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PHOTOFERROELECTRIC EFFECTS IN $A_vB_{vi}C_{vii}$ AND BaTiO$_3$-TYPE FERROELECTRICS

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Abstract. — In ferroelectrics possessing photoconductivity a number of specific effects may be observed. They consist in the influence of illumination on the phase transition, domain structure and ferroelectric properties (photoferroelectric effects). In this paper photoferroelectric effects were for the first time studied for BaTiO$_3$.

The existence of photoconductivity in some ferroelectrics stipulates a number of interesting effects consisting in the influence of nonequilibrium carriers on the phase transition, domain structure and ferroelectric properties of the crystal. Previously these effects called by us as photoferroelectric were thoroughly studied for $A_vB_{vi}C_{vii}$-type ferroelectrics, particularly for SbSI, and pyroelectric HgI$_2$ [1][2]. To these effects we may attribute the influence of illumination on Curie temperature [3], temperature hysteresis (photohysteresis effect [1]), domain structure (photodomain effect [4][5]) etc.

The discovery of considerable photoconductivity in BaTiO$_3$ crystal made possible, for the first time, to observe the influence of nonequilibrium carriers on the high temperature transition from tetragonal phase into cubic, namely, the influence of illumination on the phase transition temperature and temperature hysteresis value [6]. A remarkable feature of BaTiO$_3$ comparing with SbSI crystal is the possibility of optical observing of domain structure. This made possible in the present work to observe photoferroelectric phenomena and, particularly, the photodomain effect in BaTiO$_3$ both by means of dielectric measurements and by the optical method. Spectral distribution of intrinsic photoconductivity in BaTiO$_3$ has a maximum in the violet region near $\lambda \approx 410 \text{ nm}$ that corresponds to the energy gap $E_g \approx 3 \text{ eV}$ [7], [8], [9]. According to this fact for the observing of photoferroelectric effects the crystal was illuminated with a mercury-discharge-lamp through a filter, cutting off the longwave region $\lambda > 600 \text{ nm}$. Thus the measuring of dielectric constant $\varepsilon$ was made in the region of high temperature phase transition in the dark and under illumination. Crystals were grown by Remeika method. A field was applied in plane (001), silver paste was used as electrodes. Measurements were made alternatively in the dark and with illumination in thermostating regime displaying good reproducibility. Obtained results are presented in figure 1. From the curves of figure 1, it will be seen that illumination simultaneously shifts the phase transition temperature to the low temperature side and reduces the temperature hysteresis value. In
addition, illumination increases the \( \varepsilon_{\text{max}} \) value in heating regime. The study of spectral distribution of these effects showed that according to the spectral distribution of intrinsic photoconductivity, photoferroelectric effects in \( \text{BaTiO}_3 \) occur in the violet region of spectrum for \( \lambda < 470 \text{ mp} \).

From temperature dependencies of inverse dielectric constant corresponding to curves of figure 1, the dark and light values of phase transition temperature \( T_c \) \( (T_{c1} \text{ corresponds to heating, } T_{c2} \text{ to cooling}) \), and temperature hysteresis \( \Delta T = T_{c1} - T_{c2} \), were determined. These data demonstrate that the shift of phase transition temperature is

\[
\Delta T_c \simeq -3^\circ \text{ and } \Delta T_c \simeq -2.3^\circ
\]

and, consequently, the average value of shift is

\[
\Delta T_c \simeq -2.6^\circ.
\]

Simultaneously illumination decreases the temperature hysteresis, \( \Delta T \) being \( \simeq -0.7^\circ \) and, therefore,

\[
\delta \Delta T / \Delta T \simeq -0.3.
\]

The analysis of curves presented in figure 1 also shows that for all curves the well-known thermodynamic relation \( s(T_c) \) \( (T_c - T_0) \approx C/2 \) is satisfactorily fulfilled.

Here \( C \)-Curie Weiss constant, \( T_0 \)-Curie-Weiss temperature. Thus, it will be seen that the decrease of \( (T_c - T_0) \) with illumination results in the increase of \( s(T_c) \).

Observation of domain structure and phase transition for the same crystal was performed in the polarizing microscope. The observation was carried out in the passing polarized light in C-axis direction. For revealing photoferroelectric effects observation was performed alternatively in the longwave region \( (470 < \lambda < 600 \text{ mp}) \), where \( \text{BaTiO}_3 \) is nonphoto sensitive, and in the shortwave region \( (360 < \lambda < 600 \text{ mp}) \), where photoconductivity and photoferroelectric effects occur. In figure 2 and 3 there are given the photomicrographs of crystal for different temperatures, one series of the photographs corresponding to the observing of crystal in nonphotosensitive longwave region of spectrum («dark»), and the other-in the photosensitive shortwave region of spectrum («light»).

Photomicrographs in figure 2 were obtained for a single cycle of heating and cooling; photomicrographs in figure 3 were obtained after repeated passing of crystal through Curie point. The analysis of these results leads to the following conclusions:

1. Optical observation of phase transition in \( \text{BaTiO}_3 \) reveals both the domain structure and the coexistence of polar and nonpolar phases near the phase transition. For example, in the photograph of figure 2, corresponding to temperature 127 \(^\circ\text{C}\), it may be seen that the appearing of a paraelectric phase inside an illuminated crystal occurs for a lower temperature than for a non-illuminated one. This is connected with the shift of Curie point to the low temperature side when
illuminating the crystal in the intrinsic photosensitivity region. The decrease of temperature hysteresis value with illumination is registered by the same method (photomicrographs, corresponding to the crystal cooling are not given in figure 2).

The values of Curie temperature shift and photohysteresis effect are in agreement with the corresponding values obtained from dielectric measurements and given above. The decrease of temperature interval of phase coexistence with illuminating BaTiO$_3$ is also observed. Previously this effect was observed with SbSI.

2. As it may be seen from photomicrographs of figures 2 and 3, illumination of BaTiO$_3$ in intrinsic photosensitive region of crystal essentially influences its domain structure. If BaTiO$_3$ domain structure is near to equilibrium, illumination influences it only near phase transition (Fig. 2). If domain structure is nonequilibrium, as it, apparently, occurs in figure 3, illumination influences it even far from phase transition.

3. If in the dark BaTiO$_3$ domain structure is of «square-net» type, illumination changes it into the layer type. This may be especially well seen in microphotographs of figure 3. Then for the illuminated crystal when approaching the phase transition the layer boundary changes from (100) to (010) turning by 90°.

Let us discuss the obtained results. The influence of illumination on domain structure is related with spontaneous polarization screening and correspondingly the decrease of domain electrostatic energy. The latter accounts for the transition of domain structure to equilibrium at given temperature. Therefore nonequilibrium structure is influenced by illumination even far from the phase transition. The influence of illumination on phase transition in BaTiO$_3$ may be understood on the basis of previously developed thermodynamic and microscopic theories [10], [11], [12], [13]. Thus, the direction of phase transition temperature shift with increase of nonequilibrium carrier concentration conforms to the conclusions of the theory. The phase transition temperature shift value and photohysteresis effect value, as it is shown in [6], also are in agreement with thermodynamic calculations [10], [11].

References


