

Original article

DOI: <https://doi.org/10.18721/JPM.15201>

THE ROLE OF THE ELECTRET EFFECT IN THE FORMATION OF THE PIEZOELECTRIC STATE IN THE POLYVINYLIDENE FLUORIDE-TETRAFLUOROETHYLENE COPOLYMER FILMS

Yu. I. Sotova , *Yu. A. Gorokhovatsky*, *D. E. Temnov*

Herzen State Pedagogical University of Russia, St. Petersburg, Russia

 juliasotova1992@mail.ru

Abstract: In this work, the phenomenon of polarization of polyvinylidene fluoride-tetrafluoroethylene copolymer (P(VDF-TFE)) polymer films in the field of a corona discharge at elevated temperatures has been studied in order to elucidate the mechanism of formation of the piezoelectric state. The TSD spectroscopy was used to analyze the charge accumulation and relaxation processes occurring in the (P(VDF-TFE)) films during polarization. The results obtained made it possible to reveal an interrelationship of forming the electret and piezoelectric states in the (P(VDF-TFE)) as well as to explain the mentioned mechanism. On this basis a polarization procedure in the field of the corona discharge was developed and tested. This procedure permitted reducing the probability of electrical breakdown leading to mechanical damage of the films and allowed improving key characteristics of the objects under question.

Keywords: electret state, polyvinylidene fluoride, tetrafluoroethylene, piezoelectric effect, TSD spectroscopy

Funding: The research was supported by the Ministry of Education of Russian Federation as a part of a state task (project No. FSZN-2020-0026).

Citation: Sotova Yu. I., Gorokhovatsky Yu. A., Temnov D. E., The role of the electret effect in the formation of the piezoelectric state in polyvinylidene fluoride-tetrafluoroethylene copolymer films, St. Petersburg Polytechnical State University Journal. Physics and Mathematics. 15 (2) (2022) 8–16. DOI: <https://doi.org/10.18721/JPM.15201>

This is an open access article under the CC BY-NC 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)



Научная статья

УДК 538.9

DOI: <https://doi.org/10.18721/JPM.15201>

РОЛЬ ЭЛЕКТРЕТНОГО ЭФФЕКТА В ФОРМИРОВАНИИ ПЬЕЗОЭЛЕКТРИЧЕСКОГО СОСТОЯНИЯ В ПЛЕНКАХ СОПОЛИМЕРА ПОЛИВИНИЛИДЕНФТОРИДА С ТЕТРАФТОРЭТИЛЕНОМ

Ю. И. Сотова [✉], Ю. А. Гороховатский, Д. Э. Темнов

Российский государственный педагогический университет им. А. И. Герцена, Санкт-Петербург, Россия

[✉] juliasotova1992@mail.ru

Аннотация. С целью выяснения механизма формирования пьезоэлектрического состояния, в работе изучено явление поляризации полимерных пленок сополимера поливинилиденфторида с тетрафторэтиленом (П(ВДФ-ТФЭ)) в поле коронного разряда при повышенной температуре. Для анализа процессов накопления и релаксации зарядов, происходящих в П(ВДФ-ТФЭ) при поляризации, применялась спектроскопия токов термостимулированной деполяризации. Полученные результаты позволили обнаружить взаимосвязь процессов формирования электретного и пьезоэлектрического состояний в П(ВДФ-ТФЭ), а также объяснить указанный механизм. На этой основе была разработана и опробована методика поляризации в поле коронного разряда, позволяющая снизить вероятность электрического пробоя, приводящего к механическим повреждениям пленок, а также улучшить ключевые характеристики исследованных объектов.

Ключевые слова: электретное состояние, поливинилиденфторид, тетрафторэтилен, пьезоэлектрический эффект, спектроскопия токов термостимулированной деполяризации

Финансирование: работа выполнена при финансовой поддержке Государственного задания Минобрнауки Российской Федерации (проект № FSZN0026-2020-).

Для цитирования: Сотова Ю. И., Гороховатский Ю. А., Темнов Д. Э. Роль электретного эффекта в формировании пьезоэлектрического состояния в пленках сополимера поливинилиденфторида с тетрафторэтиленом // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 2. С 8–16. DOI: <https://doi.org/10.18721/JPM.15201>

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)

Introduction

The piezoelectric properties were first discovered in polyvinylidene fluoride (PVDF) by Heiji Kawai in 1969. However, producing piezoelectric films from the PVDF homopolymer comes with challenges due to a high coercive field (of the order of 10^8 V/m, which is two orders of magnitude higher than that of piezoceramics) [2], so piezoelectric polymers with lower coercive fields are commonly used as piezoelectric elements: these are composites based on vinylidene fluoride copolymers with trifluoroethylene, P(VDF-TrFE), and with tetrafluoroethylene, P(VDF-TFE). Notably, both the PVDF homopolymer and its copolymers only exhibit piezoelectric properties after repeated pre-stretching, causing the sample to extend by several times compared to the initial length [3, 4].

