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The final stages of polarization and monodomain state stability of the Rochelle salt crystals

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Based on the direct domain observations in the Rochelle salt crystals, the final stages of polarization and the dependence of polarized state stability on the electric field strength E and on the electric pulse duration is investigated.

The conclusion is made that there exists a high electric field strength, at which small domains are displaced. At higher fields, electrooptical effects are obviously developed and the invisible network of defects is changed.

The stability of the polarized state and the degree of polarization are determined by the electric field pulse, the duration τ and the electric strength of which E are connected by equation $\ln\tau \sim k/E + b$. For incomplete polarization, the rate of polarization decay when the pulse is finished is proportional to the deviation of the domains from the initial state of the sample.

Key words: *domains, polarization, stability of the polarized state, defects*

PACS: *75.60.-d, 77.22.Ej, 61.72.Bb, 75.60.Ch*

1. Introduction

The attention to the twin structure of ferroelectrics has been renewed lately [1–5]. Apart from its own significance, this is important for the investigation of the laws of polarization of ferroics, and for measurements of fundamental characteristics of materials (spontaneous polarization, electric permittivity, dielectric losses, coercive field, piezoelectric, piezooptical and other parameters). Besides high-frequency processes [6], a particular attention is now paid to the slow ones, in which appreciable changes are possible in the defect network of the sample. In particular, for DKDP crystals, a set of relaxation times of polarization ($\sim$ 1 hour) is detected, and the absence of an accurate value of coercive field [1] is stated. The investigation of the domain motion has been started not only under the effect of an electric field, or a mechanical stress associated with spontaneous polarization of the sample, but under the effect of several stresses (ferrobielastics) [5]. Corresponding results can be also important for classic investigations of polarization for the samples with some internal mechanic stress.

Innovative solutions to the issues of domain formation and motion under the effect of external fields are presented in [2,3] in spite of the numerous papers devoted to these problems at the initial stages of twins investigation [7–14]. Specifically, repolarization is interpreted as a phase transition of the second type.

As before, most of these papers have an indirect relation to the domains and to the defects, because they do not deal with them directly.

2. Experimental techniques

In this paper the laws of growth, saturation, and spontaneous decay of the polarized state of the Rochelle salt (RS) crystals, were investigated by means of photographic and photo-electric registration of polarization process dynamics [10,11]. Using both of these techniques made it possible to enlarge the polarization time duration interval from 10^4 to 10^{-3} s. The upper limit of polarization time duration is difficult to reliably realize using a routine electronic registration of domain changes due to the conductivity of the sample.

An example of photographic and photo-electric registration of the changes of the domain structure of the Rochelle salt crystals is presented in figure 1.

Figure 1a illustrates the change of the domain areas during the decay of the monodomain state under the effect of different shearing stresses Y_z (marks 1, 2, 3).

