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CONTRIBUTION OF FERROELECTRIC AND NON-FERROELECTRIC FACTORS TO *P–E* HYSTERESIS LOOPS OF $CuInP_2S_6$-TYPE SINGLE CRYSTALS

I. Zamaraitė [a], A. Džiaugys [a], Yu. Vysochanskii [b], and J. Banys [a]

[a] *Faculty of Physics, Vilnius University, Saulėtekio 9, 10222 Vilnius, Lithuania*

[b] *Institute of Solid State Physics and Chemistry, Uzhgorod University, 46 Pidgirna St., 88000 Uzhgorod, Ukraine*

Email: ilona.zamaraite@ff.vu.lt

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A defining property of ferroelectricity is the switching between different states by the application of an electric field. Hysteresis loops serve like a fingerprint of ferroelectric materials giving some useful information. Sometimes the interpretation of information extracted from hysteresis measurements can be challenging due to the non-ferroelectric factors such as electrical conductivity, defect dipole presence and/or dielectric properties. In this paper, the ferroelectric and non-ferroelectric factors on *P–E* hysteresis loops were investigated in a $CuInP_2S_6$-type single crystal. The analysis of data obtained for this single crystal allowed extracting the reliable values in the materials with a low polarization and a high conductivity.

Keywords: ferroelectrics, dielectric spectroscopy, hysteresis

1. Introduction

The most distinguishing feature of ferroelectric (FE) materials is a hysteresis loop in the polarization–electric field (*P–E*) characteristics, providing two stable polarization states which form the basis for the memory devices, including ferroelectric random-access memory, energy storage devices, ferroelectric tunnel junctions and ferroelectric field-effect transistors [1–3]. Therefore, a huge amount of useful information, such as coercive field and spontaneous and remanent polarization, can be extracted from *P–E* hysteresis loops that will further guide the preparation of superior ferroelectric materials. However, because of the contribution of electric conductivity, dielectric permittivity, and other non-ferroelectric factors, *P–E* hysteresis loops can become unsaturated or even round [3, 4].

$CuInP_2S_6$ (CIPS) has attracted much attention in recent years due to its van der Waals layered structure and ferroelectric properties at room temperature [5, 6]. The structure of this layered material is defined by the sulfur framework where the octahedral voids are filled with Cu and In cations, whereas P–P pairs form a triangular pattern within the interlinked sulfur cages [7]. The symmetry reduction from the paraelectric to the ferrielectric, at the first-order phase transition, occurs at $T_C = 315$ K, and is driven by the ordering in the copper sublattice and the displacement of cations from the centrosymmetric positions in the indium sublattice (C2/c to Cc symmetry). According to the experimental results, the direction of the spontaneous polarization vector, at the onset of phase transition into the ferrielectric phase, is perpendicular to the layered planes [6, 8].

The spontaneous polarization of CIPS was estimated to be around 3 μC cm^{-2} at room temperature [9]. However, the accurate determination of the polarization value of CIPS is complicated due to the low polarization and high leakage current. The dielectric spectra of CIPS single crystals and CIPS-based selenide compounds $CuInP_2(S_xSe_{1-x})_6$ were extensively studied to estimate the conductivity of these compounds [10]. A hopping mechanism for copper ions in the CIPS crystal has been suggested [11]. A noticeable ionic conductivity was found in layered compounds $CuInP_2S_6$, $CuInP_2Se_6$ and

$CuInP_2S_6$ with a small amount of selenium impurities and in indium-rich $CuIn_{1+\delta}P_2S_6$ crystals [11–13].

To the best of our knowledge, introducing appropriate amounts of selenium into $CuInP_2S_6$ can effectively change the characteristics of ferroelectric phase transition, suppress the ferroic order and even change the crystallographic symmetry [14]. In this work, the contribution of electric conductivity, dielectric permittivity and domain switching to the properties of $CuInP_2S_6$-based ferroelectric crystals was determined by preparing $CuInP_2(Se_{0.02}S_{0.98})_6$ crystals. The mechanism by which ferroelectric and non-ferroelectric factors affect the shape of *P–E* hysteresis loops was expounded.