PVDF displays polymorphism, existing in five different crystalline modifications, denoted as α -, β -, γ -, δ - and ϵ -phases [5]. The β -phase has attracted the greatest attention from researchers due to its piezoelectric properties [6].

There are several approaches to generating a piezoelectric state in PVDF-based polymer films. A traditional method is film polarization by a corona discharge at elevated temperatures. This method is popular because larger field strengths can be achieved under corona polarization (compared to those obtained by the direct contact method) [7]. However, corona polarization at elevated temperatures induces electrical aging in polymer films: the probability of electrical breakdown increases with increasing polarization temperature, leading in turn to mechanical damage to the polymer films.

The goal of this study consisted in establishing the relationship between the electret and piezoelectric states generated in P(VDF-TPE) films, as well as in modifying the technology for inducing a piezoelectric state in PVDF-based polymer films, which can serve to decrease the probability of electrical breakdown in the given sample, preserving or even improving its key characteristics.

Experimental samples and procedure

The experimental sample was a mechanically pre-stretched F2ME-type P(VDF-TFE) copolymer film with a thickness of 20 μm . A piezoelectric state was induced in the samples with a corona discharge but under different polarization conditions.

The accumulation and relaxation of charges in P(VDF-TPE) under polarization was studied by the method of thermally stimulated depolarization currents (TSDC). TSDC measurements were carried out with a TSC II thermal analyzer (from Setaram, Lyon, France).

The piezoelectric coefficient d_{33} was measured by the dynamic method using a D33 test meter (Yangzhou, China).

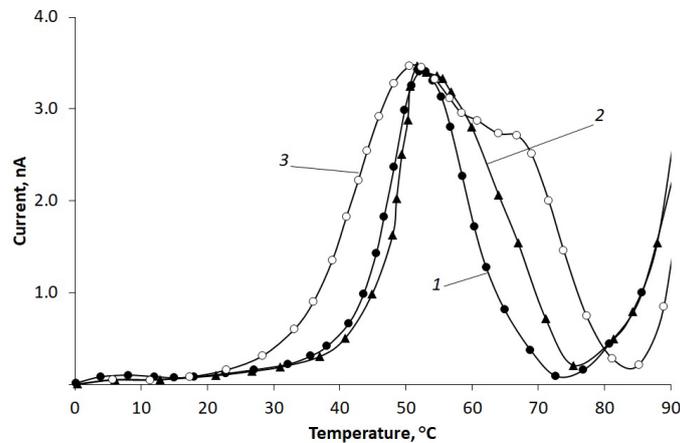


Fig. 1. Thermally stimulated depolarization currents in P(VDF-TPE) films polarized by negative corona discharge at different polarization temperatures, °C: 50 (1), 70 (2) and 80 (3)

Experimental results and discussion

The traditional procedure for inducing a piezoelectric state in the P(VDF-TPE) copolymer by a corona discharge field is as follows: the sample is placed in the given field at an elevated temperature, held in it for 10 minutes (maintaining a constant temperature), and then cooled to room temperature in the same field. It was experimentally established in earlier studies that polarization must be carried out with a negative corona discharge to achieve better electret characteristics [8].

The electric field strength required to obtain a high piezoelectric coefficient d_{33} is equal to 1.2 MV/cm [9]. We varied the polarization temperature from 50 to 80 °C.

Fig. 1 shows the TSDC curves in P(VDF-TPE) films polarized by negative corona discharge at different polarization temperatures. As evident from the data obtained, a single peak is observed on the TSDC curves for low polarization temperatures (50–60 °C) at about 50 °C, while two strongly overlapping peaks appear on the curves (near 40–70 °C) with increased polarization temperatures (70 and 80 °C). A possible explanation for this difference is that the homocharge is captured by deep near-surface traps in films polarized by the negative corona discharge. The actual homocharge in the P(VDF-TPE) sample does not contribute to the piezoelectric effect, but orientation of the polar structures occurs in the internal electric field generated by the homocharge (constituting the piezoelectric β -phase of PVDF). Apparently, there are two classes of polar structures with different activation energies. Polar structures of only one type (with lower activation energies, their current peak is located at about 50 °C) are oriented in the internal electric field of the homocharge under corona polarization at 50–70 °C, while increasing the polarization temperature to 80 °C produces orientation in both types of polar structures, which is manifested as two strongly overlapping peaks on the TSDC curves (in the temperature range of 40–70 °C).

