Stimulated Polarization in LiNbO$_3$ and Ba$_2$NaNb$_5$O$_{15}$ Crystals

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Abstract

Thermally Stimulated Conductivity (TSC) and thermoelectret state in LiNbO$_3$ and Ba$_2$NaNb$_5$O$_{15}$ were measured as a function of temperature and time in dark and under UV excitation at liquid nitrogen temperature. Effect of polarization and the other external influences on thermoelectret were investigated. The thermal activation energy levels of traps were determined from TSC measurements as well as parameters (electric field, temperature, etc.) which are necessary for characterizing thermoelectrets were obtained.

1.   Introduction

One of the most important and numerous groups of ferroelectrics is the family of oxygen-octahedral crystals. The structure of these crystals is a combination of oxygen octahedra in the centers and voids of which other ions are located. The family of oxygen octahedral ferroelectrics has three basic structures:

1. Perovskite Structure (BaTiO$_3$ et al.)
2. Trigonal Pseudoilmenite Structure (LiNbO$_3$ et al.), and
3. Distorted Potassium-Tungsten Bronze Structure (Ba$_2$NaNb$_5$O$_{15}$).

Outstanding representatives of the second and third groups of crystals, diligently investigated in the last twenty years, are single crystal LiNbO$_3$(LN) and Ba$_2$NaNb$_5$O$_{15}$ (BNN). The great interest in these compounds is due to their strong optical nonlinearity [1-3] . Further investigations of these compounds have shown them to be promising for the purpose of optical reduction of information and holographic data storage [5-8]. The holographic writing (and reading) is accomplished by nonuniform illumination of the crystal which is formed when the photoexcited charge carriers diffuse under external (or internal) polarization and are captured in the traps thereby forming a space charge field, i.e. photoelectret (or thermoelectret) which modulates the refractive index. To understand the physical processes involved in these storage systems, the mechanism for hologram writing and for selecting the optimum conditions of writing, it is necessary to know about the thermo- and electrical characteristics of active ions within the LN and BNN crystals. With this interest we studied photoelectric properties of LN and BNN crystals by using thermo- and photoactive spectroscopy methods.

2.   Experimental Details

The LN and BNN crystals used for our measurements were grown by the Czochralsky method and their ferroelectric phase transition occured at temperature $T_c = 815$ K (BNN) and 1460 K (LN) [3]. The LN and BNN samples for the investigation of the electric properties were cut from blanks and measured 8x5xd mm^3

along the crytallographic axes. The crystal thickness d ranged from 0.1 to 4 mm. The crystals were first mechanically ground and polished, and then bright-dipped (polishing etchant: 40% HF and 70 % HNO_3 in a 1:1 ratio). The crystals, ready for electric measurements, were then annealed to remove their elastic stresses. All the measurements were made on polished z- and xy - cut faces of crystals. Light impulses of different pulse widths were obtained from UV laser (Ar, Cd-He), and a flash lamp by using a light chopper (singal's rise time is 10^{-2} s, the time constant of the measuring system of the order 10^{-7} s). The photoresponse due to impulse excitation was displayed on a storage oscilloscope. The static conductivity $I \geq 10^{-15}$ A and polarization was recorded with the help of lock-in amplifier in dark and under light excitation. Measurements were made in the field from 10^2 Vcm^{-1} up to 3.5x10^4 Vcm^{-1} in vacuum of order 10^{-3} torr. To measure the temperature of TSC, the sample was mounted in a cryostat in vacuum and the temperature was measured via a copper-constantan thermocouple. The signal from the amplifier (or oscilloscope) output enters the in-house designed measurement channel where the data, after selection and storage, are reduced by a computer [4] . All data was subsequently entered into a PC for further reductions. The PC also directs the operator to introduce the sample data *in-situ* and to check the temperature.