2. Experiment

2.1. Crystal growth

The single crystal of $CuInP_2(Se_{0.02}S_{0.98})_6$ was grown by the vapour transport technique in an evacuated quartz tube using I_2 as a transport agent. The synthesis of the starting material in a polycrystalline form was carried out using high-purity elements Cu (99.99%), In (99.999%), P (99.999%), S (99.99%) and Se (99.99%), in atomic percentage. The required amount of copper, indium, phosphorous, sulfur and selenium was placed into the quartz tube for further homogenization at 650°C during one week. After that, the recrystallization by vapour transport between the hot zone at 650°C and the cool zone at 630°C took three days. At the next stage, the cool zone was cleaned by heating, and further this zone was cooled to 615°C and kept at this temperature until the appearance of visually observed crystal nucleus. From this moment, the monocrystal growth started with a duration of near one month. At the finish of the growth process, the hot zone of the quartz tube was absolutely clean, which gave evidence that a full mass transport and a growth of a monocrystal with needed stoichiometry was achieved.

2.2. Ferroelectric switching and dielectric properties

In a wide temperature and low frequency (from 20 Hz to 1 MHz) range, the capacitance and loss tangent of the sample was measured with a *Hewlett Packard* 4284 precision LCR meter. For all measurements the silver paste electrodes were painted on the largest (001) face to ensure the electrical contact. This surface is nearly at right angles to the spontaneous polarization. Measurements were performed during the continuous temperature variation on a cooling cycle with a cooling rate 0.05 K/min near the phase transition temperature and 0.5 K/min far from the phase transition temperature. All measurements were performed on cooling and heating but most of the presented results are on cooling. The samples were cooled using the liquid nitrogen.

Ferroelectric properties were measured by a commercial ferroelectric test system (TF Analyzer 2000E with FE-Module, *AixACCT*, Germany) with the TREK 609E high voltage set-up. The external high voltage amplifier allows voltage pulses ranging from 200 V to 4 kV to be applied to the sample via the probes. The measurements were performed in the temperature range from 180 to 350 K. The TF-Analyzer 2000 system is modular; attaching an FE-module will allow hysteresis loops to be measured. The FE-module can be replaced by three other modules to investigate different ferroelectric behaviours. Polarization hysteresis, which allows a fast characterization of the ferroelectric samples, was considered a standard technique. Ferroelectric hysteresis loops have been obtained using the dynamic hysteresis mode (DHM). In the DHM method, four bipolar triangular excitation signals of frequency ν_0 are applied with the delay time τ between them. The frequency of the triangular signal was varied in a range of 3–30 Hz in accordance with the sample parameters.

3. Results and discussion

The temperature dependence of the complex dielectric permittivity of $CuInP_2(Se_{0.02}S_{0.98})_6$ crystal is shown in Fig. 1. The real part of complex dielectric permittivity is characterized by a broad anomaly at about 300 K, which can be attributed to the first-order phase transition. In previous studies it was found that the layered crystal $CuInP_2S_6$ becomes ferrielectric below T_C ~ 315 K. Chemical substitution of impurities is a tool that tunes the characteristic of ferroelectric phase transitions and modifies the ferroic order. At the substitution of sulfur for selenium in $CuInP_2S_6$ the first-order phase transition temperatures decrease very rapidly. Even the substitution of only 2% of selenium leads to the phase transition temperature decrease from 315 to 300 K (Fig. 1). The phase transition temperature reduction