In this case, it is possible to estimate the activation energies and the frequency factors for the polar structures in the P(VDF-TPE) samples, characterized by lower activation energies (Table 1); the samples were subjected to polarization at different temperatures. The calculations were performed by two methods: initial current rise and heating rate variation [10].

We also estimated the activation energy of the homocharge for a negatively polarized corona electrode (the release of the homocharge from the near-surface traps shown in Fig. 1 appears as an increase in current above 80 °C) by the initial rise method. The resulting value amounted to (1.90 ± 0.09) eV. A similar calculation for a positively polarized corona electrode gave an activation energy of the homocharge equal to (1.20 ± 0.06) eV.

Analyzing the dependence of the piezoelectric coefficient d_{33} on the polarization temperature (Fig. 2), we can conclude that the values of the piezoelectric coefficient are high (in the range of 24–26 pC/N) immediately after polarization (curve 1) and only slightly depend on the polarization temperature. However, it is not only the actual magnitude of the piezoelectric coefficient but also its thermal stability that is an important characteristic of the piezoelectric properties.

Table 1

**Key characteristics of polar structures
in P(VDF-TPE) films
polarized at different temperatures**

| Method for determining W | Activation energy W , eV, for polarization temperature | | |
|--|---|-----------------|-----------------|
| | 50 °C | 70 °C | 80 °C |
| Initial rise method | 0.82 ± 0.04 | 0.82 ± 0.04 | 0.83 ± 0.04 |
| Heating rate variation method | 0.84 ± 0.03 | 0.83 ± 0.03 | 0.83 ± 0.03 |
| The frequency factor found by varying the heating rate was equal to $\omega = 10^{10} \text{ s}^{-1}$ for the three polarization temperatures | | | |

Notes. 1. The results are given for polar structures characterized by lower activation energies (see Fig. 1 and explanations in the text). 2. The values of ω were determined up to a half decade.

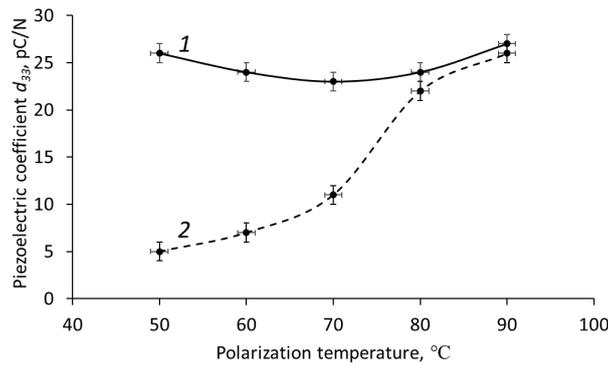


Fig. 2. Dependences of the piezoelectric coefficient d_{33} in P(VDF-TPE) films on the polarization temperature, obtained immediately after polarization (1) and after 2.5 hours of subsequent annealing at 70 °C (2)

To test the thermal stability of the values obtained for the piezoelectric coefficient d_{33} , P(VDF-TFE) films were kept in a thermostat at 70 °C for two and a half hours. We then discovered that the piezoelectric coefficient in P(VDF-TFE) films polarized at a low temperature (50–70 °C) decreased considerably after exposure in a thermostat (see curve 2 in Fig. 2).

Thus, this quantity turns out to be unstable at polarization temperatures below 70 °C. On the other hand, polarization at 80–90 °C yields stable values of the piezoelectric coefficient.

As noted above, exposing the film to the corona discharge at elevated temperatures often leads to electrical breakdowns, mechanically damaging the film as a result. We used polarization in the internal field of the homocharge to reduce the risk of electrical breakdown: P(VDF-TPE) films were first subjected to polarization at room temperature under negative corona discharge for 10 minutes (the electric field strength was 1.2 MV/cm), then heated (the sample was in the open state, i.e., in the absence of an external electric field) to a different temperature, and finally cooled to room temperature. Fig. 3 shows the TSDC curves in P(VDF-TPE) films polarized by this method.