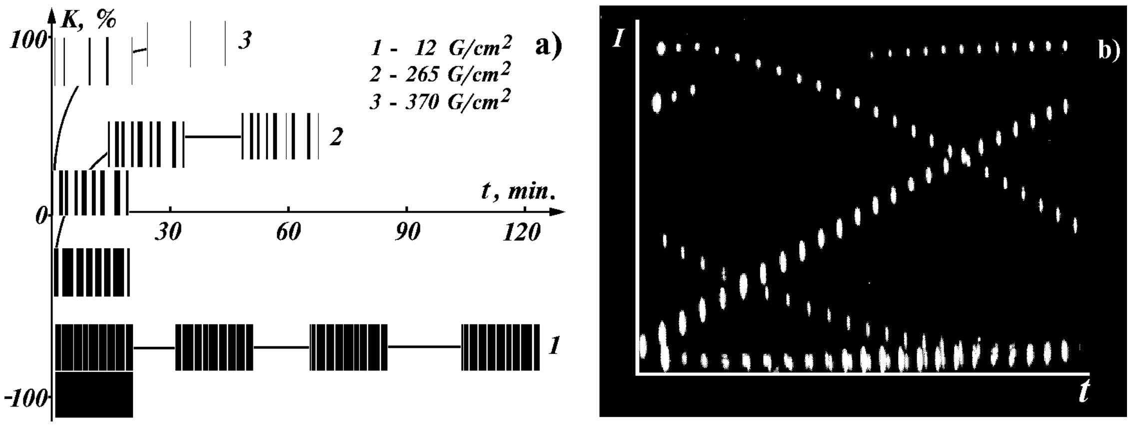

Figure 1. An examples of photographic (a) and photoelectric (b) registration of the time dependence of domains during the polarization of the Rochelle salt crystals (dots on (b) – are time marks). Here $K = S_l/(S_l + S_d)$, I – photocurrent, which is proportional to K. Curves 1, 2, 3 – the kinetics of depolarization under the action of the different shearing stresses Y_z .

Figure 1b illustrates the changes of the normalized area of the light domains of the sample under the effect of the E_x electric field, and the spontaneous decay of the polarized state after the removal of the electric pulse. The general picture is created by the shift of the corresponding sections of the oscillograph record along the abscissa axis. The time distance between the time marks is 10^{-4} s. The similar pictures are observed under the effect of the other fields, but with another time duration between the time marks. In the presented figure, the duration of the whole process is 10^{-2} s.

The field dependence of domain changes is described by the relationship between the areas of light and dark components of the twins, or by changes of the photocurrent I, caused by the light flux, which passed through the system of the crossed nicols and the investigated sample, which is put between the nicols in a diagonal position in accordance with the following relation

$$I = I_0 \frac{S_l}{S_l + S_d} \sin^2 2\varphi \sin^2 \frac{\pi d (n_2 - n_3)}{\lambda}. \tag{1}$$

Here, S_l and S_d – areas of light and dark (installed for the extinction of light) components of the twins, φ – an angle of spontaneous turn of the crystallophysic axis of domain, d – thickness of sample, λ – wavelength of light, $(n_2 - n_3)$ – birefringence of beams of light which propagate in the crystal along the polar axis X_1, I_0 – intensity of the incident beam of light.

The values of the area of the light beam $(S_l + S_d)$ and the intensity I_0 were kept constant for the whole set of experiments.

The values S_l, φ and $(n_2 - n_3)$ depend on the electric field strength. Maximal changes of intensity are related with $S_l(E)$. The change of the axis of the domain optical indicatrix φ is defined by the linear electrooptic effect (EOE) [15]

$$\Delta\varphi = \frac{r_{41} \cdot n_2^2 \cdot n_3^2 \cdot E_1}{n_2^2 - n_3^2}, \tag{2}$$

and the change of the main refractive indices $(n_2 - n_3)$ – by relationship

$$\Delta(n_2 - n_3) \simeq -\frac{n^3}{2} (R_{2211} - R_{3311}) \cdot E_1^2 , \tag{3}$$

where r_{41} – an actual coefficient of the linear electrooptic effects; R – corresponding coefficients of the quadratic electrooptic effect, E_1 – the electric strength of the external electric field, applied along the polar axis of the sample X_1. The field dependence of the sample's thickness is neglected.

3. Field and time dependences of domains

The field dependences of polarization, described by the change of the twins areas, or by the photocurrent I, are presented in figure 2 and figure 3. Here, the origination, i.e., a visible side growth, and general mass domain changes at coercive field take

