Features of the Manifestation of Surface Electrochemical Processes in Ferroelectric Crystals with Low-Temperature Phase Transitions

N. S. Kozlova*, E. V. Zabelina*, M. B. Bykova*, and A. P. Kozlova*

*National University of Science and Technology MISIS, Moscow, 119049 Russia

*e-mail: kozlova_nina@mail.ru

Received January 16, 2019

Abstract—The short-circuit current flow in crystals with the low-temperature phase transitions including Rochelle salt NaKC₄H₄O₆ · 4H₂O and triglycine sulfate (CH₂ · NH₂ · COOH)₃ · H₂SO₄ is investigated. The experiments are conducted on polar cut samples without preliminary polarization with the symmetric indium conducting coatings. The short-circuit currents remaining for a fairly long time and the current decay with time are observed at room temperature on all the samples. The temperature dependences of the short-circuit currents in the temperature ranges of 16 to 45°C for Rochelle salt and 16–110°C for triglycine sulfate are obtained. The short-circuit currents are observed in these crystals both in the ferroelectric and paraphase. It is shown that, upon heating in the ferroelectric phase, the total short-circuit current is determined by competing processes: the pyroelectric currents and electrochemical decomposition currents. In the paraphase, the short-circuit currents are the electrochemical self-decomposition currents. Based on the experimental results obtained, it is demonstrated that the short-circuit current flow through the polar cut samples of Rochelle salt and triglycine sulfate crystals is induced by the intrinsic emf caused by the electrochemical self-decomposition of the opposite surfaces of the sample polar cuts when in contact with the conducting coatings due to the anisotropy of these surfaces. A model of the electrochemical self-decomposition in such crystals is proposed.

Keywords: polar classes, ferroelectrics, triglycine sulfate, Rochelle salt, low-temperature ferroelectric phase transition, pyroelectric effect, short-circuit currents

DOI: 10.1134/S1063739719080092

INTRODUCTION

Ferroelectric crystals are widely used in various fields of high-technology production due to the piezoelectric and pyroelectric effects and nonlinear optical properties. These crystals should have stable characteristics throughout the life of the device. The operational stability of the crystals is determined by their nonequilibrium state.

The nonequilibrium state can be caused by the properties of a crystal itself and its prehistory or under the influence of external factors, including electric fields, high temperatures, and pump radiation. It was established [1–6], however, that some processes determining the changes in the crystals can occur without external factors. An example is the formation of conducting coatings on the polar cut surface, which can induce short-circuit currents (SCCs). The SCCs in polar materials were observed by many authors [3–6]. In particular, in [3], an emf ranging from several tenths of a volt to several volts was detected on the polar cut of a KLiSO₄ crystal belonging to the polar class (sp. gr. P6₃) with silver conducting coatings, which gave rise to SCCs without preliminary polarization. The temperature investigations of the SCCs in the KLiSO₄ crystals revealed the nonmonotonic temperature dependence with sharp peaks and jumps near the temperature of the phase transformation of this crystal. In other materials with the polar class symmetry, SCCs of about 10⁻¹³ A were detected [4–6] without preliminary external effects.

It is well known [7] that, in solid dielectrics, SCCs can be induced using the preliminary stimulating thermo-, photo-, electro-, and piezoeffects; after that, the symmetric (identical) conducting coatings are deposited onto the surface of materials. This underlies the current relaxation thermoactivation spectroscopy technique for studying the properties of high-resistance dielectrics. A crystal sample with symmetric conducting coatings deposited onto its opposite surfaces can be considered as a galvanic or electrochemical M/M₁/E/M₁/M cell, where M is the material of the pressure electrodes, M₁ is the conducting coating material, and E is the solid electrolyte. In such an electrochemical cell with a solid electrolyte, the SCCs can only be caused by preliminary stimulating effects [7]. The SCCs without preliminary stimulation of dielectric samples can be observed when asymmetric conductive coatings are deposited onto their surface [8]. In this case, the SCCs are induced by the difference
between the oxidizing or reducing electrochemical processes at the contact of the dielectric surface with different conducting coating materials.