It can be seen from the TSDC curves in Fig. 3 that the peak on the curve rises with increasing heating temperature, and the area under the curve increases. We should note that the TSDC curves have a similar appearance to low-temperature equivalents in Fig. 1 (in terms of their shape and the positions of the peaks on the temperature axis), suggesting that the homocharge is held in deep near-surface traps in this case, while orientation of the polar structures occurs in the generated internal electric field. Thus, the mobility of polar structures increases with increasing heating temperature, more of them have time to orient themselves, so both the maximum value and the area under the curve grow.

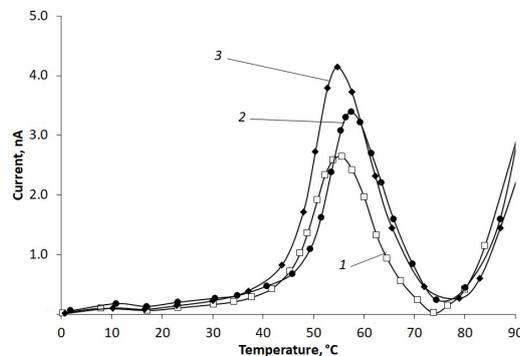


Fig. 3. Thermally stimulated depolarization currents in P(VDF-TPE) films polarized under negative corona discharge at room temperature, followed by heating (in the absence of an electric field) to different temperatures, °C: 50 (1), 70 (2) and 80 (3)

Table 2 gives the activation energies and frequency factors (with an accuracy up to half a decade) of polar structures in P(VDF-TFE) films polarized at room temperature, subsequently subjected to heating to different temperatures and further cooling to room temperature (in the open state, i.e., in the absence of an electric field), calculated by methods of initial rise and variation of the heating rate.

Table 2

**Key characteristics of polar structures in P(VDF-TPE) films
heated to different temperatures after polarization**

| Method for determining W | Activation energy W , eV, at heating temperature | |
|--|--|-----------------|
| | 70 °C | 90 °C |
| Initial rise | 0.81 ± 0.04 | 0.83 ± 0.04 |
| Heating rate variation | 0.83 ± 0.03 | 0.84 ± 0.03 |
| The frequency factor found by varying the heating rate was equal to $\omega = 10^{10} \text{ s}^{-1}$ for the two heating temperatures | | |

Notes. 1. Film samples were heated after polarization under negative corona discharge at room temperature. 2. The values of ω were determined up to a half decade.

We estimated the activation energy of the homocharge; in this case, the homocharge release from near-surface traps was manifested as an increase in depolarization current after it reaches 80 °C. (see Fig. 3). The value obtained by the initial rise method was (1.90 ± 0.09) eV, as in the case of the traditional polarization method.

Fig. 4 shows the dependence of the piezoelectric coefficient d_{33} on the heating temperature measured immediately after polarization (curve 1) and after two and a half hours of exposure in a thermostat at 70 °C (curve 2). Apparently, in the first case, the piezoelectric coefficient measured immediately after following the steps of the procedure (including polarization at room temperature, heating to a given temperature, then cooling to room temperature) increases with increasing heating temperature, reaching a maximum (25 mC/N) at a heating temperature of 90 °C. However, in the second case, when the procedure includes exposure in a thermostat after heating to a given temperature, the piezoelectric coefficient in P(VDF-TFE) samples, heated to 50–70 °C, decreased significantly, while the piezoelectric coefficient of the samples heated to 80–90 °C practically did not change. The optimal heating temperature was 90 °C, yielding the maximum value of the piezoelectric coefficient d_{33} (25 pC/N). On the other hand, heating to a higher temperature led to mechanical deformation of the samples.

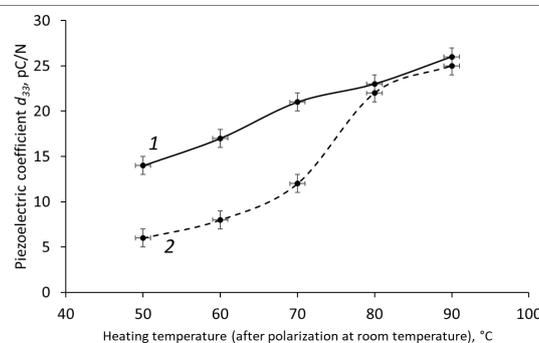


Fig. 4. Dependences of the piezoelectric coefficient d_{33} in polarized P(VDF-TPE) films on further heating temperature, obtained without subsequent annealing (1) and after 2.5 hours of subsequent annealing at 70 °C (2)
The films were polarized at room temperature

We can therefore argue that the technique proposed for inducing a piezoelectric state allows achieving the value of the piezoelectric coefficient comparable to that obtained by the traditional method in P(VDF-TFE) films; moreover, the probability of electrical breakdown (and mechanical damage to the sample) is significantly reduced.