3.   Thermally Stimulated Conductivity (TSC) In Ba$_2$NaNb$_5$O$_{15}$

The measurement of TSC involves measurement of the dark current under dynamic heating conditions for both filled (I_f) and partially filled (I_p) electron traps:

$$I_{TSC} = I_f(T) - I_p(T) \ . \tag{1}$$

In measuring $I_p(T)$ we observed a feature which is associated with the temperature dependence of the dielectric permittivity (Fig. 1). As the heating started a current appeared in the opposite direction to the applied external field E and it was only for $T > 400$ K that $I_p(T)$ and E exhibited the same sign. The current, which was opposite to the field, was found to be proportional to the rate of heating (v = 0.06 degr./ sec.), was a maximum at 480 V/cm and decreased for higher fields. It did not occur when a cleaved crystal was used. This observed effect can be explained by displacement currents. Under dynamic heating conditions

$$I = I_c + I_d \quad , \tag{2}$$

where I is the measured, I_c is the conduction and I_d is the displacement currents; and

$$I_d = EA\frac{\partial D}{\partial t} = -EA\epsilon_o v\frac{C}{(T - T_c)^2} \quad , \tag{3}$$

where A is the contact area, ϵ_o is the dielectric constant of vacuum, C is the Curie constant, and T_c is the Curie temperature for compound. On heating I_c and I_d are opposite and for $I_d > I_c$ the measured current I is in the opposite direction to the external field.

This feature, which is obviously a property of all ferroelectrics in the paraelectric phase, must be taken into account when interpreting the TSC. In curve 2 of Fig. 1 we show the temperature dependence of the dark current I_f after the crystal has been illuminated for 4 min at 200 K. When we take into account the directions of the currents represented by these curves, the TSC current can be written as

$$I_{TSC} = I_{fc}(T) - I_{pc}(T) = I_f(T) - I_p(T) \quad , \tag{4}$$

(see Fig. 1, curve 3). If the currents represented by curves 1 and 2 are comparable, the inclusion of I_d then means that there is a considerable difference between $I_f(T)$ and I_{TSC}. An estimate of the displacement current in BNN gives $I_d \simeq 6.5$x10^{-11} A. If the current due to charges freed from the traps is less than I_d, these traps cannot be observed by the TSC method. This evidently is the reason for the absence in Fig. 1 curve 2 of the peak at T=220 K which would correspond to the trap level responsible for the thermoluminescence [9]. The thermal activation energies of the trap levels, as determined from the TSC, is 0.62 eV.
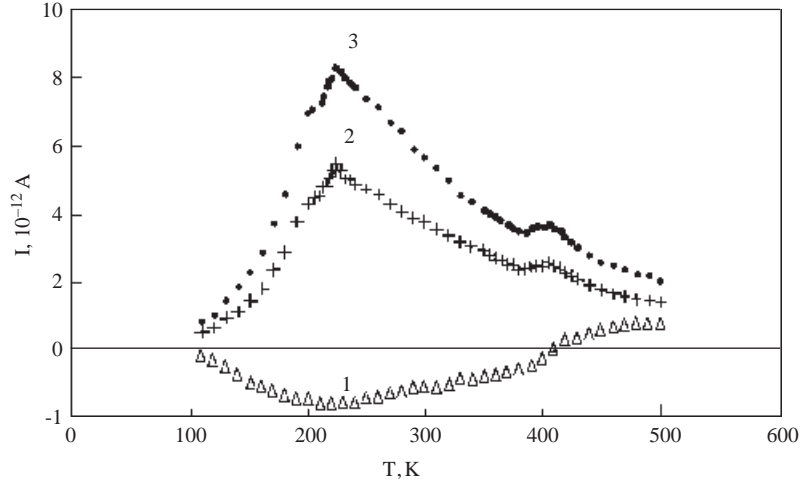
Figure 1. Temperature dependences of dark current for partially filled trap levels (1), dark current for occupied trap levels (2) and thermostimulated current (3) in $Ba_2NaNb_5O_{15}$.

