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Abstract
It has been shown that the hysteresis loop of the uniaxial triglycine selenate ferroelectric can be gradually suppressed in an inhomogeneous electric field not parallel to the ferroelectric axis. Such a field was generated by a constant electric potential applied to silver paste measurement electrodes painted on a single-crystal sample of the form of a small round plate with an additionally attached grounded silver side (ring) electrode. No changes in the coercive field were visible during the remanent polarization decay over time. A reduction of remanent polarization persisted for many days after disconnecting the inhomogeneous electric field if no alternating electric field was applied. The original dielectric properties could be easily restored by annealing the sample above the critical temperature. The mathematical formula for the remanent polarization decay in time is discussed.

1. Introduction

As is well known, the electric polarization of a ferroelectric crystal placed in an alternating electric field parallel to the polar axis exhibits a hysteresis loop. If such a crystal is simultaneously exposed to a constant electric field also parallel to this axis, the hysteresis loop is shifted in the horizontal direction. This has been a very well-known experimental fact for years. On the other hand, the influence of an electric field perpendicular to the ferroelectric axis on dielectric properties of such popular uniaxial ferroelectrics as triglycine sulfate $((NH_2CH_2COOH)_3H_2SO_4$, also abbreviated as TGS) and the Rochelle salt $(KNaC_4H_4O_6) \cdot 4H_2O)$ has been observed quite recently ([1–8] and cited therein). As became evident, a prolonged action of the transverse electric field leads to a gradual disappearance of the remanent polarization. What is more, such a reduction can persist after disconnecting this field. However, due to the requirements regarding the sample shape it is rather inconvenient to investigate the influence of a field not parallel to the ferroelectric axis. It was supposed that only the perpendicular parallelepiped form of the crystals could be used in this case.

It has been shown in the present paper that the remanent polarization can be permanently reduced also in crystal plates, used for years in classic dielectric measurements, provided a special electrode configuration is used. The ferroelectric triglycine selenate crystal $((NH_2CH_2COOH)_3H_2SeO_4$, abbreviated as TGSe) was chosen as a sample. Its transition to the ferroelectric phase occurs at $T_C = 22.4 \pm 0.1\,°C$.

2. Experiment

Figure 1 presents the sample, of width $w = 1.4$ mm and diameter 3.6 mm. Three silver paste electrodes are attached to the crystal. The same constant electric potential $V_C = 500$ V could be applied to both circular measurement electrodes (perpendicular to the ferroelectric b-axis and placed in the centre of the plate surface), each 2 mm (± 0.1 mm) in diameter. Since two blocking capacitors, each of 2 μF, were connected to the circuit, the hysteresis loops could be measured simultaneously by means of the Sawyer–Tower method [9, 10]. An alternating voltage applied between the points A and B was the source of the driving (measuring) electric field $E = E_0 \sin(2\pi f_m t)$ of the frequency $f_m = 100$ Hz. The application of such a field led to a periodic reorientation of dipoles in the sample. The relation between the polarization P and the field E (the hysteresis loop) could be then investigated. In figure 1 one can see also a side electrode painted around the circular sample. Its potential was equal to zero (the grounded electrode). The power supply and two resistors used in the experiment have been also shown schematically in figure 1. All the elements presented in this figure were treated together as a 'sample' connected at points A and B to the typical Sawyer–Tower circuit.
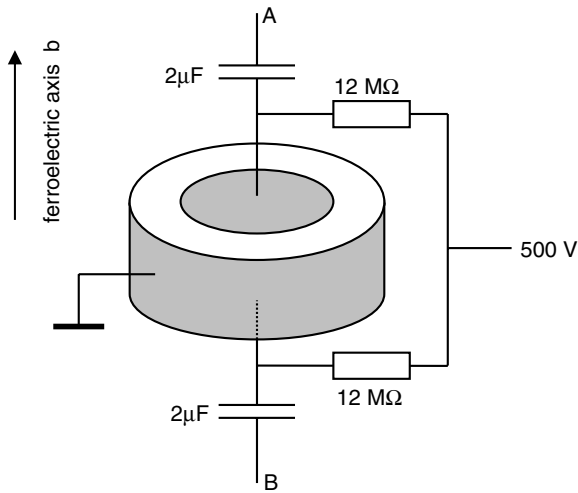
Figure 1. The crystal with electrodes (grey), two blocking capacitors and two resistors as a 'sample' investigated by means of the Sawyer–Tower method.
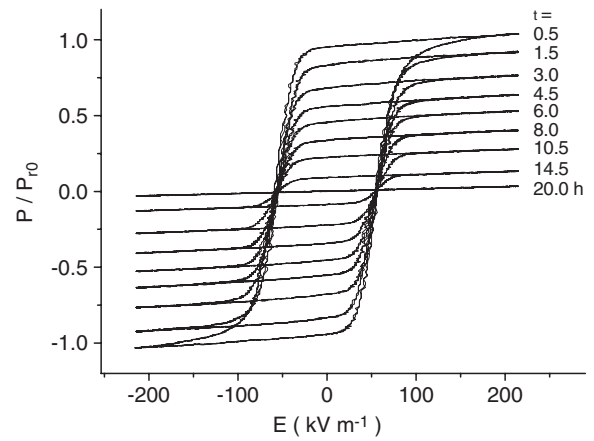