Conclusion

As a result of the studies carried out by the method of thermal activation spectroscopy, we have proposed a mechanism for polarization in polymer films of the copolymer P(VDP-TPE): a homocharge is trapped by deep near-surface traps during polarization in corona discharge field, which itself does not contribute to the magnitude of the piezoelectric coefficient. However, orientation occurs in the internal electric field of the homocharge and the oriented state of the polar structures is preserved. Increasing the polarization temperature increases the contribution of dipoles with higher activation energies (this appears as two strongly overlapping peaks on the TSDC curves). Thus, homo and hetero charges coexist under corona discharge for polarized P(VDP-TPE) films. The activation energy of polar structures amounts to (0.82 ± 0.03) eV, and the frequency factor to 10^{10} s^{-1} (up to half a decade). The activation energy of the homocharge for a negatively polarized corona electrode is much higher than that for polar structures and amounts to (1.90 ± 0.09) eV. A similar calculation for a positively charged corona electrode gives an activation energy of the homocharge equal to (1.20 ± 0.06) eV.

Thus, we have established that the electret and piezoelectric states emerging in P(VDF-TPE) films are interconnected. Inducing an electret state in these samples is necessary to produce and preserve piezoelectric properties.

The traditional method of polarization in the corona field at elevated temperature often leads to electrical breakdowns, and, consequently, to mechanical damage to polymer films. The method for polarization in the internal field of the homocharge proposed in this study significantly reduces the risk electrical breakdown; furthermore, the values of the piezoelectric coefficient d_{33} obtained by this method in P(VDF-TPE) films are not inferior in their level and thermal stability to the piezoelectric coefficient d_{33} obtained in the samples by polarization using the traditional approach.

REFERENCES

1. **Kawai H.**, The piezoelectricity of poly (vinylidene fluoride), *Jap. J. Appl. Phys.* 8 (6) (1969) 975–983.
2. **Lushcheykin G. A.**, New polymer-containing piezoelectric materials, *Physics of the Solid State.* 48 (6) (2006) 1023–1025.
3. **Ting Y., Suprpto Y., Chiu C.-W., Gunawan H.**, Characteristic analysis of biaxially stretched PVDF thin films, *J. Appl. Polym. Sci.* 135 (36) (2018) 46677.
4. **Marandi M., Tarbutton J.**, Additive manufacturing of single- and double-layer piezoelectric PVDF-TrFE copolymer sensors, *Procedia Manuf.* 34 (2019) 666–671.
5. **Begum S., Ullah H., Kausar A., et al.**, Fabrication of epoxy functionalized MWCNTs reinforced PVDF nanocomposites with high dielectric permittivity, low dielectric loss and high electrical conductivity, *Comp. Sci. Technol.* 167 (20 October) (2018) 497–506.
6. **Kalimuldina G., Turdakyn N., Abay I., et al.**, A review of piezoelectric PVDF film by electrospinning and its applications, *Sensors.* 20 (18) (2020) 5214.
7. **Sukumaran S., Chatbouri S., Rouxel D., et al.**, Recent advances in flexible PVDF based piezoelectric polymer devices for energy harvesting applications, *J. Intell. Mater. Syst. Struct.* 32 (7) (2021) 746–780.
8. **Gorokhovatskiy Yu. A., Temnov D. E., Sotova Yu. I.**, Rheological parameters effect on the electric properties of polyvinylidene fluoride, *St. Petersburg State Polytechnical University Journal: Physics and Mathematics.* 13 (4) (2020) 39–46 (in Russian).
9. **Mahadeva S. K., Berring J., Walus K., Stoeber B.**, Effect of poling time and grid voltage on phase transition and piezoelectricity of poly(vinylidene fluoride) thin films using corona poling, *J. Phys. D: Appl. Phys.* 2013. Vol. 46 (28) (2013) 285305.
10. **Gorokhovatskiy Yu. A., Bordovskiy G. A.**, Termoaktivatsionnaya tokovaya spektroskopiya vysokomnykh poluprovodnikov i dielektrikov [Thermal activation spectroscopy of high-resistance semiconductors and dielectrics], Nauka, Moscow, 1991 (in Russian).