In [3–6], SCCs were observed on the samples with symmetric electrodes without preliminary polarization, which does not correspond to any of the conventional models [7, 8]. Several explanations of the origin of these phenomena were proposed [3–6]:

(i) **Background currents.** In [3], the occurrence of the SCC is explained mainly by the sample’s inhomogeneity and the nonuniformity of the space charge distribution over the crystal surfaces. This induces the emf; therefore, the SCC, assumed by the authors to be the background SCC, was detected.

(ii) **Pyrocurrents.** Since SCCs were observed in the temperature regions before the phase transitions (PTs), i.e., in the ferroelectric phase, the total electric response of the samples can be caused by the total pyroelectric component \( I_\text{p} \) and currents of different origins. In the order–disorder-type ferroelectric crystals, e.g., Rochelle salt and triglycine sulfate (TGS), the residual pyrocurrents remain in the paraphase due to the presence of residual domains in it [9].

(iii) **Currents of different origins.** These can be the currents caused by the structure of the material and chemical bonds [9, 10]. The occurrence of the currents in ferroelectric crystals with complex composition, which contain bound crystallization water or hydrogen bonds, for example, TGS and Rochelle salt, upon variation in the external conditions, in particular, with increasing temperature, changes the state of hydrogen bonds, which leads to a change in the electrical parameters of the crystals [10].

(iv) **Effects of other forces** [11]. Thus, the observed currents can be induced by various, including competing, processes. However, the proposed explanations are incomplete. The identification of the processes leading to the occurrence of SCCs and determining their origin and orders in ferroelectric crystals can be fundamentally important due to the high intensity of some effects [12–18].

For the first time, in the \( \alpha \)-LiIO\(_3\) lithium iodate polar crystals of a hexagonal modification (point symmetry group 6), SCCs of about \( \times 10^{-12} \)–\( 10^{-8} \) A were detected together with the intrinsic emf, which induces a weak electric field of about ten millivolts generating these currents [1, 2]. The observed processes were thoroughly investigated to identify their origin. On the surface of the samples without preliminary stimulations, symmetric conducting coatings were formed. After closing the circuit, the current decayed with time to a stationary value according to the law [19]

\[
I = I_0 \left( \frac{t}{t_0} \right)^{-\alpha}, \tag{1}
\]

where \( \alpha \) is the characteristic coefficient, \( I_0 \) is the initial current detected upon connecting to the circuit, and \( I \) is the steady-state current, which took a constant value in time \( t \).

The orientation dependence of the SCC was established: the current was not observed in the samples cut parallel to the polar (6th-order) axis and was pronounced in the samples cut perpendicular to it. SCCs were observed for any conducting coating materials used. The steady-state value was independent of the sample thickness; its value and flow direction depended on the conducting coating material. This indicates that the observed SCCs are caused by the near-electrode processes.

Next, the temperature dependences of the SCCs were examined. It was found that they are nonmonotonic with pronounced peaks, the position of which is independent of the conductive coating material used. The material of the conducting coatings significantly affects the SCCs’ value and flow direction. The X-ray photoelectron spectroscopy study of the surface state before, during, and after the temperature tests of the SCCs revealed different phase states of the surfaces. It was shown that the same processes occur on both surfaces but at different rates. The \( \alpha \)-LiIO\(_3\) anisotropy, which leads to the anisotropy of the chemical reaction rates, gives rise to SCCs. It was established that, in these crystals, the SCCs have an electrochemical nature and are explained by the electrochemical decomposition of the crystal; i.e., these are the electrochemical self-decomposition currents \( I_\text{ESC} \). The electrochemical self-decomposition currents can significantly contribute to fixed SCCs. This effect was also detected at room temperature \( T_\text{room} \) in other polar- and polar neutral-classes (CH\(_2\) · NH\(_2\) · COOH)\(_3\) · H\(_2\)SO\(_4\), Ba\(_2\)Na\(_2\)Nb\(_2\)O\(_{15}\), KH\(_2\)PO\(_4\), NaK\(_2\)H\(_4\)O\(_6\) · 4H\(_2\)O (Rochelle salt), LiNbO\(_3\), and LiTaO\(_3\) crystals on the samples cut perpendicular to the polar axes. However, we did not study such processes on these crystals in detail; the published data were not found. In the crystals that do not belong to the polar classes (CaCO\(_3\), KCl), the SCCs were not observed [1, 2].