Figure 2. Hysteresis loop suppression with time in an inhomogeneous electric field not parallel to the ferroelectric axis generated by the electric potential $V_C = 500$ V; the given successive times correspond to the hysteresis loops drawn from top to bottom.

3. Results

Figure 2 depicts some hysteresis loops measured at different times after switching on the potential $V_C = 500$ V. The amplitude E_0 of the sinusoidal driving electric field E (continuously applied during the V_C application) was always equal to 214 kV m^{-1} ($= 300/W$). The measurements were carried out at the temperature $T = 19.5\,°C$. The parameter P_{r0} is the numerically fitted value of $P_r(0)$, as presented below. It should be stressed that the gradual suppression of the hysteresis loop is not accompanied by any changes in the coercive field. Figure 3 shows the time dependence of the remanent polarization $P_r(t)$ when the potential V_C and the driving field are simultaneously applied. The empirical formula for the $P_r(t)/P_r(0)$ ratio can be written as follows:

$$\frac{P_r(t)}{P_r(0)} = \frac{t_0 - t}{t_0} \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where the numerically fitted parameters are $t_0 = 19.4 \pm 0.2$ h and $\tau = 14.1 \pm 0.3$ h. Only the experimental points obtained at $V_C = 500$ V (solid circles) have been taken into account during the fitting procedure. The value of the parameter $P_r(0)$ is not given because it could possibly contain an experimental error connected with the geometry of the sample–electrode system. Such an error is reduced if the ratios $P_r(t)/P_r(0)$ or $P/P_r(0)$ are considered. One can easily see that the dependence shown in figure 3 is not simple exponential decay over time. Apparently, we deal here with a more complex molecular mechanism of a gradual suppression of polarization. A prolonged voltage application between the measurement electrodes and the side one leads to a freezing of dipoles that cannot be reversed any longer in the alternating field. It should be pointed out that the crystal does not have to be transversely polarized as a whole then, contrary to what might be inferred from previous papers (e.g. [6]).

Between the times $t_1 = 20$ h and $t_2 = 25$ h (figure 3), no electric field was applied to the sample. No remanent
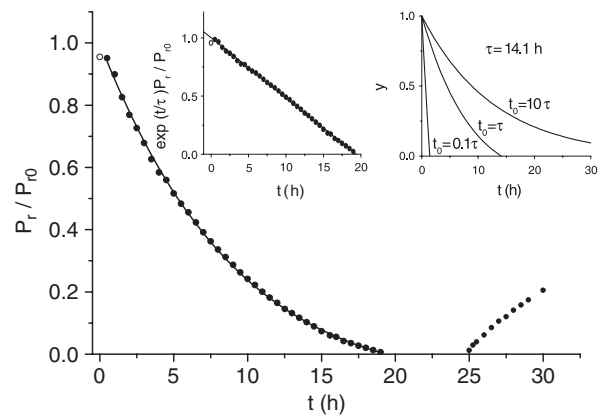

