

Electrical second harmonic generation and temperature autostabilized nonlinear dielectric element in ferroelectric solid solutions $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$

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Abstract. Second harmonic generation and temperature autostabilized nonlinear dielectric element (TANDEL) effect have been studied for ferroelectric solid solutions $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$ in the vicinity of the Curie temperature. The generated second harmonic is linear for low biasing d.c. fields with zero off-set. The deviations from linear behaviour and a sharp decrease in the amplitude of second harmonic is observed at higher d.c. bias voltages. The TANDEL elements, in the autostabilized state, adjust their impedance against the variation of applied a.c. voltage. The observed zero off-set might be due to the presence of defects which give internal bias and generate second harmonic.

Keywords. Ferroelectrics; second harmonic generation; thermoautostabilized state (TANDEL).

1. Introduction

Second harmonic generation (SHG) in the autostabilized state has been studied by Malek *et al* (1964) for TGS from the harmonic analysis of current response. Similar effect has been observed for barium titanate and potassium dihydrogen phosphate by Miller (1964). Abe *et al* (1971) studied SHG for triglycine sulphate using external temperature arrangement and observed zero off-set. They suggested the use of TGS in electrometer circuit. Mansing and Eswar Prasad (1977) studied SHG and TANDEL effects in triglycine sulphate and suggested that the zero off-set might be due to the presence of defects which in turn give rise to an internal bias. Chavan and Patil (1980) reported that the defects and dislocations in the crystal give rise to an internal bias for TGSe and TGS-Se.

Our studies on SHG and TANDEL effects for ferroelectric solid solutions sodium-potassium vanadate $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and sodium-lithium vanadate $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$ are reported in this paper.

2. Experimental

The crystalline solids of sodium vanadate (NaVO_3), potassium vanadate (KVO_3) and lithium vanadate (LiVO_3) were prepared from a stoichiometric mixture of M_2^+CO_3 ($\text{M}^+ = \text{Na}, \text{K}$ and Li) and V_2O_5 . This mixture was heated in a platinum crucible inside a globar furnace at 750°C for 4 hr and then allowed to cool up to room temperature. The solid solutions of $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$ were

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prepared from their respective vanadates by firing in the platinum crucible at 900°C for 3 hr and then allowed the furnace to cool. The samples formed were confirmed by scanning them on x-ray diffractometer. The pellets of the solid solutions in the form of discs (diameter 1 cm and thickness about 1 mm) were prepared by applying 5 tonnes pressure using a hydraulic press. These pellets were sintered on a platinum foil at 500°C for 3 hr. The two sides of the pellets were coated with a thin layer of silver paste for good electrical contact.

The experimental set-up (figure 1) is similar to that used by Mansing and Eswar Prasad (1977) and Chavan and Patil (1980). We have studied voltage response of TANDEL elements of $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$ with a pure resistor of 10 ohm connected in series with them. A frequency of 10 kHz was used during the entire course of study. The experiments were carried out near the Curie temperatures of different samples using a temperature controller arrangement. The Curie temperatures of these samples were investigated by using a modified form of Sawyer and Tower (1930) circuit. The investigated Curie temperatures of $(\text{Na}_{0.75}\text{K}_{0.25})\text{VO}_3$, $(\text{Na}_{0.50}\text{K}_{0.50})\text{VO}_3$ and $(\text{Na}_{0.25}\text{K}_{0.75})\text{VO}_3$ are 425, 460 and 485°C respectively and of $(\text{Na}_{0.75}\text{Li}_{0.25})\text{VO}_3$, $(\text{Na}_{0.50}\text{Li}_{0.50})\text{VO}_3$ and $(\text{Na}_{0.25}\text{Li}_{0.75})\text{VO}_3$ are 490, 470 and 445°C respectively. The second harmonic voltage response for TANDEL elements of $(\text{Na}_{0.50}\text{K}_{0.50})\text{VO}_3$ is shown in figure 2. The other compositions of sodium-potassium vanadate series also show similar nature as in figure 2. The second harmonic voltage response for TANDEL elements of $(\text{Na}_{0.50}\text{Li}_{0.50})\text{VO}_3$ is shown in figure 3. The other compositions of sodium-lithium vanadate series also show similar type of graphical nature as in figure 3.