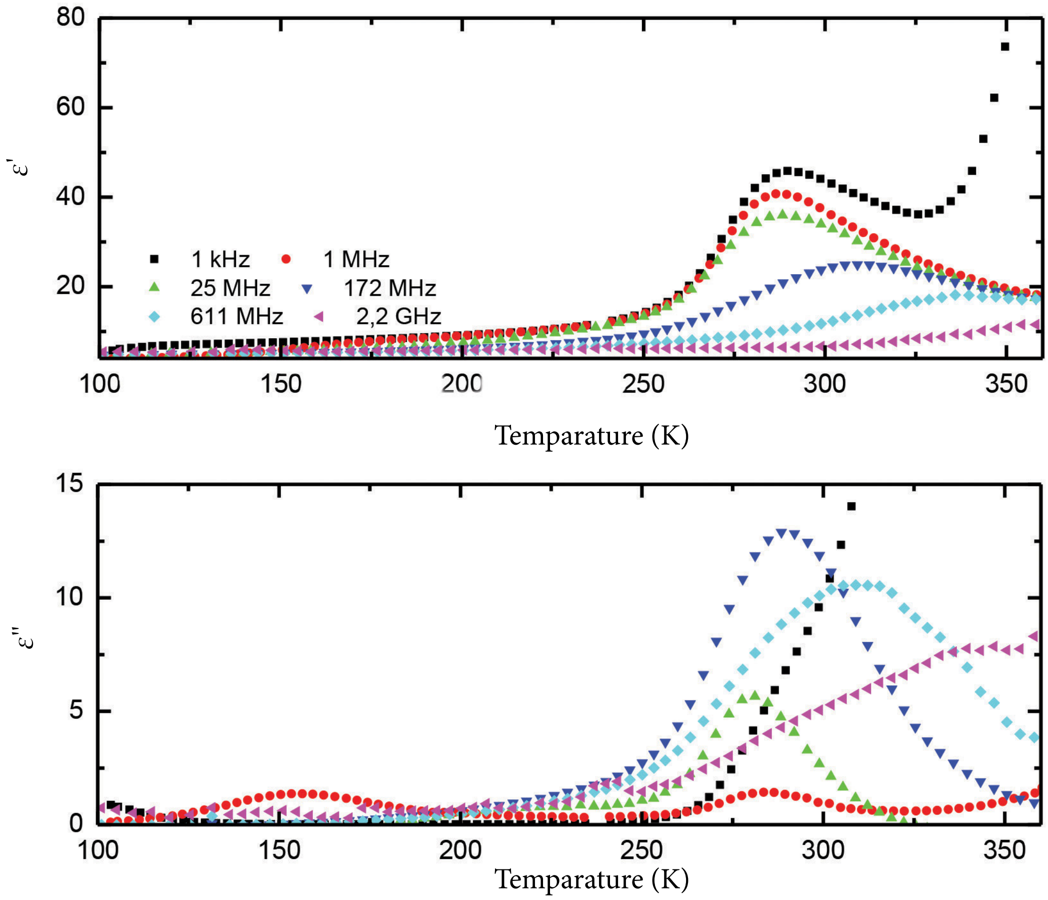

Fig. 1. Temperature dependence of the complex dielectric permittivity of $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal.

in the selenium-mixed compound can be attributed to the higher covalency and larger ionic radius of the selenium anion, which relieves the potential constraint for Cu cation hopping compared to the sulfide analog [15].

At low frequencies, the conductivity phenomena dominate in the dielectric spectra of $CuInP_2(Se_{0.98}S_{0.02})_6$ single crystals. The imaginary part of complex dielectric permittivity corresponds to the energy losses mainly due to the current conduction. This effect was already observed in $CuInP_2S_6$ pure and selenium-mixed crystals. It was explained by a high electrical conductivity caused by the ion migration. The conductivity phenomena of $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal has already been discussed in Ref. [10]. To extend the study to the real DC limit, current–voltage (I–V) curves were recorded at room temperature, as shown in Fig. 2. The crystal shows the prominent DC current at room temperature (up to 15×10^{-11} A). The thermal hysteresis between the forward and reverse sweeping of I–V curves is also obvious. Many ferroelectric CIPS-type crystals possess semiconductive properties, but such behaviour is not common for the electronic type conductors, it is more a typical signature of ionic conduction. These results

