Features of nonlinear optical properties of thin-film phthalocyanine coatings obtained by femtosecond hardware-software Z-scan measurement complex

K S Khorkov¹, R V Chkalov¹, D A Kochuev¹, A V Kazak², V E Pushkarev³ and A Yu Tolbin³

¹Vladimir State University, 87 Gorky St., Vladimir 600000, Russia
²Ivanovo State University, 39 Ermak St., Ivanovo 153025, Russia
³Institute of Physiologically Active Compounds, RAS, 1 Severnyi Pr., Chernogolovka 142432, Russia

E-mail: kirill.khorkov@gmail.com

Abstract. In this paper, we study the nonlinear optical properties of thin-film phthalocyanine coatings based on the developed femtosecond hardware-software complex Z-scan. As a control of the complex, a combined system is used to ensure the synchronization of all components of the installation, as well as to automate the process of data collection and processing, which greatly simplifies the process of conducting the Z-scanning experiment. The results of measurement of nonlinear optical properties of the phthalocyanine thin films using femtosecond laser radiation are presented.

1. Introduction

Currently, the production of materials with nonlinear optical properties is a dynamically developing field of physics, which allows to solve a number of important applied scientific problems. Therefore, studies of nonlinear optical properties of thin-film materials are an actual task in the creation of active media, saturable absorbers, optical limiters and other elements of fiber optics, integrated optics and photonics. Materials such as porphyrins and phthalocyanines are aromatic organic macrocyclic molecules with a huge number of delocalized π electrons [1-4]. These materials demonstrate large nonlinear responses, which is beneficial for various nonlinear optical and photonic devices [5-7].

This work aims to obtain nonlinear optical characteristics of thin-film coatings based on phthalocyanines using the developed femtosecond hardware-software Z-scan complex.

2. Hardware and software Z-scan complex measurements

2.1. Samples

The compound, later called phthalocyanine, was first obtained in the industrial production of ortho-disubstituted benzene derivatives [8]. Linstead was the first who described the structure of phthalocyanine, also he carried out the synthesis of some of its metal complexes [9]. Robertson using the X-ray diffraction [10] later described the phthalocyanine structure. Phthalocyanines are not found in nature, they are synthetic compounds.
Phthalocyanines and their derivatives demonstrate high nonlinear optical responses and are currently the focus of many studies [11-13]. Phthalocyanines possess high thermal and chemical resistance, and their highly polarized macrocyclic electronic system promotes multiphoton absorption of light. In the case of subnanosecond and shorter laser pulses, the absorption cross-section of the excited states of phthalocyanines increases, which opens up prospects for the protection against ultrashort laser pulses.

In this work, the investigation of nonlinear optical properties of the phthalocyanine thin-film coatings obtained by a Langmuir–Blodgett method has been carried out. The Langmuir–Blodgett technique allows obtaining the oriented multi-molecular layers on various solid surfaces by successive transfer of the monolayer from the surface of the aqueous solution to a solid substrate.

2.2. Z-scan technique
The Z-scan method introduced by Sheik-Bahae [14] is a well-known technique used to study the nonlinear properties of optical materials. The method allows not only to determine the value and sign of the nonlinear refractive index, but also the two-photon absorption coefficient [15-17]. The method is based on the effect of self-focusing of laser radiation at a sample with nonlinear optical response. If the sign of the nonlinear refractive index is such that it increases in the region occupied by the beam, then this area becomes optically denser and the peripheral rays are deflected to the center of the beam. To determine the nonlinear refractive index, a closed-aperture technique is used. The nonlinear absorption index is determined in the experiment with an open aperture.

The method of determining nonlinear constants consists in moving the sample along the optical axis near the focus of the lens used to form a convergent Gaussian beam and measuring the power of the radiation transmitted through the sample.

2.3. Experimental setup
Experiments on the study of nonlinear optical characteristics were carried out using the developed hardware-software Z-scan complex. The setup uses a femtosecond Yb:KGW laser system TETA-10 as a radiation source. The system characteristics: \( \lambda = 517 \text{ nm} \) (second harmonic), pulse repetition rate \( f = 10 \text{ kHz} \), energy of the pulse \( E_{\text{max}} \approx 150 \mu \text{J} \), pulse duration \( \tau \approx 280 \text{ fs} \). The sample is moved by means of a motorized positional platform equipped with a bipolar stepper motor. To control the engine, a specialized driver with a high pitch division is used, which ensures micro-dimensional positioning accuracy and smooth movement. Control and registration of the output laser radiation power values is carried out using the Nova II power meter (Fig. 1).