3. Results and discussion

Figures 2 and 3 show that the generated second harmonic is linear with applied d.c. voltage for low biasing fields in accordance with equation (1) given by Mansing and Eswar Prasad (1977), viz

$$V_{sh} = 6\omega CRdBP_0 P_\omega^2 \cos 2\omega t, \quad (1)$$

where C is the capacitance of the TANDEL element, d the thickness of the pellet, R

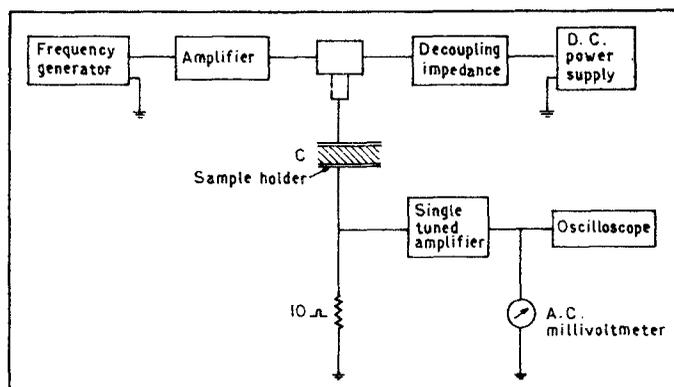


Figure 1. Experimental set-up.

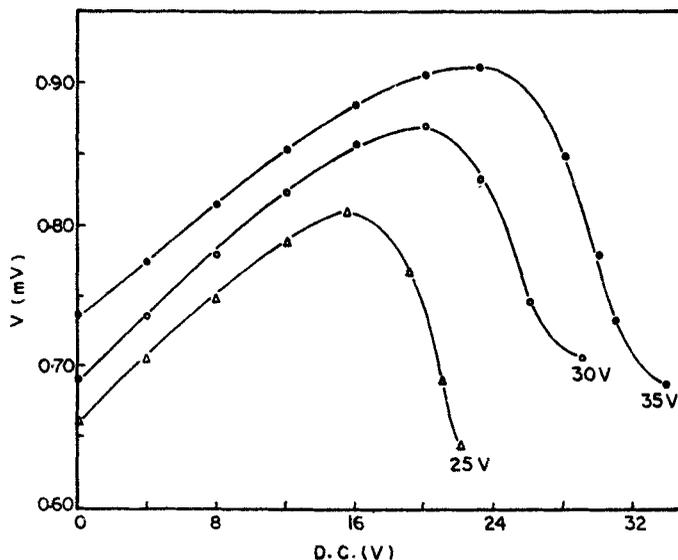


Figure 2. Variation of second harmonic voltage with D.C. bias for different a.c. voltages for $(\text{Na}_{0.50}\text{K}_{0.50})\text{VO}_3$.

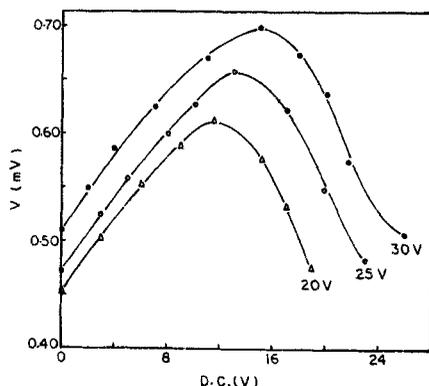


Figure 3. Variation of second harmonic voltage with d.c. bias for different a.c. voltages for $(\text{Na}_{0.50}\text{Li}_{0.50})\text{VO}_3$.

the small series resistance, ω the sinusoidal frequency and B the material specific constant. From (1) the generated second harmonic is proportional to polarization P_0 (which is proportional to applied d.c. bias) and to P_ω^2 (which is proportional to the square of the applied a.c. voltage). Similar results were reported by Malek *et al* (1964) and Mansing and Eswar Prasad (1977) for TGS and by Chavan and Patil (1980) for TGSe and TGS-Se. The region over which the second harmonic is linear with the applied d.c. bias can be extended by increasing the a.c. voltages. This is due to the fact that for low biasing fields the polarization is counteracted by d.c. bias fields so that the second harmonic is generated.