Figure 3. Remanent polarization decay over time for $V_C = 500$ V (the driving electric field applied continuously), for five hours without any electric field and the first hours of rejuvenation only in the driving electric field, at the constant temperature $T = 19.5\,°C$; the solid line is the numerical fit of equation (1); insets: the linear factor as a function of time (with the solid line as a linear fit) and three theoretical dependences (equation (1)) each for $\tau = 14.1$ h and for $t_0 = 0.1\tau$, τ and 10τ, drawn for $y > 0$.

polarization was measured then, either. For $t > t_2$ the crystal was exposed only to the alternating electric field (driving electric field, the same as for $t < t_0$). The first hours of this rejuvenation process at $V_C = 0$ are presented in the diagram.

4. Discussion

The relation (1) has been chosen as the best empirical formula from among different functions containing both power and exponential dependences. It is worth stressing that the function (1) is the solution of a differential equation, known for the critically damped harmonic oscillator:

$$\frac{d^2 y}{dt^2} + \frac{2}{\tau}\frac{dy}{dt} + \frac{1}{\tau^2}y = 0 \tag{2}$$

for $y = P_r(t)/P_{r0} > 0$, $P_{r0} = P_r(0)$, $y(0) = 1$ and $dy/dt|_{t=0} = -(\tau^{-1} + t_0^{-1})$. Negative values of y do not seem to have any physical meaning. However, a negative derivative dy/dt at $t = t_0$ means that after the change of voltage sign from $+500$ to -500 V the remanent polarization initially increases, then reaches an extremum and finally tends to the zero value.

Two mechanisms of the polarization decay over time can be considered from the phenomenological point of view. One of them, characterized by the time τ, seems to be connected with inherent chemical and structural properties of the crystal. During the application of the inhomogeneous electric field more and more nuclei of frozen molecule groups are appearing in the sample. This means that the number of active (being repolarized) dipoles decreases exponentially with the relaxation time τ. On the other hand, one can imagine the nuclei to grow linearly with time at a rate proportional to t_0^{-1}. The parameter t_0 seems to be connected to the actual domain structure and therefore may vary from sample to sample. The domain structure observation followed by dielectric measurements of the same sample could help us to answer the question of to what extent such a correlation exists. In the inset of figure 3 the linear factor has been separated from the time dependence (1). Crystals with $t_0 \ll \tau$ can be frozen relatively easily, almost linearly with time. On the other hand, the relation $t_0 \gg \tau$ means that the sample exhibits 'almost' exponential remanent polarization decay over time in a field not parallel to the ferroelectric axis. The second inset of figure 3 shows three time dependences of y calculated from the formula (1) for the common value of $\tau = 14,1$ h and $t_0 = 0.1\tau$, τ and 10τ.

Although the results obtained with the electrode–sample system shown in figure 1 have not yet been published, there are some other examples of how the transverse electric field operates. There is every indication that in these cases some parameters analogous to t_0 and τ can also be considered while interpreting the experimental data. For triglycine sulfate, probably due to different values of t_0, more or less 'pure' exponential decay over time was observed [6, 7]. As follows from the experimental results [7, 11], both t_0 and τ are expected to depend on temperature and on the strength of the electric field not parallel to the ferroelectric axis. The temperature dependence of t_0 and τ (for a sample of the shape of a perpendicular parallelepiped) was investigated for the ferroelectric Rochelle salt [10]. The examples mentioned above suggest that it is also in triglycine selenate that the parameters t_0 and τ should depend on temperature. In particular, they are expected to become smaller and smaller when the temperature tends to the critical point. For the required 'degree of freezing' of the crystal decreases with rising temperature (below T_c).