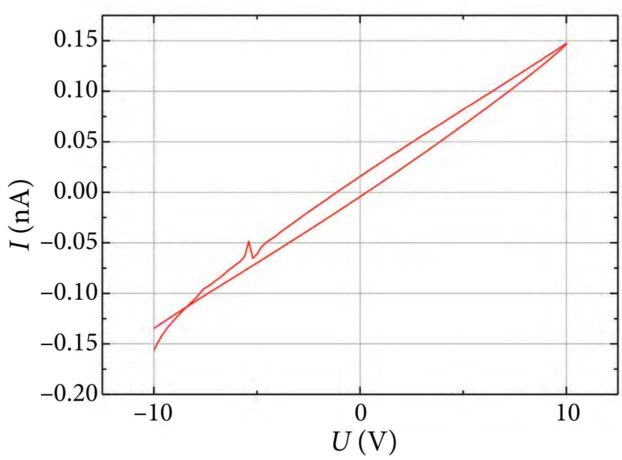

Fig. 2. The current–voltage (I–V) characteristic of $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal at room temperature.

further support the opinion about ionic conductivity in $CuInP_2S_6$-type ferroelectric layered crystals.

For ferroelectric materials, it is extremely important to understand the polarization switching dynamics that directly affects the operation speed and performance of ferroelectric devices [16]. Maisonneuve and coworkers estimated the P_s of $CuInP_2S_6$ to be around 3 μC cm^{-2} at room temperature, and their experimental result of 2.55 μC cm^{-2} is close to the estimated value [7, 9]. According to the same study, a coercive field of 77 kV cm^{-1} was reported in $CuInP_2S_6$ only at room temperature. Another study presented the thermal evolution of a ferroelectric hysteresis loop for the bulk $CuInP_2S_6$ crystal in the temperature region from 193 to 313 K [17]. The ferroelectric *P–E* loops offset was observed and attributed to the stabilized defects: an antisymmetric shape of the loops is associated with the pinning of domain walls [3, 18, 19]. The bending of the hysteresis loop at temperature close to T_C = 315 K is related to a quite high ionic conductivity in this material. Figure 3 shows the ferroelectric hysteresis (*P–E*) and *I–U* loops of $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal.

Figure 3 shows the polarization hysteresis *P–E* loops measured at applying a triangular signal of 3 Hz and 10 kV cm^{-1}. Meanwhile, the *P–E* loops of CIPS were measured at the higher external triangular signal: 100 Hz and 80 kV cm^{-1} [20]. This decrease of external field characteristics can be attributed to the effect of conductivity. Apparently, due to the unstabilized defects in the mixed crystal, it suffers from the more extensive leakage current. *P–E* constricted loops measured from 180 to 250 K support the idea of the unstabilized defects in the $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal. The constricted *P-E* loop starts to open at 260 K and becomes fully open at 300 K. This suggests that the defect dipoles can respond to the external field at high temperatures and switch even along with the polarization at higher temperatures. This also provides evidence that the defects can migrate and/or be identified as the ions.

The values of current peaks decreased with increasing temperature up to the phase transition at

