

Figure 2 Variation of coefficients of thermal expansion of silver thiogallate with temperature.

dence of these coefficients are represented by the following equations

$$\alpha_{\parallel} = -(7.6652 \times 10^{-6} + 1.5124 \times 10^{-9} T + 6.5514 \times 10^{-11} T^2) \quad (1)$$

$$\alpha_{\perp} = (8.8576 \times 10^{-6} - 3.5404 \times 10^{-10} T + 3.7901 \times 10^{-11} T^2) \quad (2)$$

where α_{\parallel} and α_{\perp} are expressed in $^{\circ}\text{C}^{-1}$ and T in $^{\circ}\text{C}$. The mean coefficients of thermal expansion of AgGaS_2 between 30 and 394°C obtained from the present data are $\alpha_{\parallel} = -10.80 \times 10^{-6} \text{C}^{-1}$ and $\alpha_{\perp} = 10.93 \times 10^{-6} \text{C}^{-1}$. It can be seen from Fig. 2, that the positive value of α_{\perp} increases non-linearly while the value of α_{\parallel} is negative at room temperature and its numerical value increases non-

linearly with increasing temperature as in the case of AgGaSe_2 [2].

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Internal field and photovoltaic effect in non-homogeneous ferroelectric SBN

Photorefractive and photovoltaic effects [1] and photocurrents [2] in ferroelectric single crystals of SBN have been studied. The results show that

the photovoltage measured externally (several volts cm^{-1}) does not correspond to the change in birefringence, equivalent to an electric field of hundreds of volts cm^{-1} . Photocurrents show a maximum around 320nm .

In a previous paper [3] the results obtained in a

study of photocurrents and photovoltaic effect in single crystals of SBN, and polycrystalline SBN and PLN, with or without cationic impurities were reported. In polycrystalline samples without dopants an inversion of the sign of the stationary current around 450 nm was observed. In ferroelectric materials with layered structure ($\text{Sr}_2\text{Nb}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$, $\text{La}_2\text{Ti}_2\text{O}_7$) Stefanovich [4] found a photocurrent in which the sign of the stationary part was opposed to that of the pyroelectric transient. Finally, Land [5] reported a clear asymmetry in the distribution of the intensity of light scattering as a function of the applied field in PLZT ceramics. These results lead us to consider the existence of strong internal electric fields that modify photoelectric behaviour in these materials.

In this paper we try to confirm the appearance of internal electric fields in single crystal SBN and its influence on commutation and photovoltaic processes.

Single crystals of SBN ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) were grown by the floating zone method in an image furnace*. Hysteresis loops of single crystals were determined applying electric fields of triangular shape and a frequency of 0.05 Hz. Photocurrents were measured in short circuits, and photovoltages were determined either in open circuits or by measuring photocurrents while applying very small external fields. In order to determine the polarization state, measurements were made of the pyroelectric transient, after applying different electric fields. It was thus possible to observe the effect of illumination on the commutation process.

A superpressure mercury vapour lamp was used which provided light intensities of 17.5, 12.3 and 12.0 mW cm^{-2} at wavelengths (λ) of 370, 410 and 440 nm, respectively.

The hysteresis loop at room temperature of a single crystal sample not previously illuminated does not show asymmetries, and values of $E_c = 1900 \text{ V cm}^{-1}$ and $P_s = 21.6 \mu\text{C cm}^{-2}$ are obtained. (E_c is coercive field and P_s is spontaneous polarization.)

When the sample, having been polarized to saturation, was illuminated for 2 h with a light of wavelength 410 nm and intensity 12.5 mW cm^{-2} , was made to describe the hysteresis loop again, it

TABLE I

Wavelength (nm)	E_c (V cm^{-1})	E_1 (V cm^{-1})	E_2 (V cm^{-1})	E_i (V cm^{-1})
Darkness	1860	2875	850	1010
370	1450	2025	875	575
440	1375	1700	1050	325

was necessary to apply an external field of 2900 V cm^{-1} in order to invert the original polarization, and 900 V cm^{-1} to take it to its initial state. In other words, a 1000 V cm^{-1} displacement of the loop along the electric field axis had taken place.