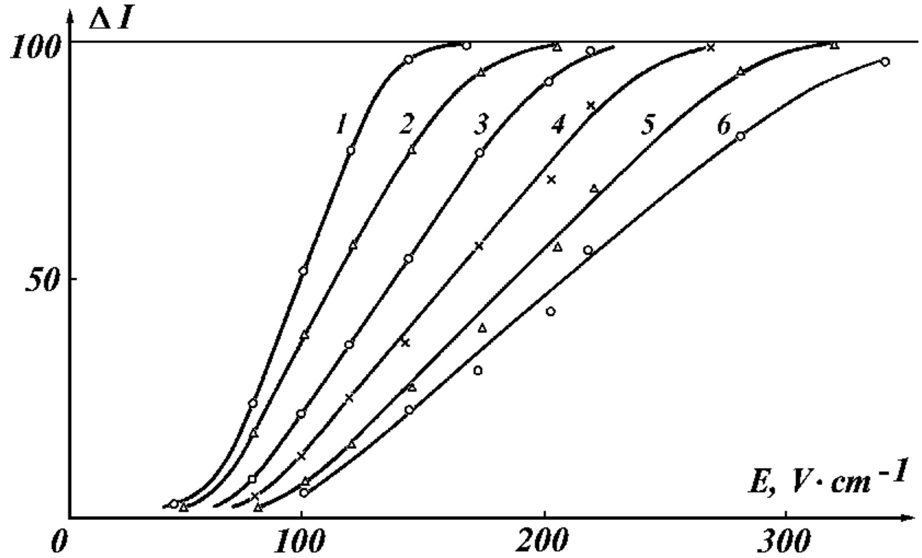

Figure 2. Polarization of the RS crystals in a weak fields for different pulse duration: 1 – 2 s, 2 – 1 s, 3 – 0.4 s, 4 – 0.15 s, 5 – 0.07 s, 6 – 0.03 s. Temperature 15 °C.

place (figure 2), and then we observe linear sections in the vicinity of saturation field, and fixing of monodomain state fields (figure 3). At relatively low fields (< 200 V/cm) it is possible to neglect the field changes of optical indicatrix, but in the higher fields just these changes are registered. In this case, it is necessary to take into consideration the clamping degree of the disappearing domains, which is a simultaneous action of electric and mechanic fields. Vanishingly small slope of the middle area of the plot in figure 3 can be caused by some factors. Among them there are different signs of electrooptic and piezooptic coefficients r_{41} and π_{2323} [16], and fixing of the small domains on the defects, when the area of domains is not changed.

At higher fields (E > 500 V/cm), obviously the full monodomainization takes place, and now the main factor becomes the deformation of the optical indicatrix of one twin component.

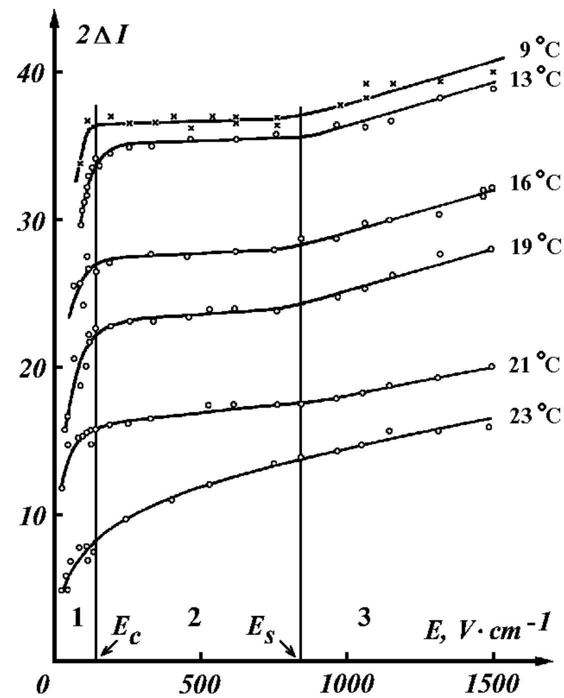

Figure 3. An example of polarization of RS crystals in the strong electric fields. Areas 1, 2, 3 – correspond to the different field changes of the domains. E_c – coercive field, E_s – saturation field.