It is not the aim of this paper to explain the effect of hysteresis loop disappearance from the microscopic point of view. One can mention here only a possibility of reorientation of dipoles and their transition to metastable states, domain structure rearrangement and freezing as well as free electric charge injection as potential origins of the suppression of remanent polarization. The linear contribution to the time dependence of y may be a result of an elongation of stripe-like rigid domains in the c-direction observed in the transverse electric field in triglycine sulfate [3, 6, 8]. The spontaneous polarization decay over time presented in [7] does not have the exponential form and can probably be described by a modified formula (1):

$$y = \frac{t_0 - t}{t_0} \exp\left[-\left(\frac{t}{\tau}\right)^n\right] \qquad (3)$$

where the exponent $n > 1$ give a rounding in the $P_r(t)$ dependence for short times [7]. A similar effect was sometimes observed for TGSe during the first few hours of the V_C potential application and could be interpreted as the first and rather unpredictable reaction of the domain structure to the transverse field application. In figure 3 of the present paper only one point—but the one measured just before the application of voltage V_C—lies beyond the dependence $P_r(t)$.

The suppression of the hysteresis loop shown in figure 2 is permanent if, after disconnecting the potential V_C, the sample is kept in a zero electric field and if the crystal is not heated. The remanent polarization reduction by not less than 99.7% could be observed at zero electric field for a few days (the observation was continued for five days) after a previous exposure of the sample to the same fields as those described in section 3 (i.e. $V_C = 500$ V, $E_0 = 214$ kV m^{-1}, $f_m = 100$ Hz) for 48 h at the temperature 16.4 °C.

It is an interesting experimental fact that no changes in the coercive field are observed during the remanent polarization decay over time. This means that the mechanism of the hysteresis loop reduction should preferably be considered from the macroscopic point of view. In fact, although the crystal is gradually frozen in the transverse field, there must still exist relatively large (macroscopic) active regions which give rise to polarization. They are supposed to behave as ferroelectric domains, with the remanent polarization and the coercive field equal to those for the original sample. On the other hand, more and more frozen regions are growing here and there in the crystal and spread in the 'ferroelectric sea'. Due to such gradual freezing, the number of active dipoles decreases with time but the remaining ones are still being repolarized collectively like in the original sample. Consequently, only the measured remanent polarization decreases. No changes in the coercive field are then expected unless almost all frozen domains become large enough to merge (after a sufficiently long time of transverse field action). This probably takes place only when the remanent polarization is too small to be measured with reasonable accuracy.

There are two methods of restoring the original dielectric properties: a prolonged application of the Sawyer–Tower-type driving electric field and a much more effective method, i.e. an annealing above the critical temperature (cf [2]).

Thanks to a possibility of determining theoretically the inhomogeneous electric field space distribution inside the crystal, the cylindrical symmetry of the sample–electrode–voltage arrangement shown in figure 1 seems to be suitable for investigations into the influence of an electric field not parallel to the ferroelectric axis on dielectric properties of uniaxial ferroelectrics. A possibility of programming different values of the remanent polarization by adjusting E and V_C

in a small cylindrical plate with three electrodes, without any change in the coercive field, appears to be interesting for various practical applications. It is worth stressing that the blocking capacitors might not be required if the constant potential V_C were applied to the side electrode rather than to the measurement ones.

5. Conclusions

Summing up the results shown in the present paper one can state that:

(1) A suppression of the hysteresis loop in a prolonged electric field not parallel to the ferroelectric axis takes place in the triglycine selenate ferroelectric.
(2) The effect can be easily observed in a single-crystal plate with two conventional measurement electrodes and an additional side one; a perpendicular parallelepiped shape of the sample is not required.
(3) The value of the remanent polarization can be adjusted by means of a voltage between the measurement and side electrodes; no changes in the coercive field value are observed then.
(4) Two molecular mechanisms, characterized by the times t_0 and τ, are responsible for the suppression of the hysteresis loop in the transverse electric field.

(5) The cylindrical symmetry of the sample–electrode system will be very useful when comparing experimental and theoretical results.

Acknowledgments

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