If the loop was described while the sample was being illuminated, variations were observed both in the width and in the displacement of the loop. In Table I the coercive fields obtained before damaging with light, the electric fields E_1 and E_2 necessary to switch polarization in both directions after illuminating for 2 h and thus damaging the material, and the internal field E_i inferred from the displacement of loops are shown. These quantities have been measured in the darkness and on illumination with 370 and 440 nm light.

These results allow us to state that light produces a strong asymmetry in the hysteresis loop due to the action of an internal electric field of fixed direction, E_i . This is a result of electric charges produced by illumination due to spontaneous polarization. These charges accumulate in some region of the sample, which may be next to the surface assuming E_i to be of the same origin as the field due to space charge, E_{sc} , observed by Land [5] in PLZT ceramics.

This electric field is an obstacle to the switching of polarization in one direction and favours switching in the opposite direction; it is thus normal for the hysteresis loop to show an asymmetry in the field axis. On the other hand, the results of Table I show a wavelength dependent decrease in coercive field and in the internal field when the sample is under illumination. That is, illuminating with an electric field present favours the switching process and tends to eliminate the internal electric field. These results agree with those of Land [6] in PLZT ceramics.

All this leads us to think that the origin of the internal electric field observed in our experiments

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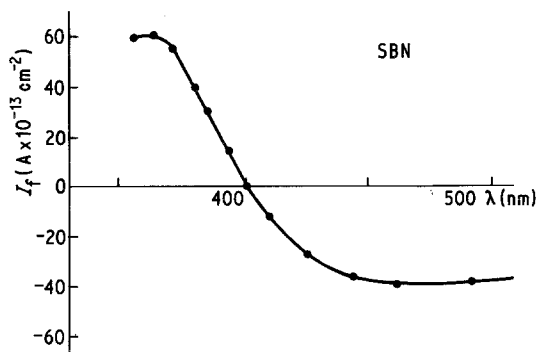


Figure 1 Stationary part of the photocurrent as function of λ , (SBN).

is to be found in space charges produced by illumination.

The build-up of the field E_i can be observed through the study of the evolution of the shape of the photocurrents. These are measured in the first minutes after illuminating a sample that initially does not present asymmetry in the hysteresis loop. The results of Fig. 1 show a change in the sign of the stationary current when the wavelength is made to vary between 300 and 500 nm. This effect appears in the first experiment independently of the direction in which λ is varying, and also, after some time, for a fixed λ , around 400 nm, depending on light intensity. That is, the shape of the photocurrent changes from normal at the beginning (pyroelectric peak of the same sign as the stationary photocurrent) to "anomalous" (different sign) at the end (Fig. 2).

Once the inversion of the stationary photocurrent has taken place, it keeps this anomalous shape; if the polarization with an electric field is inverted the shape of the photocurrent is always normal (Fig. 2a).

This behaviour, that could be interpreted as a photocommutation process, is not, because pyroelectric transients produced by heat pulses, superposed to illumination when polarization is saturated, do not change sign. It is thus possible to follow the build-up of an internal electric field due to illumination, through the study of the shape of the photocurrent as a function of exposure time and light intensity. This field remains fixed in the sample, in such a way that it strongly influences commutation processes.

In Table II the voltages V_i and V_λ (internal voltage and photovoltage) computed from measurements of photocurrents applying voltages of ± 1 V for both signs of spontaneous polarization are presented.

These voltages would correspond to fields of the order of 10^4 V cm^{-1} ; assuming for the charge diffusion zone a width of the order of 10^{-5} cm , which is normal in this type of material.

There is a dependence on wavelength, and a maximum for 410 nm. V_λ is always smaller than V_i , and, therefore, a stationary photocurrent is always governed by V_i .