Table 1. Relationship of amplitude E, polarizing pulse duration τ_i and the time constant $\beta(E)$ for the Rochelle salt crystals at 15 °C.

E, V/cm	50	80	130	163	195	235	315	500	500	1000
τ_i, s	$7 \cdot 10^3$	360	2	1	0.4	0.07	0.03	$5 \cdot 10^{-4}$	$15 \cdot 10^{-4}$	$25 \cdot 10^{-5}$
$\beta(E)$, s^{-1}	$63 \cdot 10^{-5}$	0.01	1.72	3.45	8.5	50	106	$7 \cdot 10^{-3}$	2500	$14 \cdot 10^3$

The slope being a bit higher than the predicted slope of the last area of the plot of polarization can be caused by the quadratic electrooptic effect. This explanation is confirmed by the fact, that for different samples this area of the plot has a little bit different slope. It is connected with the one of the three components of the relative increase $\Delta I/I$, which follows from (1) and depends on the difference in the optical beam path in the sample:

$$-\cot \frac{\pi d(n_2 - n_3)}{\lambda} \left\{ \frac{\pi d}{\lambda} \cdot \frac{n^3}{2} (R_{2211} - R_{3311}) \cdot E_1^2 \right\}.$$

Thus, at least in the strong fields, the polarization of RS crystals is connected not only with the change of twin areas relationship but with the change of the angle of monoclinity of the separate component of the twins over the value, typical of the present temperature.

Using a single voltage pulses with a large period of repetition we exclude the link of the observed effects with heating of the sample. Moreover, the heating may lead to the opposite changes of the light beam intensity.

The presence of two linear areas (figure 3) indicates that there exist two critical fields: the first – coercive E_c, at which there appears a massive domain motion, and the second – saturation field E_s, a field, in which the small domain disappears. The second field, first of all, produces an effect on the precision of the measurement of spontaneous polarization and the related values.

It is shown that the time dependence of the array of the increasing twin component S_l is described by the equation

$$S_l = S\left[1 - \exp\{-\beta(E)t\}\right], \qquad (4)$$

where E – electric field strength; t – polarization time, and $\beta(E)$ – depends sharply on the field strength, time and temperature. Information about its field dependence is given in table 1, where only those pairs E and τ_i are presented, to which there corresponds practically the same polarization state (equal value of the index of exponent). Theoretical papers predict exponential dependence of polarization rate on E^{-1}. As it is seen from figure 4, such a dependence can be presented by three linear areas, described by the following relations

$$\ln \tau_i = k E_i^{-1} + b_i\,.$$

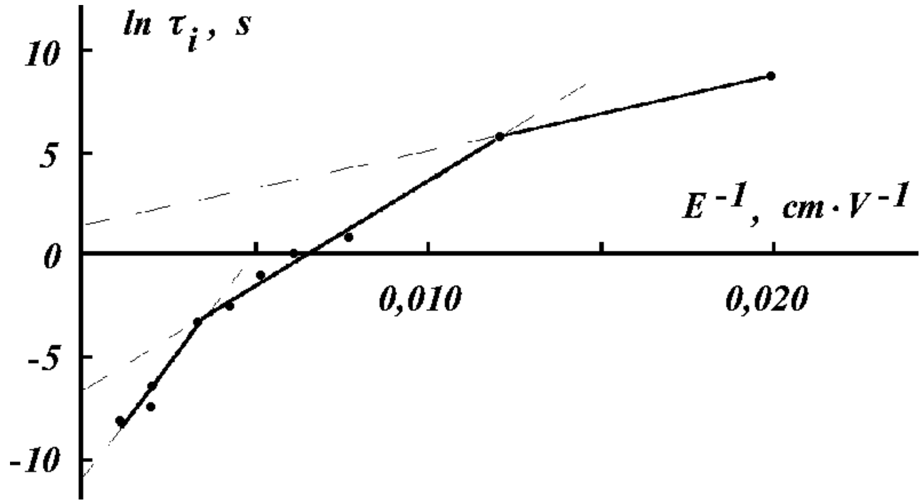

Figure 4. The relation between the duration and the amplitude of the pulses, capable of providing the same polarization level of the sample.