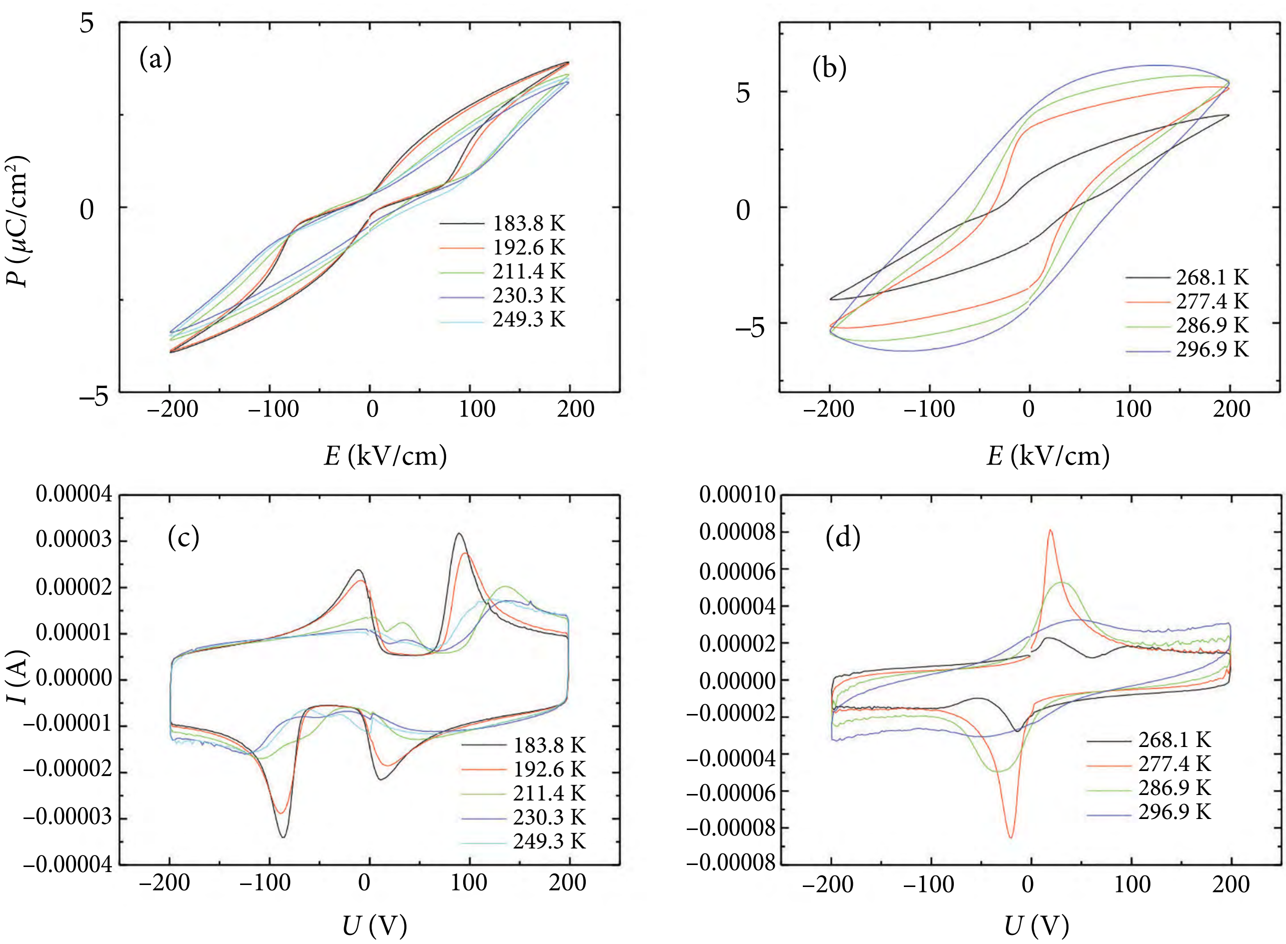

Fig. 3. Polarization–electric field (*P–E*) hysteresis of the as-grown $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal.

about 300 K. P corresponding to the maximum applied field increased with increasing temperature, which is consistent with the increasing influence of non-ferroelectric factor to the ferroelectric hysteresis loops – increasing the contribution of conductivity. In the I–U loops, the current peaks may also contain the contribution from ionic conductivity beside the contribution from dielectric permittivity and domain switching.

The nature of the ferroelectric-paraelectric phase transition of $CuInP_2S_6$ has traditionally been recognized as displacive. However, it has been shown to be intermediate between displacive and order–disorder phase transitions [21–23]. Obviously, in the mixed crystal system, the situation is much more complicated. From the presented I–U loops it can be clearly seen that at 180–250 K the polar nanoregions nucleate and begin to grow, and at about 268 K, the polar nanoregions begin to move cooperatively. This is consistent with the domain switching peaks in the I–U loops. It can suggest that below the phase transition temperature, the paraelectric phase is stable and the ferroelectric phase is pseudo stable.