![Functional scheme of the Z-Scan complex.](image1)

![Graphical interface of the developed Z-scan software.](image2)
To control the complex, a combined system is used, which includes both PC software that allows for interaction between devices at the API level and a microcontroller designed to work at a lower level. This approach allows to ensure the synchronization of all components of the installation, as well as to automate the process of data collection and processing, which greatly simplifies the experimental process.

Interaction with the system is carried out through the graphical user interface (Fig. 2). The software allows for a full cycle of sample scanning in automatic mode based on the specified parameters. The result of this cycle is a graph of the laser radiation power at the output of the sample from the scanning depth.

3. Results
As a result of the measurements, graphs of the laser radiation power transmitted through the sample and the coordinates of the sample position were obtained. It should also be noted that in order to achieve the self-focusing effect, on which the Z-scan technique is based, the power must reach a certain critical value. The coatings were deposited on a quartz substrate. Figure 3 (left graph) shows changes in transmittance from the power of the incident laser radiation. The right graph depicts the corresponding approximation curves. It is seen that nonlinear effects begin to appear when the power value exceeds 10 mW.

![Figure 3](image.png)

**Figure 3.** Dependences of the laser radiation power transmitted through the substrate on the position coordinate.

Note the significant contribution of the substrate. In the course of the experiment, the threshold value of the power required for triggering nonlinear behavior of the substrate deposited phthalocyanine was established. Figure 4 shows the transmittance dependences at different power. Thus, at power values below 3 mW, nonlinear processes are practically not observed. At the same time, at a power of 5 mW, a pronounced nonlinear response begins to be observed. The pronounced manifestation of the nonlinear properties of the substrate using the Z-scan technique take place at the power value of 10 mW, a further increase in the power leads to irreversible changes in the sample structure and destruction of the thin film.
Figure 4. Dependences of the laser radiation power transmitted through the sample on the position coordinate.

4. Conclusion
As an experimental result of the nonlinear optical study of the phthalocyanine thin-film samples, dependence of the material response on the power of the transmitted femtosecond laser radiation was obtained. A hardware-software Z-scan complex was developed, which allows to automate the collecting and processing of the information and essentially simplifies the experimental process.

Acknowledgement
This work was performed within the framework of the State Assignment of 2019 (Theme 45.5 Creation of compounds with given physicochemical properties). The work was also supported by the Ministry of Education and Science of the Russian Federation in the framework of the state task for Ivanovo State University (Grant No 16.1037.2017/4.6) and partially supported by the RFBR (Grant No 19-57-04002). We also acknowledge support of the study by the Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant MD-3847.2019.3).

References
[1] Bharati M S S, Bhattacharya S, Krishna J S et al 2018 Optics & Laser Technology 108:418-425
[2] Kazak A V, Usol’tseva N V, Smirnova A I et al 2015 Macroheterocycles 8(3):284–289
[3] Chausov D N, Dadivanyan A K, Noah O V, Belyaev V V 2015 Mol Cryst Liq Cryst 611(1):21–26
[4] Chausov D N, Kurilov A D, Konstantinov M S, Belyaev V V, Bogdanov D L 2015 Liq Cryst and their Appl 15(2):35–43
[5] Zongo S, Dhlamini M S, Neethling P H et al 2015 Optical Materials 50:138-143
[6] Chumakov A S, Al-Alwani A J, Gorbachev I A et al 2017 BioNanoScience 7(4):666–671
[7] Kazak A V, Usol’tseva N V, Smirnova A I et al 2016 Crystallography Reports 61(3):493–498
[8] Braun A V, Tcherniac J 1907 Berichte der deutschen chemischen Gesellschaft 40(2):2709-2714
[9] Linstead R P 1934 Journal of the Chemical Society (Resumed) 1016-1017
[10] Robertson J M 1936 Journal of the Chemical Society (Resumed) 1195-1209
[11] Hanack M, Dini D, Barthel M, Vagin S 2002 The Chemical Record 2(3):129–148
[12] De la Torre G, Claessens C G, Torres T 2007 Chemical communications 20:2000-2015
[13] Tolbin A Yu, Saveliev M S, Gerasimenko A Yu, Tomilova L G, Zefirov N S 2016 Phys Chem. Chem. Phys 18(23):15964–15971
[14] Sheik-Bahae M, Hutchings D C, Hagan D J, Van Stryland E W 1991 IEEE Journal of quantum electronics 27(6):1296-1309
[15] Castro-Marín P, Castro-Olvera G, Garduño-Mejía J et al 2017 Optics express 25(13):14473-14482
[16] Zheng X, Chen R, Shi G et al 2015 Optics letters 40(15):3480-3483
[17] Zheng X, Zhang Y, Chen R, Xu Z, Jiang T 2015 Optics express 23(12):15616-15623