The numerical values of the constants are: $k = 371$ V/cm, $b = 1.43$ ($E > 500$ V/cm; $k = 1046.9$ V/cm, $b = -6.78$ ($500 > E > 190$ V/cm), and $k = 2238.2$ V/cm, $b = -11.0$ (for $E < 190$ V/cm). These data are consistent with the number of areas, predicted in [13], and with the field dependence of the number of new polarity domain nuclei [2,3]. There is a correlation of coefficients k for weak and middle fields as well. Logarithmic time dependences are also obtained during the investigations of ageing of the triglycine sulphate group crystals [14].

4. Stability of the polarized state

The direct observations of the domains showed that the stability of the polarized state depends on the initial geometry of domain structure and the regime of the sample's polarization [11]. It is shown, that the polarized state easily decays when small domains of new polarity, areas of joint b- and c-domains and mechanical defects are present. Apart from visible changes of the domain structure, which are registered by microphotographs, or by photocurrent (figure 5), during the polarization of the sample, some invisible changes take place, probably – of the defect network, and the internal fields associated with them. Just this can explain the dependence of stability of monodomain state upon the polarization pulse duration and the value of the electric field.

Actually, it was shown that at the same polarization level after the end of the polarizing pulse, the polarization decays more quickly if it had been created by a more short voltage pulse.

At a given temperature, the initial rate of decay of the induced, not-fully polarized state, depends on the level of deformation of the initial domain structure, and is defined by the following relations (figure 6):

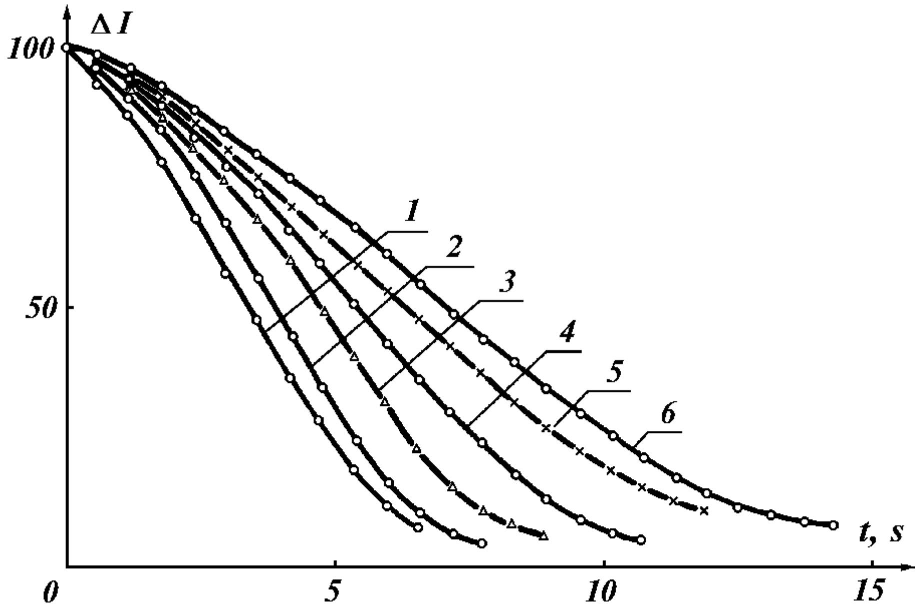

Figure 5. Examples of spontaneous decay of the monodomain RS crystals state after the end of the polarizing pulse for different polarizing pulse durations: 1 – 0.04 s, 2 – 0.34 s, 3 – 2.4 s, 4 – 10 s, 5 – 40 s, 6 – 80 s. Measured at $E = 300$ V/cm, $T = 16$ °C.