Thus, the phenomenon of the electrochemical self-decomposition of the polar cuts of the dielectric crystals, which is caused by different electrochemical activities of the opposite sample surfaces perpendicular to the polar axis was established for the first time [1, 2, 20].

This effect is of fundamental importance for the physics of dielectrics and the electrochemistry of solid electrolytes and studying the phase transitions in the materials [21, 22]; in addition, it is important for application. The SCCs caused by the near-electrode processes should be taken into account, since they can significantly contribute to the total electric response.

This phenomenon was studied in sufficient detail for the new functional material \( \text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14} \) lanthanum gallium tantalate (point symmetry group 32), the polar cuts of which are used in high-temperature sensors based on the direct piezoelectric effect [23–25].

These processes in ferroelectrics with the low-temperature phase transitions, including Rochelle salt
NaKC₄H₄O₆ · 4H₂O and triglycine sulfate (CH₂NH₂COOH)₃ · H₂SO₄ (TGS) crystals, are of particular interest. The characteristics of these crystals are given in Table 1.

Rochelle salt and TGS undergo type-II ferroelectric phase transitions. The TGS crystal is in the ferroelectric phase at temperatures below 49°C and the Rochelle salt ferroelectric phase is limited by the temperature range from –18 to +24°C. In the ferroelectric phase, both crystals are unipolar ferroelectrics.

The aim of the study was to investigate the SCCs and their temperature dependences in Rochelle salt and TGS crystals in the temperature ranges including the temperatures of ferroelectric phase transitions.

**EXPERIMENTAL**

The experiments were conducted on the TGS and Rochelle salt crystal samples in the form of plane-parallel plates cut perpendicular to the polar axis [010]; the indium foil used for forming electrode coatings was deposited onto the sample surface at room temperature. The samples were not subjected to preliminary polarization or other stimulating effects.

The SCCs were studied by current spectroscopy [7, 8, 11] using an IMT-05 low-current meter, which allows currents of any polarity in the range from 10⁻¹⁴ to 10⁻⁶ A to be measured with an error of not more than ±1.5%. The samples were placed between two identical steel pressure electrodes of a crystal holder according to the sample polarity and installed in a heat chamber at room temperature. The test consisted of two stages.

*Stage I. Room temperature investigations.* The first stage consists in measuring currents of a short-circuited sample at T = 16°C without a voltage source in the circuit, except for the crystal itself. In this measurement, the sample is not heated and the voltage is not applied. The samples are kept in this mode until the stationary SCC value is established.

*Stage II. Heating.* The linear heating of the samples was performed to a temperature above the phase transition temperature at a rate of 1.5°C/min using a temperature-control heater supply system. The SCC measurements upon heating the sample are illustrated in Fig. 1. The SCCs are detected during the entire heating process.

| Crystal                          | Space and point symmetry groups | Polar axis | T_{PT}, °C | T_{d*}, °C |
|----------------------------------|---------------------------------|-----------|------------|------------|
| Rochelle salt NaKC₄H₄O₆ · 4H₂O | P₂₁ and 2                       | [010]     | –18; +24   | 55         |
| Triglycine sulfate (CH₂NH₂COOH)₃ · H₂SO₄ (TGS) | P₂₁ and 2                       | [010]     | 49         | 150        |

* T_{d} is the crystal decomposition temperature.