At higher biasing voltages a deviation from linear behaviour and a sharp decrease

in the amplitude of second harmonic is observed for TANDEL elements $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$. At high d.c. fields the polarization is counteracted to the extent at which the elements fall out of the state of autostabilization. Higher d.c. bias is required to drive the TANDEL elements out of the state of autostabilization for higher a.c. voltages. This can be explained from the impedance voltage hysteresis given by Malek *et al* (1964).

The generated second harmonic should be proportional to the square of the applied a.c. voltage according to (1). But in the present studies, as also in the work of Mansing and Eswar Prasad (1977) and of Chavan and Patil (1980), no such variation was observed perhaps due to the basic TANDEL behaviour. The TANDEL element adjusts its impedance against the variations of applied a.c. voltage, so that the product CP_ω^2 in (1) remains constant which is in agreement with the theory of TANDEL given by Dvorak *et al* (1964). From figures 2 and 3 it is clear that when the d.c. bias voltage is zero there is still some second harmonic output. This is in agreement with the results of Abe *et al* (1971), Mansing and Eswar Prasad (1977) and of Chavan and Patil (1980). This zero off-set might be due to the presence of defects, giving rise to an internal bias, which in turn generates second harmonic. Table 1 summarizes our observations of threshold peak voltage for transition to the autostabilized state, amplitude of a.c. signal used for different samples, magnitude of second harmonic at zero bias and magnitude of d.c. bias at which samples go out of the autostabilized state.

Table 1. Values of various parameters of $(\text{Na}_x\text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{Li}_{1-x})\text{VO}_3$ solid solutions.

Sample	Threshold peak voltage for autostabilization (V)	Peak a.c. voltage (V)	Magnitude of second harmonic at zero bias (mV)	Magnitude of d.c. bias for going out of autostabilization (V)
$(\text{Na}_{0.75}\text{K}_{0.25})\text{VO}_3$	18	25	0.70	14.0
		30	0.75	18.5
		35	0.78	23.0
$(\text{Na}_{0.50}\text{K}_{0.50})\text{VO}_3$	16.5	25	0.66	15.5
		30	0.69	20.0
		35	0.74	23.0
$(\text{Na}_{0.25}\text{K}_{0.75})\text{VO}_3$	14	25	0.62	17.0
		30	0.65	20.5
		35	0.69	24.5
$(\text{Na}_{0.75}\text{Li}_{0.25})\text{VO}_3$	10	20	0.42	12.0
		25	0.44	14.5
		30	0.50	17.0
$(\text{Na}_{0.50}\text{Li}_{0.50})\text{VO}_3$	12	20	0.45	11.5
		25	0.47	13.0
		30	0.51	15.0
$(\text{Na}_{0.25}\text{Li}_{0.75})\text{VO}_3$	14.5	20	0.49	9.0
		25	0.50	12.0
		30	0.53	14.0

The following observations could be noted

- (i) The threshold peak voltage for transition to the autostabilized state and the magnitude of zero off-set increases as the proportion of NaVO_3 increases in the solid solution $(\text{Na}_x \text{K}_{1-x})\text{VO}_3$ and decreases in the solid solution $(\text{Na}_x \text{Li}_{1-x})\text{VO}_3$.
- (ii) The zero off-set might have been caused due to the presence of defects, giving rise to an internal bias, which generates second harmonic.
- (iii) Higher d.c. bias is required to drive the ferroelectric solid solutions out of the state of autostabilization at higher a.c. voltage.
- (iv) The d.c. bias voltage that drives the TANDEL element out of autostabilization increases as the proportion of NaVO_3 in the solid solution $(\text{Na}_x \text{K}_{1-x})\text{VO}_3$ decreases and in the solid solution $(\text{Na}_x \text{Li}_{1-x})\text{VO}_3$ increases.
- (v) Our results establish that the solid solutions $(\text{Na}_x \text{K}_{1-x})\text{VO}_3$ and $(\text{Na}_x \text{Li}_{1-x})\text{VO}_3$ can be used as TANDEL elements.

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