4. Thermoelectret State In $Ba_2NaNb_5O_{15}$ and $LiNbO_3$

When the sample is exposed to the external polarization field, a polarization charge is formed therein. The charge value may be determined, for example, from the depolarization charge (q) in the short-circuited crystal during the thermostimulated disturbance of polarization. At the polarization temperature T_p the crystal was exposed to the field E_p for the time Δt. When the field was switched off, after a time, Δt, the crystal was cooled down to 200 K at 25 K/min. Then in the process of heating at constant heating rate of 8 K/min, a depolarization current was recorded with a maximum at the temperature T_{dp}. Upon integrating the curve of depolarization current over the time, we can determine the depolarization charge q, and is found to be equal numerically to the polarization charge of free carriers. The result of measurement carried out for LN and BNN crystals have shown that at the given temperature T_{dp} the charge q increases linearly with the polarization field up to E_p=10700 V/cm. The dependence of q upon T_p at E_p= 8800 V/cm for LN and at E_p=1280 V/cm for BNN are shown in Fig. 2-3.
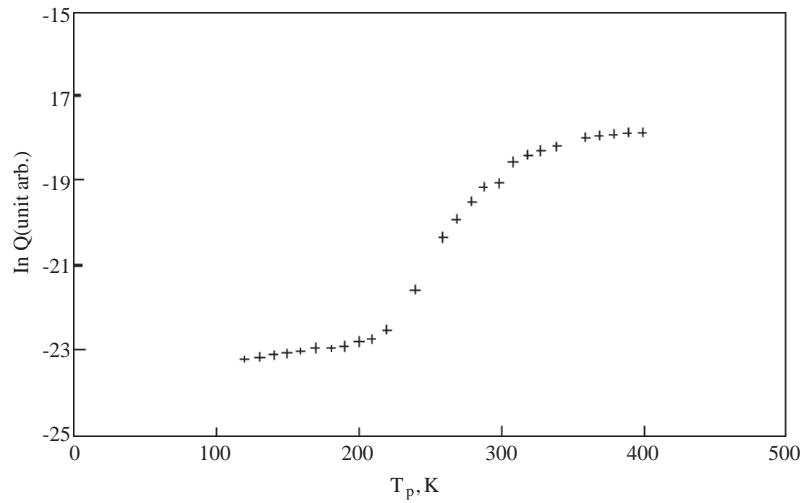

Figure 2. Thermoelectret charge (Q) as a function of polarization temperature T_p at E_p=1500 V/cm in $Ba_2NaNb_5O_{15}$.

The relaxation characteristics of the induced polarization after switching off the polarization field can be obtained in the following way. The sample is exposed to the polarization field (at a certain temperature T_p), which induces the depolarization charge q. Then, at the same temperature T_p, the polarization field is switched off. The relaxation of the polarization will be characterized by the q charge variation in the sample for a time Δt_1 (before sample cooling). Figure 4 presents such a dependence for the two temperatures T_p. It is seen from Fig. 2, 3 that the relaxation decelerates with decreasing T_p. These measurements have shown that a quick cooling of the polarized crystal down to 180 K maintains a long-term induced polarization in the crystal. Hence, as seen from Fig. 2, 3 and 4, the most appropriate condition for maximum polarization in the dark is E_p=7800 V/cm, $T_{pol} \sim 350$ K and a quick cooling of the crystal after the polarization field is switched off.
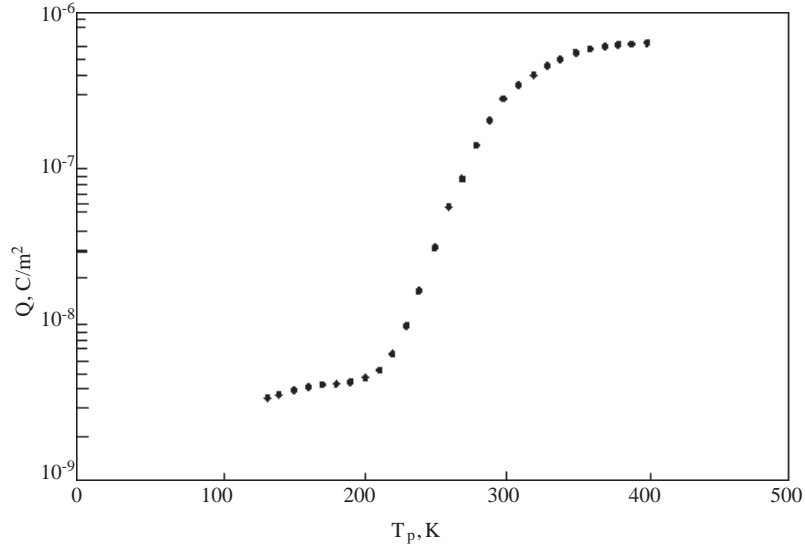

Figure 3. Thermoelectret charge (Q) as a function of polarization temperature T_p at E_p=8200 V/cm in LiNbO$_3$.