After placing the samples in a crystal holder, the current sharply decreased with time and then took a stationary value, which remained constant for a fairly long time. The SCC decay with time (Fig. 2) demonstrates a characteristic relaxation dependence, which can be divided into three regions: the rapid current decay, which takes several minutes; the transition process; and the current saturation process, for an unknown time period. Figure 2 shows that the current value before attaining the stationary value changes by two orders of magnitude for both the TGS and Rochelle salt crystals (from 10⁻¹¹ to 10⁻¹³ A and from 10⁻¹² to 10⁻¹⁴ A, respectively). In the repeated measurements, the time dependence of the current is not repeated.

**Temperature Dependences of the SCC for Rochelle Salt**

The Rochelle salt samples were heated twice from 16 to 45°C; the temperature dependences of the SCCs for Rochelle salt are presented in Fig. 3. Upon first heating (Fig. 3a), the initial stationary SCC value was 4 × 10⁻¹⁴ A. During heating at T = 18°C, the current changed its direction and its value sharply increased to
that observed during the initial heating; the current continues growing to \(10^{-13}\) A up to \(45^\circ\text{C}\). The differences are observed also in the cooling zone. First of all, the current during the repeated experiments in the cooling region exceeds the current in the cooling region during the initial heating by a factor of about 1.5 and amounts to \(10^{-13}\) A. Then, near \(T\approx40^\circ\text{C}\), the current decreases to \(5 \times 10^{-14}\) A. As the temperature decreases to \(30^\circ\text{C}\), the current returns to a value of \(10^{-13}\) A and remains unchanged up to \(20^\circ\text{C}\). After that, it decreases monotonically.

It is worth noting that the current is maintained throughout the heating interval both in the ferroelectric and paraphase. The currents observed in the ferroelectric and paraphases of the Rochelle salt crystals can be explained as follows. In the temperature region before the phase transition, in the ferroelectric phase, the observed currents are determined, first of all, by the pyroelectric effect and the resulting pyrocurrents \(I_p\) (Table 2) comparable with the experimentally detected current values.

However, the observed SCC values do not completely coincide with the values of the pyrocurrents and, depending on the temperature range, they either exceed them by an order of magnitude or are lower by an order of magnitude. Thus, the SCCs observed in the ferroelectric phase cannot be caused by the pyrocurrents only. In the paraphase region, residual pyrocurrents can be observed but their value should be lower than in the ferroelectric phase. Since the process occurs in a natural mode and the cooling rate is nonlinear, then, at the decisive contribution of the pyrocurrents, the dependence of the SCC would be nonlinear; therefore, the contribution of the residual pyrocurrents in the paraphase is insignificant. The induced currents could be attributed to the rearrangements of the hydrogen bonds. Indeed, upon first heating, the temperature dependences of the SCC change sharply (the change in the direction of the current flow) at temperatures of 18 and \(37^\circ\text{C}\), i.e., close to the temperatures of the rearrangement of the hydrogen bonds (20 and \(36^\circ\text{C}\)). However, upon repeated heating, such changes are observed only at \(18^\circ\text{C}\), while upon cooling they are not observed at all. Consequently, the contribution of the rearrangements of the hydrogen bonds to the SCC can only be significant near \(20^\circ\text{C}\).