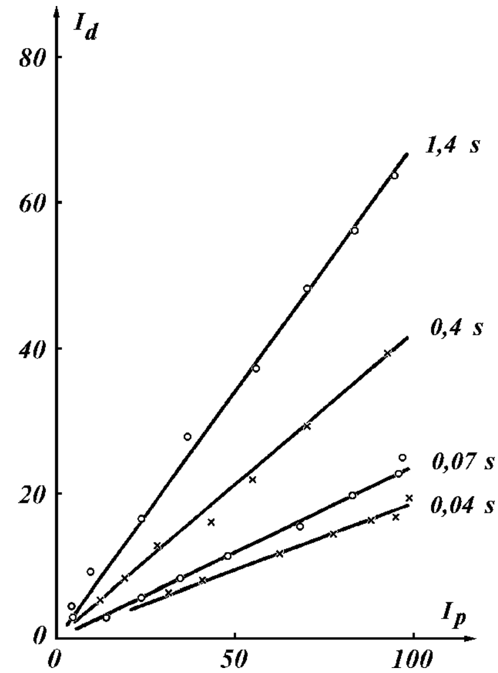

Figure 6. The dependence of the spontaneous polarization decay I_d on I_p. The decay is registered in 0.06 s after the end of the polarizing pulse. The duration times of polarization processes are placed near the corresponding plots

$$\left\{ \begin{array}{l} I_d = k(I_p - I_0), \\ I_d \sim 1 - \exp\{\beta(t) \cdot t\}, \\ \alpha = b - A \ln \tau_i \, . \end{array} \right\}$$

Here I_0 corresponds to the initial state of the domain structure, I_p – to polarized state, A and b – some constants. Thus, here the forces act, which are similar to quasi-elastic, and initial and final stages differ from linearity.

Repolarization under the effect of internal fields has a different time dependence than the polarization, caused by an external field. Time constant of this process is a function of the logarithm of polarizing pulse duration τ_i at a constant field, or a function of the logarithm of electric field – when τ is constant (figure 7). That is, already at polarization pulse duration $10^{-2} \ldots 10^{2}$ s, the dependence of stability of polarized state from polarization pulse duration is displayed.