The fact that polarization temperature T_p coincides with depolarization temperature T_{dp} (Fig. 5) is important, but it is not explained so far. This leaves in doubt the electron polarization mechanism explaining the appearance of polarization charges by trapping free carriers in the deep traps, or requires the assumption of the existence of quasi-continuum trap distribution in the energy gap.
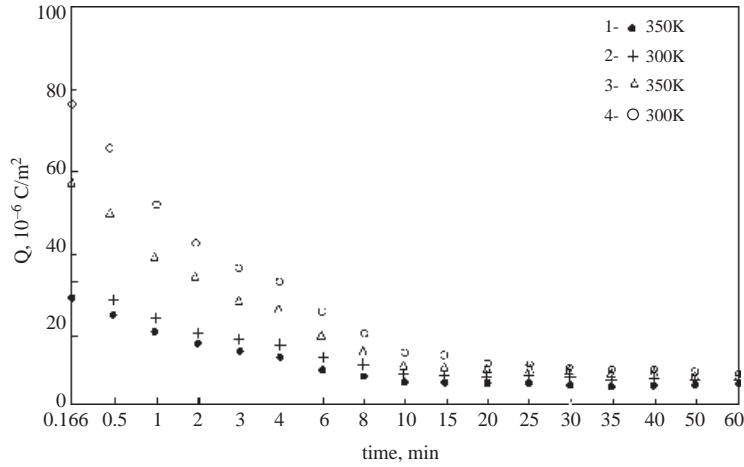

Figure 4. Thermoelectret charge (Q) as a function of time Δt during which the short-circuited crystal is in the dark at polarization temperature T_p before cooling: T_p=300 K (curves 1, 3), T_{pol}=350 (curves 2, 4) for Ba$_2$NaNb$_5$O$_{15}$ (curves 1, 2) and LiNbO$_3$ (curves 3, 4).
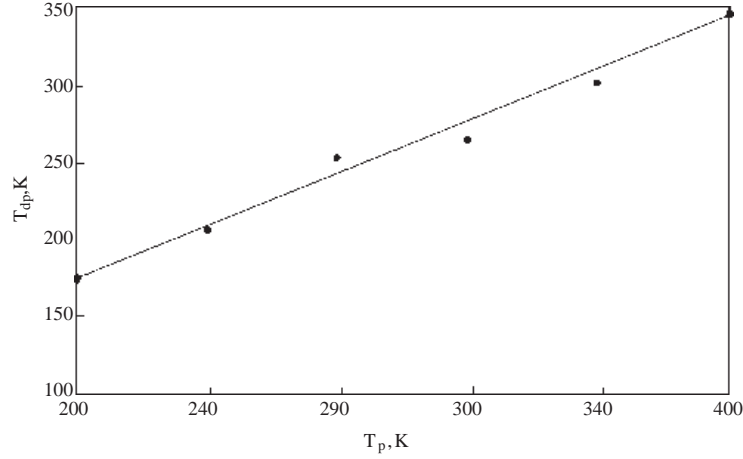
Figure 5. The dependence of polarization temperature (T_p) upon the depolarization temperature (T_{dp}) for $Ba_2NaNb_5O_{15}$ (The same behavior of T_p upon the T_{dp} in $LiNbO_3$ are to be observed).

The mechanism of polarization charge appearance under the influence of an external field is not discussed so far, but we should like to point out that these charges must be screened by free carriers after the external field is switched off and the sample is short-circuited. The screening time of this polarization is determined from the dielectric permittivity (ϵ) and conductivity (σ), and we might suppose that no overall screening takes place during our experiments because of extremely small dark conductivity, $\sigma < 10^{-12}\Omega^{-1}$ cm^{-1}. For this reason, at low temperature the internal field induced by non screened polarization charges in the polarized crystal is non-zero and can be calculated from the magnitude of surface density of the non-screened polarization. When the crystal under the internal polarization field is illuminated by the photoactive light, the photocurrent appears in the crystal. Then, in time the photocarriers screen polarization and the current drops to zero. Estimating the photocharge q for overall screening of internal field, we obtain thereby the magnitude of the internal field. When the crystal is polarized in dark at E=1300 V/cm, the non-screened polarization charge at 250 K determine by photocharge in the short circuited crystal is equal to q=4x10^{-4} C/m^2; in this case $E_1 = 4x10^5$ V/cm.

Crystal polarization in the external field and under illumination, when the photocarrier concentration is two (or three) orders of magnitude higher than the dark concentration, causes both the rise of thermostimulated depolarization current and non-screened polarization, and, hence, of the internal field at a low temperature.

5.   Conclusion

TSC and thermoelectret measurements from LN and BNN have been essentially applied to study of their thermoelectrets properties. We examined the dependence of charge of the thermoelectret to the temperature and applied electric field. Hence, electric field and temperature values for thermoelectrect's describing were found.

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