Thus, the main (decisive) contribution to the SCC should be made by other effects. Based on the results of the study of the near-electrode processes in lithium iodate crystals and the model from [1, 2, 20] explain-

### Table 2. Pyrocoefficients \(\gamma\), pyrocurrents \(I_p\), and SCCs for Rochelle salt and triglycine sulfate crystals

| Crystal                        | \(\gamma\), C/cm² K⁻¹ | \(I_p\), A | SCC, A          | References |
|-------------------------------|------------------------|------------|-----------------|------------|
| Rochelle salt NaKC₄H₆O₆ · 4H₂O | \(4 \times 10^{-10}\) | \(1 \times 10^{-11}\) | \(5 \times 10^{-12}–10^{-14}\) | [26]       |
| Triglycine sulfate (NH₂CH₂COOH)₃ · H₂SO₄ | \(4 \times 10^{-9}\) | \(1 \times 10^{-10}\) | \(1 \times 10^{-11}–10^{-13}\) | [27, 28]   |
ing these processes, we may state that this effect is the electrochemical decomposition at the interface between the crystal and conducting coating and the currents induced by it are $I_{ESC}$. Thus, it can be assumed that, in Rochelle salt with indium conducting coatings, two types of currents flow in the ferroelectric phase, pyrocurrents $I_p$ and electrochemical self-decomposition currents $I_{ESC}$, which can have different directions. When they are codirected, the resulting current exceeds the pyrocurrents and, when the currents are directed differently, the resulting current is weaker than the pyrocurrents. The occurrence of the SCC in the paraphase can also be explained based on the data on the lithium iodate crystals from [1, 2, 20] as follows. When the crystal polar cut sample is in the ferroelectric phase, even before its heating to the phase transition temperature, the state of the opposite sides of the polar cut is already different due to the anisotropy of their chemical potentials. When the conducting coatings are deposited onto these surfaces, decomposition products (new phases) can be released on them either in different amounts or different composi-

![Temperature dependences of the SCCs in the Rochelle salt: (a) first heating and (b) repeated heating.](image-url)
tions, which are retained in the paraphrase. This causes the presence of the SCCs in the paraphase, which are the electrochemical self-decomposition currents. However, Rochelle salt in the paraelectric phase belongs to the polar-neutral 222 class. In [23], the SCCs and their temperature dependences were studied on polar cuts of the lanthanum-gallium tantalate crystals belonging to the polar-neutral 32 class. The X-ray phase analysis showed that, on the opposite sides of the sample polar cuts coming into contact with the conducting coating, different products of the electrochemical reactions were formed, which induced the electrochemical SCCs. Similarly, in the surface regions of the Rochelle salt in the paraphase, either different electrochemical reactions or reactions at different rates can also occur; then, the SCCs are also $I_{ESC}$.

Thus, we may assume that, even in Rochelle salt with the indium conductive coatings, only the $I_{ESC}$ currents flow in the paraphase.

**Temperature Dependences of the SCCs in Triglycine Sulfate**

The TGS samples were heated to 80°C and reheated to 110°C. The temperature dependences of the SCCs in the TGS are shown in Fig. 4. The initial stationary SCC value was $4 \times 10^{-14}$ A. At the beginning of heating at $T = 18^\circ$C, the current value and direction changed sharply. At $T = 25^\circ$C, the current was $3 \times 10^{-11}$ A, which is comparable with the pyrocurrents $I_{p} = 10^{-11}$ A (Table 2). Further, upon heating, the current behaves monotonically and, at $T = 45^\circ$C, it is $I = 2 \times 10^{-11}$ A.

![Fig. 4. Temperature dependence of the SCC in the TTC crystal: (a) first heating and (b) repeated heating.](image-url)
Then, at the Curie point $T_{PT} = 49^\circ C$, the current passes through a sharp peak. At temperatures above $49^\circ C$, the current decreases; at $T = 60^\circ C$, it changes direction and monotonically increases to a heating temperature of $80^\circ C$. As for the Rochelle salt in the paraphase, the current is nonzero. Upon cooling after $60^\circ C$, the current sharply increases by two orders of magnitude to a maximum of $\sim 10^{-11} A$ in the region of the phase transition temperature and then sharply decreases again to $3 \times 10^{-14} A$. Upon cooling, the current monotonically decreased to room temperature to a value of $3 \times 10^{-14} A$, remaining almost constant. Reheating (Fig. 3b) to $110^\circ C$ did not drastically change the temperature dependence; however, after $T_c$, the current decreased less sharply and changed direction at $T \approx 70^\circ C$, taking a stationary value and retaining it up to $110^\circ C$. Upon cooling to $T \approx 75^\circ C$, the current remains stationary. The form of the dependence upon further cooling repeats its form in the initial experiment.