4. Conclusions

In conclusion, the constricted P–E loop observed in the $CuInP_2(Se_{0.98}S_{0.02})_6$ crystal is caused by a constriction of the ionic conductivity. The dopants-ions of selenium form tunnels for more favourable migrations of copper ions in these materials. The dielectric and electrical measurements confirmed increased conductivity in the mixed crystals.

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References

[1] H. Yan, F. Inam, G. Viola, H. Ning, H. Zhang, Q. Jiang, T. Zeng, Z. Gao, and M.J. Reece, The contribution of electrical conductivity, dielectric permittivity and domain switching in ferroelectric hysteresis loops, J. Adv. Dielectr. **1**, 107–118 (2011).

[2] I. Fina, L. Fábrega, E. Langenberg, X. Mart, F. Sánchez, M. Varela, and J. Fontcuberta, Nonferroelectric contributions to the hysteresis cycles in manganite thin films: A comparative study of measurement techniques, J. Appl. Phys. **109**, 074105 (2011).

[3] L. Jin, F. Li, and S. Zhang, Decoding the fingerprint of ferroelectric loops: comprehension of the material properties and structures, J. Am. Ceram. Soc. **97**, 1–27 (2014).

[4] M. Maglione and M.A. Subramanian, Dielectric and polarization experiments in high loss dielectrics: A word of caution, Appl. Phys. Lett. **93**, 032902(2008).

[5] S. Zhou, L. You, H. Zhou, Y. Pu, Z. Gui, and J. Wang, Van der Waals layered ferroelectric $CuInP_2S_6$: Physical properties and device applications, Front. Phys. **16**, 13301-1–30 (2021).

[6] M.A. Susner, M. Chyasnavichyus, M.A. McGuire, P. Ganesh, and P. Maksymovych, Metal thio- and selenophosphates as multifunctional van der Waals layered materials, Adv. Mater. **29**, 1602852 (2017).

[7] V. Maisonneuve, M. Evain, C. Payen, V.B. Cajipe, and P. Molinié, Room-temperature crystal structure of the layered phase $Cu^{I}In^{III}P_2S_6$, J. Alloys Compd. **218**, 157–164 (1995).

[8] A. Belianinov, Q. He, A. Dziaugys, P. Maksymovych, E. Eliseev, A. Borisevich, A. Morozovska, J. Banys, Y. Vysochanskii, and S. Kalinin, $CuInP_2S_6$ room temperature layered ferroelectric, Nano Lett. **15**, 3808–3814 (2015).

[9] V. Maisonneuve, V. Cajipe, A. Simon, R. von der Muhll, and J. Ravez, Ferrielectric ordering in lamellar $CuInP_2S_6$, Phys. Rev. B **56**, 10860–10868 (1997).

[10] J. Macutkevic, J. Banys, and Y. Vysochanskii, Electrical conductivity of layered $CuInP_2(S_xSe_{1-x})_6$ crystals, Phys. Status Solidi B **252**(8), 1–5 (2015).

[11] V. Maisonneuve, J. Reau, M. Dong, V. Cajipe, C. Payen, and J. Ravez, Ionic conductivity in ferroic $CuInP_2S_6$ and $CuCrP_2S_6$, Ferroelectrics **196**, 257–260 (1997).

[12] J. Banys, J. Macutkevic, R. Grigalaitis, and Yu. Vysochanskii, Influence of small amount of $CuInP_2Se_6$ to conductivity of $CuInP_2S_6$ crystals, Solid State Ion. **179**, 79–81 (2008).

[13] A. Dziaugys, J. Banys, and Y. Vysochanskii, Broadband dielectric investigations of indium rich $CuInP_2S_6$ layered crystals, Z. Kristallogr. **226**, 171–176 (2011).

