magnitude of d.c. bias for going out of auto-stabilization (v)
$(Pb_{0.8}\text{-}Ba_{0.2})TiO_3$	20	25	0·66	17
		30	0·69	20
		35	0·71	23
$(Pb_{0.6}\text{-}Ba_{0.4})TiO_3$	20	25	0·65	14
		30	0·67	17
		35	0·69	22
$(Pb_{0.5}\text{-}Ba_{0.5})TiO_3$	20	25	0·62	13
		30	0·64	16
		35	0·67	20
$(Pb_{0.8}\text{-}Sr_{0.2})TiO_3$	15	20	0·55	15
		25	0·57	18
		30	0·60	21
$(Pb_{0.6}\text{-}Sr_{0.4})TiO_3$	15	20	0·53	14
		25	0·57	16
		30	0·60	19
$(Pb_{0.5}\text{-}Sr_{0.5})TiO_3$	15	20	0·51	12
		25	0·53	15
		30	0·56	18

of applied a.c. voltage. Table 1 summarizes the observations on the threshold voltages for transition to autostabilized state, amplitude of a.c. signal used in the different experiments, magnitude of second harmonic at zero bias and magnitude of d.c. bias at which samples go out of the autostabilized state.

4. Conclusions

From our present investigation the following conclusions could be made (i) Zero off-set goes on decreasing as the proportion of $PbTiO_3$ decreases. (ii) The d.c. bias voltage that drives the TANDEL out of autostabilization also decreases as the proportion of $PbTiO_3$ decreases. (iii) As a.c. voltage is increased, higher d.c. bias would be required to drive the ferroelectric solid solution out of the state of autostabilization. (iv) The zero off-set voltage goes on increasing as the applied a.c. voltage is increased. (v) Our results establish that $(Pb_x\text{-}Ba_{1-x})TiO_3$ and $(Pb_x\text{-}Sr_{1-x})TiO_3$ can be used as TANDEL elements.

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