As in the Rochelle salt crystals, the currents in TGS are observed both in the ferroelectric and paraelectric phases. The rearrangement of the hydrogen bonds occurs at 20, 36, 50, 65, and 76°C [10]; however, if we identify these temperatures with the temperature dependences of the SCCs, we will see that the changes in them occur at $18^\circ C$, as in the Rochelle salt, and at 50°C; in TGS, we have $T_{PT} = 49^\circ C$. At other temperatures of the rearrangement of the hydrogen bonds, sharp transitions are not observed in the temperature dependences of the SCCs. Thus, at the beginning of heating in the region of 20°C, the observed currents are determined mainly by the electrochemical decomposition currents. Upon further heating to $T_{PT}$, the observed currents are the resulting currents $I_p$ and the electrochemical self-decomposition currents $I_{ECS}$. At temperatures above the temperature of the ferroelectric phase transition, the observed currents are only electrochemical ($I_{ECS}$).

**DISCUSSION**

The experiments above showed that in the Rochelle salt and TGS crystal samples without preliminary external effects with symmetric electrodes, SCCs are observed at room temperature and kept for a long time. Upon heating, the value and direction of the currents change. SCCs are observed both in the ferroelectric and paraphase.

The occurrence of an SCC can be explained using the electrochemical model proposed in [1] for the lithium iodate crystals.

The crystal polar cuts can be represented in the form of electrochemical cells with symmetric electrodes M$_i$/M$_{1,2}$/Pr$_i$/E/Pr$_i$/M$_i$/M, where M is the pressure electrode material, M$_i$ is the conducting coating material, Pr$_i$ and Pr$_2$ are the products of the electrochemical reactions, and E is the solid electrolyte cut perpendicular to the polar axis (TGS, Rochelle salt). If we consider a crystal between two electrodes to be a galvanic cell, its emf can be written in the form [8]

$$\varepsilon = \varphi_{\text{Pr}_i}^E - \varphi_{\text{Pr}_i}^E + \varphi_{\text{Pr}_i}^{\text{Pr}_2} = E_2 - E_1,$$

where $E$ is the potential of the $i$th electrode and $\varphi$ is the Galvani potential at the corresponding boundaries.

Thus, the short-circuited polar crystal appears to be substantially nonequilibrium: in the short-circuited state, these processes can be observed for an arbitrarily long time until the crystal is completely decomposed. The rates of the near-electrode processes on the opposite polar cut surfaces are different and the resulting reactions can be accelerated if the electrons can be transferred through an external circuit, i.e., at the short circuiting. The crystal heating also additionally intensifies the process. The gradient of the electrochemical potentials and temperature field induces the emf in such an electrochemical cell, which generates the SCCs.

**CONCLUSIONS**

In the polar crystals of Rochelle salt NaKC$_4$H$_4$O$_6$·4H$_2$O and TGS (CH$_2$·NH$_2$·COOH)$_3$·H$_2$SO$_4$ with the low-temperature phase transitions, SCCs were observed over the entire range from room to the decomposition temperature when applying the symmetric electrodes both in the ferroelectric and paraelectric phases even without external effects. At room temperature, the presence of SCCs, which remain for a fairly long time due to the electrochemical phenomena in the surface layers—i.e., these are the electrochemical self-decomposition currents—was established.

Upon heating from room temperature $T_{\text{room}}$, there are two competing processes: pyrocurrents and electrochemical self-decomposition currents. Above the Curie temperature, the observed currents are only electrochemical. In the temperature range of the phase transitions, the current flow direction changes sharply.