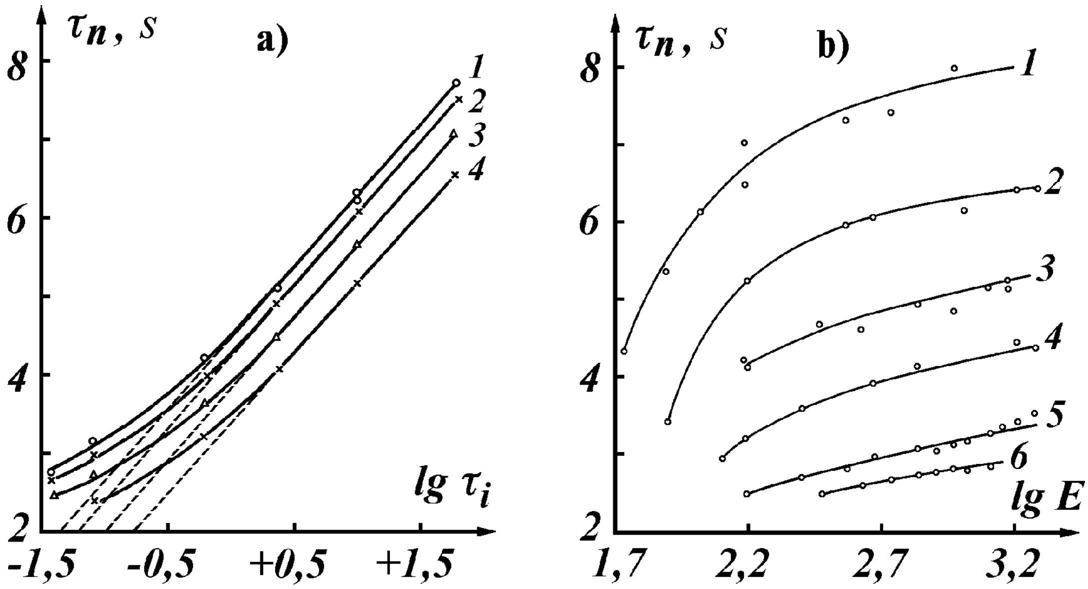

Figure 7. The dependence of the time of the half-decay of polarization τ_p from (1 – 1250 V/cm, 2 – 700 V/cm, 3 – 300 V/cm, 4 – 156 V/cm) the pulse duration τ_i, and (1 – 60 s, 2 – 10 s, 3 – 2.4 s, 4 – 0.63 s, 5 – 0.08 s, 6 – 0.04 s) electric field strength amplitude E. Measured at 16 °C.

Considering the time constant $\beta(t)$ as a function of time, we can come to a conclusion about the time changes of the defect structure of the crystal and the related internal fields.

A strong field at small τ_i, changes mainly the domains, while a network of defects, being more stable and inertial, remains practically unchanged. That is why we have a fast decay of the polarized state (domains adjustment to the old defect fields).

If the weak field during the short pulses does not change noticeably, neither the domains, nor the defects network, then in the initial moment the decay is fast as well (but the general changes are small, and are difficult to be registered).

With the growing of the polarization time, both the domains and the defects are changed. That is why the stability of the new polarized state increases, and after the monodomainization of the sample only the defects suffer some changes, and the stability of their new configuration grows.

The internal field is revealed more distinctly in the crystals with the specially introduced defects (doped and irradiated crystals). Here it is worthy to distinguish such special features as:

1. Just after irradiation, and even more – after the repolarization cycle – domain walls in the RS crystals are not distinct. They become distinct after 10–20 minutes, that is an evidence of slowdown of relaxation processes.

2. The coercive field depends on the irradiation dose, and on the time of ageing of the sample. After keeping a sample of RS with defects in the monodomain

state it can increase in dozens of times, unlike a pure sample, where the same procedure gives the increase of the coercive field in 2–3 times only.

3. If the sample is irradiated in a paraelectric phase, or during the process of repolarization of the irradiated crystals, the trapping of the rhombic areas in monoclinic phase is possible, which creates an unstable phase. This phase is capable of being polarized by the field of any sign, and looks like the mechanism of repolarization of KDP crystals [17].

4. On the defect samples of RS unipolar and double hysteresis loops are observed, the separation fields are displayed more distinctly, at which the domain motion starts to be noticeable.

5. Conclusions

Thus, polarization of the RS crystals, except the known processes of nucleation and growth of the domains of new polarity, is also connected with the slow displacement of small components of twins, which is finished at some characteristic field. When the electric field and polarization time increase, the deformation of domains takes place, and the change of the sample's defects network corresponding to the relations $\ln\tau \sim k/E + b$. This dependence is the evidence of the diffusive nature of the related processes [18].

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Про кінцеві стадії поляризації та стійкість поляризованого стану кристалів сегнетової солі

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На основі прямого спостереження доменів кристалів сегнетової солі досліджено прикінцеві стадії поляризації та залежність стійкості поляризованого стану від напруженості поля і тривалості імпульса.

Зроблено висновок, що існує високе поле витіснення дрібних доменів, після чого явно проявляються електрооптичні ефекти та зазнає змін невидима сітка дефектів.

Стійкість поляризованого стану та ступінь поляризації визначаються імпульсами поля, тривалість τ і напруженість E якого пов’язані співвідношенням $\ln\tau \sim k/E + b$. При неповній поляризації зразка втрата останньої при знятті поля пропорційна до відхилення доменів від вихідного стану зразка.

Ключові слова: *домени, поляризація, стійкість поляризованого стану, дефекти*

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