[14] A. Džiaugys, *Influence of Impurities on Dielectric Properties of Ferroelectric and Superionic Crystals* (Vilnius University Publishing House, Vilnius, 2011).

[15] A. Dziaugys, J. Banys, J. Macutkevic, and Y. Vysochanskii, Anisotropy effects in thick layered $CuInP_2S_6$ and $CuInP_2Se_6$ crystals, Phase Transit. **86**, 878–885(2013).

[16] S. Zhou, L. You, A. Chaturvedi, S.A. Morris, J.S. Herrin, N. Zhang, A. Abdelsamie, Y. Hu, J. Chen, Y. Zhou, S. Dong, and J. Wang, Anomalous polarization switching and permanent retention in a ferroelectric ionic conductor, Mater Horiz. **7**, 263–274 (2020).

[17] I. Zamaraitė, *Ferroelectricity, Dielectric and Low-frequency Noise Spectroscopic Studies of Phosphorus Chalcogenide Crystals* (Vilnius University Publishing House, Vilnius, 2019).

[18] D. Damjanovic, in: *The Science of Hysteresis*, eds. I. Mayergoyz, G. Bertotti (Elsevier, Amsterdam, 2005) pp. 337–465.

[19] D. Damjanovic, Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Rep. Prog. Phys. **61**, 1267–1324 (1998).

[20] I. Zamaraite, J. Matukas, S. Pralgauskaite, Yu. Vysochanskii, J. Banys, and A. Dziaugys, Low-frequency noise characteristics of lamellar ferrielectric crystal $CuInP_2S_6$ at the phase transition, J. Appl. Phys. **122**, 024101 (2017).

[21] Yu. Vysochanskii, T. Janssen, R. Currat, R. Folk, J. Banys, J. Grigas, and V. Samulionis, *Phase Transitions in Ferroelectric Phosphorous Chalcogenide Crystals* (Vilnius University Publishing House, Vilnius, 2008).

[22] A. Dziaugys, J. Banys, V. Samulionis, J. Macutkevic, Yu. Vysochanskii, W. Kleemann, and V. Shvartsman, in: *Ferroelectrics – Characterization and Modeling*, ed. M. Lallart (InTech, New York, 2011) pp. 153–180.

[23] J. Banys, J. Macutkevic, V. Samulionis, A. Brilingas, and Yu. Vysochanskii, Dielectric and ultrasonic investigation of phase transition in $CuInP_2S_6$ crystals, Phase Transit. **77**, 345–358 (2004).

FEROELEKTRINIŲ IR NEFEROELEKTRINIŲ VEIKSNIŲ ĮTAKA $CuInP_2S_6$ TIPO MONOKRISTALŲ *P–E* HISTEREZĖS KILPOMS

I. Zamaraitė [a], A. Džiaugys [a], Yu. Vysochanskii [b], J. Banys [a]

[a] *Vilniaus universiteto Fizikos fakultetas, Vilnius, Lietuva*

[b] *Užhorodo nacionalinio universiteto Kietojo kūno fizikos ir chemijos institutas, Užhorodas, Ukraina*

Santrauka

Viena pagrindinių feroelektrinius kristalus apibūdinančių savybių yra perjungimas tarp skirtingų būsenų naudojant išorinį elektrinį lauką. Histerezės kilpos dažnai interpretuojamos kaip feroelektrinių medžiagų pirštų atspaudai, suteikiantys naudingos informacijos apie medžiagos savybes. Kartais informacija, gauta iš histerezės matavimų, gali būti sudėtingai interpretuojama dėl neferoelektrinių veiksnių, tokių kaip elektros laidumas, defektų dipolių buvimas ir (arba) dielektrinės savybės. Šiame darbe feroelektriniai ir neferoelektriniai veiksniai *P–E* histerezės kilpose buvo nagrinėjami $CuInP_2(Se_{0,98}S_{0,02})_6$ monokristale.