Based on the experimental results, it was shown that the flow of the SCCs through the polar cut samples of the Rochelle salt crystals and TGS is caused by the intrinsic emf induced by the electrochemical self-decomposition of the opposite cut surfaces of the samples coming into contact with the conducting coating due to the anisotropy of the sides.

**ACKNOWLEDGMENTS**

This study was carried out at the Interdepartmental Educational Testing Laboratory of Semiconductor Materials and Dielectrics “Single Crystals and Stock on their Base,” National University of Science and Technology MISIS.
FUNDING
This study was supported by the Ministry of Science and Higher Education of the Russian Federation through state assignment nos. 3.2794.2017/4.6, 11.5583.2017/ITR (11.5583.2017/7.8), and 11.6181.2017/ITR (11.6181.2017/7.8) to the university.

REFERENCES
1. Blistanov, A.A., Kozlova, N.S., and Geraskin, V.V., The influence of surface states on the features of phase transformations and the formation of structural defects in lithium iodate crystals, Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall., 1996, no. 4, pp. 66–71.
2. Blistanov, A.A., Kozlova, N.S., and Geras’kin, V.V., The phenomenon of electrochemical self-decomposition in polar dielectrics, Ferroelectrics, 1997, vol. 198, no. 1, pp. 61–66.
3. Zhu, Y., Zhang, D.-F., and Xu, Zh.-Y., The electrical properties of KLiSO₄ single crystals, Acta Phys. Sin., 1982, vol. 31, no. 8, pp. 1073–1079.
4. Juhasz, C. and Gil-Zambrano, J.L., Spontaneous electric currents from nylon films, J. Phys. D: Appl. Phys., 1982, vol. 15, no. 2, pp. 327–336.
5. Sharma, R. and Sud, L.V., Temperature-dependent currents in unipolarised poly( vinyl alcohol), J. Phys. D: Appl. Phys., 1981, vol. 14, no. 9, pp. 1671–1676.
6. Srivastava, J.P., Shrivastava, S.K., and Srivastava, A.P., Thermally stimulated discharge currents from unpoled iodine doped polyvinylacetate, Jpn. J. Appl. Phys., 1981, vol. 20, no. 12, pp. 2439–2442.
7. Gorokhovatsky, Yu.A. and Borodovskii, G.A., Termoaktivatsionnaya tokovaya spekroskopiya vysokoomnykh poluprovodnikov i dielektrikov (Thermal Activation Current Spectroscopy of High-Ohm Semiconductors and Dielectrics), Moscow: Nauka, 1991.
8. Chebotin, V.N. and Perfil’yev, M.V., Elektrokhimiya tverdykh elektrolitov (Electrochemistry of Solid Electrolytes), Moscow: Khimiya, 1978.
9. Jona, F. and Shirane, G., Ferroelectric Crystals, Oxford: Pergamon, 1952.
10. Gavrilova, N.D. and Malyshkina, O.V., Polarization relaxation in Rochelle salt crystals, Phys. Solid State, 2007, vol. 49, no. 10, pp. 1953–1956.
11. Novikov, V.N., Novik, V.K., Esengaliev, A.B., and Gavrilova, N.D., Point defects and singularities of the low-temperature (T < 15 K) behavior of the pyroelectric coefficient and the spontaneous polarization of TGS, LiTaO₃ and LiNbO₃, Ferroelectrics, 1991, vol. 118, no. 1, pp. 59–69.
12. Bogomolov, A.A., Dabizada, T.A., and Malyshkina, O.V., Nonlinear pyroeffect in unipolar DTGS crystals, Ferroelectrics, 1996, vol. 186, no. 1, pp. 1–4.