**СПИСОК ЛИТЕРАТУРЫ**

1. **Kawai H.** The piezoelectricity of poly (vinylidene fluoride) // Japanese Journal of Applied Physics. 1969. Vol. 8. No. 6. Pp. 975–983.
2. **Лушейкин Г. А.** Новые полимерсодержащие пьезоэлектрические материалы // Физика твердого тела. 2006. Т. 48. № 6. С. 963–964.
3. **Ting Y., Suprpto Y., Chiu C.-W., Gunawan H.** Characteristic analysis of biaxially stretched PVDF thin films // Journal of Applied Polymer Science. 2018. Vol. 135. No. 36. P. 46677.
4. **Marandi M., Tarbutton J.** Additive manufacturing of single- and double-layer piezoelectric PVDF-TrFE copolymer sensors // Procedia Manufacturing. 2019. Vol. 34. Pp. 666–671.
5. **Begum S., Ullah H., Kausar A., Siddiq M., Aleem M. A.** Fabrication of epoxy functionalized MWCNTs reinforced PVDF nanocomposites with high dielectric permittivity, low dielectric loss and high electrical conductivity // Composites Science and Technology. 2018. Vol. 167. 20 October. Pp. 497–506.
6. **Kalimuldina G., Turdakyn N., Abay I., Medeubayev A., Nurpeissova A., Adair D., Bakenov Z.** A review of piezoelectric PVDF film by electrospinning and its applications // Sensors. 2020. Vol. 20. No. 18. P. 5214.
7. **Sukumaran S., Chatbouri S., Rouxel D., Tisserand E., Thiebaud F., Ben Zineb T.** Recent advances in flexible PVDF based piezoelectric polymer devices for energy harvesting applications // Journal of Intelligent Material Systems and Structures. 2021. Vol. 32. No. 7. Pp. 746–780.
8. **Гороховатский Ю. А., Темнов Д. Э., Сотова Ю. И.** Влияние реологических параметров на электретные свойства поливинилиденфторида // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2020. Т. 13. № 4. С. 39–46.
9. **Mahadeva S. K., Berring J., Walus K., Stoeber B.** Effect of poling time and grid voltage on phase transition and piezoelectricity of poly(vinylidene fluoride) thin films using corona poling // Journal of Physics D: Applied Physics. 2013. Vol. 46. No. 28. P. 285305.
10. **Гороховатский Ю. А., Бордовский Г. А.** Термоактивационная токовая спектроскопия высокоомных полупроводников и диэлектриков. М.: Наука. Гл. ред. физ.-мат. лит.-ры, 1991. 248 с.

THE AUTHORS**SOTOVA Yulia I.**

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russia
juliasotova1992@mail.ru
ORCID: 0000-0001-6792-2390

GOROKHOVATSKY Yuriy A.

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russia
gorokh-yu@yandex.ru
ORCID: 0000-0001-5085-2525

TEMNOV Dmitry E.

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russia
tde@herzen.spb.ru
ORCID: 0000-0002-9560-4346

СВЕДЕНИЯ ОБ АВТОРАХ

СОТОВА Юлия Ильинична – аспирантка кафедры общей и экспериментальной физики
Российского государственного педагогического университета им. А. И. Герцена.

191186, Россия, г. Санкт-Петербург, наб. р. Мойки, 48

juliasotova1992@mail.ru

ORCID: 0000-0001-6792-2390

ГОРОХОВАТСКИЙ Юрий Андреевич – доктор физико-математических наук, заведующий
кафедрой общей и экспериментальной физики *Российского государственного педагогического*
университета им. А. И. Герцена.

191186, Россия, г. Санкт-Петербург, наб. р. Мойки, 48

gorokh-yu@yandex.r

ORCID: 0000-0001-5085-2525

ТЕМНОВ Дмитрий Эдуардович – кандидат физико-математических наук, доцент кафедры
общей и экспериментальной физики *Российского государственного педагогического университета*
им. А. И. Герцена.

191186, Россия, г. Санкт-Петербург, наб. р. Мойки, 48

tde@ Herzen.spb.ru

ORCID: 0000-0002-9560-4346

Received 10.04.2022. Approved after reviewing 12.04.2022. Accepted 12.04.2022.

Статья поступила в редакцию 10.04.2022. Одобрена после рецензирования 12.04.2022.
Принята 12.04.2022.