The situation could be described in the following way:

In the darkness, the field due to polarization, E_p , remains completely shielded by a field E_A due to carriers present in the material

$$E_p + E_A = 0$$

When the sample is illuminated, this brings forth the internal field, E_i , but also the photovoltaic field, E_λ , whose origin is ascribed to several causes invoking a decrease of the spontaneous polarization of the ferroelectric material [7]. The resultant field, E_R , under illumination of these

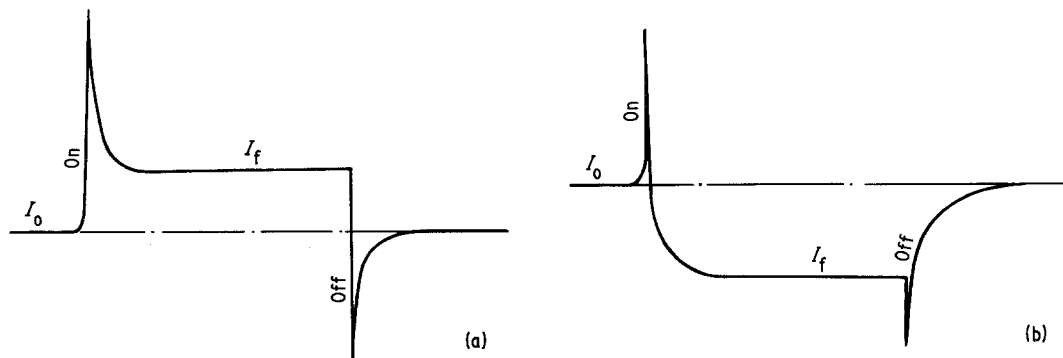


Figure 2 (a) Photocurrent at the beginning of the experiment and (b) photocurrent at the end of the experiment.

TABLE II

Wavelength (nm)	V_i (V)	V_λ (V)
White light	0.460	0.120
370	0.106	0.020
410	0.341	0.117
440	0.335	0.100

two fields of different origins would thus be

$$E_R = E_i \pm E_\lambda.$$

In our case $E_\lambda < E_i$ and the photocurrent depends on the magnitude and shape of E_i . Therefore, depending on the sign of the spontaneous polarization with respect to E_i , whose sign is fixed, the shape of the current will be normal if $\text{sign } E_i = \text{sign } E_\lambda$ and anomalous if $\text{sign } E_i \neq \text{sign } E_\lambda$. This is also the behaviour in non-doped ceramic SBN samples [3].

Light next to ultraviolet produces a fixed sign strong internal electric field E_i in ferroelectric SBN, due to space charge accumulated near the surface, of the order of 10^4 V cm^{-1} . It is possible to follow the build-up of this field studying the shape of photocurrents as a function of time and to verify that the change in sign of the stationary part is not due to photocommutation but to the influence of E_i .

In non-doped samples, the internal field is

higher than the photovoltaic field, and there is an anomalous photocurrent. The origins of these two fields are different; the former is due to space charge, and the latter to charge transfer and charges in spontaneous polarization.

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Thermal expansion of dysprosium vanadate

The rare earth vanadates with a chemical formula RVO_4 , where R is a trivalent rare earth ion, crystallize with the tetragonal zircon structure (space group $I4_1/amd$). At low temperatures, some of these crystals exhibit cooperative Jahn–Teller phase transitions from tetragonal to orthorhombic symmetry, Cooke *et al.* [1]. As a part of a general programme of X-ray investigation of zircon type compounds, the authors have studied the thermal expansion of dysprosium vanadate at high temperatures. In this communication, the precision lattice parameters and the coefficients of thermal expansion of dysprosium vanadate determined at various high temperatures are presented.

The sample used in the present study was kindly made available by Dr Wendl, Fakultät für Physik, Universität Karlsruhe, West Germany. The specimen used in the investigation was prepared by placing the sample in a thin walled quartz capillary tube. X-ray diffraction patterns were recorded at various temperatures in the temperature range 30 to 604°C, using $\text{CuK}\alpha$ radiation. The temperature could be held constant within about 2°C using a voltage stabilizer and a variac. The details of the experimental arrangement have been described in an earlier publication by Krishna Rao *et al.* [2]. The least squares method of Cohen [3] was adopted in evaluating the precision lattice parameters. The lattice parameters at different temperatures were deter-