13. Gavrilova, N.D. and Malyshkina, I.A., The influence of surface states on the features of phase transformations and the formation of structural defects in lithium iodate crystals, Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall., 1996, no. 4, pp. 66–71.
14. Golitsyna, O.M., Drozdhin, S.N., and Nikishina, A.I., Polarization relaxation in Rochelle salt crystals, Phys. Solid State, 2007, vol. 49, no. 10, pp. 1953–1956.
15. Novikov, V.N., Novik, V.K., Esengaliev, A.B., and Gavrilova, N.D., Point defects and singularities of the low-temperature (T < 15 K) behavior of the pyroelectric coefficient and the spontaneous polarization of TGS, LiTaO₃ and LiNbO₃, Ferroelectrics, 1991, vol. 118, no. 1, pp. 59–69.
16. Golitsyna, O.M., Drozdhin, S.N., and Nikishina, A.I., Polarization relaxation in Rochelle salt crystals, Phys. Solid State, 2007, vol. 49, no. 10, pp. 1953–1956.
17. Malysknina, O.V., Spatial distribution of polarization and pyroelectric effect in ferroactive materials, Doctoral (Phys.-Math.) Dissertation, Voronezh, 2009.
18. Drozdhin, S.N., Golitsyna, O.M., Nikishina, A.I., and Kostsov, A.M., Pyroelectric and dielectric properties of triglycine sulphate with an impurity of phosphorus (TGSP), Ferroelectrics, 2008, vol. 373, no. 1, pp. 93–98.
19. Oreshkin, P.T., Fizika poluprovodnikov i dielektrikov (Physics of Semiconductors and Dielectrics), Moscow: Vysshaya Shkola, 1977.
20. Blistanov, A.A., Kozlova, N.S., and Geraskin, V.V., Phenomenon of electrochemical decomposition of polar dielectric crystals, scientific discoveries, in Sb. kratkikh opisani nauchnykh otkrytii (Collection of Brief Descriptions of Scientific Discoveries), Moscow: Ross. Akad. Estestv. Nauk, 2002, p. 20.
21. Delimarsky, Yu.K. and Markov, B.F., Elektrokhimiya rasplavlennykh soley (Electrochemistry of Molten Salts) Moscow: Khimiya, 1960.
22. Mikhailova, A.M. and Ukshe, E.A., Electrochemical circuits with solid electrolytes in a silver-complex iodine electrode system, Elektrokhimiya, 1987, vol. 23, no. 5, pp. 685–688.
23. Buzanov, O.A., Zabelina, E.V., Kozlova, N.S., and Sagalov, T.B., Near-electrode processes in lanthanum-gallium tantalate crystals, Crystallogr. Rep., 2008, vol. 53, no. 5, pp. 853–857.
24. Kozlova, A.P., Kozlova, N.S., Anfimov, I.M., Kiselev, D.A., and Bykov, A.S., Lanthanum-gallium tantalate crystals and their electrophysical characterization, J. Nano-Electron. Phys., 2014, vol. 6, no. 3, pp. 03034–1–03034–4.
25. Kozlova, N.S., Buzanov O. A. Kozlova, A.P., and Anfimov, I.M., Lanthanum-gallium-tantallate crystals: surface processes and their effect on electrophysical properties, IOP Conf. Ser.: Mater. Sci. Eng., 2015, vol. 80, pp. 012017–1–012017–4.
26. Zholudev, I.S., Fizika kristallicheskih dielektrikov (Physics of Crystalline Dielectrics), Moscow: Nauka, 1968.
27. Perelomova, N.V. and Tagiyeva, M.M., Kristallofizika. Sbornik zadach s resheniyami (Crystal Physics. Collection of Problems with Solutions), Moscow: MISiS, 2013.
28. Rez, I.S. and Polplavko, Yu.M., Osnovnye svoystva i prime-neniy v elektronike (Dielectrics. Basic Properties and Applications in Electronics), Moscow: Radio Svaz, 1989.

Translated by E. Bondareva