REVIEW

of a dissertation for obtaining the scientific degree "Doctor"

Professional field: 4.1 Physical Sciences

Doctoral Program: "Electrical, Magnetic and Optical Properties of Condensed Matter"

Author of the dissertation: Blaga Hristova Blagoeva , IOMT-BAS

Scientific supervisors: Prof. Dr. Lian Nedelchev and Prof. Dr. Dimana Nazarova

Consultant: Prof. DSc. Elena Stoykova

Topic of the dissertation: " Photoanisotropic media for optical recording , sensitive in the visible and ultraviolet spectral range"

Prepared by the review: Vera Marinova Gospodinova, Professor, DSc., IOMT- BAS scientific jury, appointed by order of the Director of IOMT-BAS No. RD-15-790/21.11.2024

1. Brief biographical data about the doctoral student

Blaga Hristova Blagoeva graduated from the Bachelor's program, major in "Medical Physics" at the Faculty of Physics of Sofia University "St. Kliment Ohridski" in 2014, and in 2017 she completed her Master's program in major "Quantum Physics, electronics and laser technique" at the same University. She started working at the IOMT-BAS in 2014, and in 2018 she was enrolled in a full-time doctoral program on the topic "Photoanisotropic media for optical recording, sensitive in the visible and ultraviolet spectral range".

Since the beginning of her scientific career, Blaga Blagova has personally participated in 16 international and national conferences and seminars, where are presented 6 oral and 12 poster reports , with the total number of co -authored reports being 60.

Blaga Blagoeva is a co-author of a patent "System for improvement on polarizing parameters on holographic diffraction optical element representing circularly polarized beam splitter ", together with her colleagues from IOMT-BAS.

The doctoral candidate is the winner of the prestigious "Ivan Evstratiev Geshov" award for achievements in science direction "Nanosciences, new materials and technologies" of the Bulgarian Academy of Sciences in 2023 and the award "Outstanding Young Scientist in the Field of Optical Materials and Technologies" of the Institute of Optical Materials and Technologies "Acad. Y. Malinovski", Bulgarian Academy of Sciences, also won in 2023.

Blaga Blagoeva wins the first place for oral participation report in the field of "Nanosciences, new materials and technologies" of the 2-nd interdisciplinary doctoral forum and first award for "the Best poster" at VII National student scientific conference on physics and engineering technologies.

She served as a member of expert group associated to the National agency for assessment and accreditation (NAOA).

2. Data about the dissertation

The dissertation is dedicated to the development of photoanisotropic media (azopolymers and azodyes) sensitive in the visible and ultraviolet spectral regions for polarization holographic recording.

The photoanisotropic media, the subject of research in the Thesis work, have the unique ability to register polarization condition on light and have enormous potential for applications in polarization holography, for making diffractive optical elements, for security holograms, in virtual and augmented reality devices, imaging systems, and many others.

The dissertation consists of 146 pages and includes: Introduction, Aim and Objectives, three sections, Conclusion, Main Contributions, List of the author's publications on the dissertation, Bibliography. Participation in projects related to the topic of the dissertation is listed. The Thesis work contains of 66 figures, 12 tables and 223 cited sources.

2.1. Relevance of the problem developed in the dissertation

The aim of the dissertation is to establish the optimal parameters for inducing birefringence and implementing polarization holographic recording in photoanisotropic materials such as azopolymers and azodyes, sensitive in the visible and ultraviolet spectral regions.

The subjects of research are organic materials ranging from different groups of azopolymers – four azopolymers with azochromophores in the side chain (three amorphous and one liquid-crystalline); four azo dyes; a stilbene-based polyimide and two Schiff bases in a polymer matrix.

Undoubtedly, the topic is extremely relevant and interesting, due to the combination of two important aspects - on one hand, the development of photoanisotropic materials, sensitive in a wide spectral range, following the requirements of modern technologies for achieving high values of birefringence and reversibility of recording (high stability of the write-erase cycles) . On the other hand, the development of modern optical elements and devices, for example, polarization diffraction optical elements, optical switches, etc. In this aspect, the ability to form supramolecular chiral structures is of high importance, as the direction of the chiral structure can change when the sign of the ellipticity of the incident light changes.

Another important property of materials for optical recording and polarization holography is the possibility of multiple cycles of recording and erasing information.

The combination of these factors is of utmost importance for the development of modern experimental technologies, especially since IOMT has long-standing traditions in this field.

To achieve the goal, the doctoral student has set herself the following tasks :

- Deposition of thin homogeneous layers with high optical quality;
- Determination of the photoanisotropic parameters of the samples and tracking of the recording and erasing parameters of the birefringence Δn;
- Study of the spectral dependence of Δn induced in an azopolymer;
- Recording optical elements and devices: polarization diffraction optical elements and optical switch;
- Computer modeling of the diffraction efficiency of surface relief gratings in an azopolymer.

2.2. Knowledge of the state of the problem and analysis of literature data

The literature review covers an overview of photoanisotropic materials and their ability to transition from an isotropic to an anisotropic state under the action on linear polarized light, expressed in a change in optical properties constants (birefringence and dichroism). The phenomenon is due to the reversible trans-cis isomerization and is associated with reorientation on specific chromophores under impact on polarized light, playing an essential role in the formation on supramolecular chirality and surface relief of a grid.

The literature review examines in great detail the basic molecular processes under the influence of polarized light in some organic materials (e.g. azo compounds, stilbenes and Schiff bases), in which linear and circular birefringence are induced. The ways to achieve high values of birefringence and the importance of these values for the development of holographic optical elements are discussed.

As one of the preferred materials for work, appropriately chosen by the doctoral student is the azopolymer PAZO , well-studied material and commercially available, allowing comparison of data reported in the literature, and on the other hand easy to work with and still opening up new possibilities for applications. The azopolymer PAZO provides high values of induced birefringence (even in the short-wavelength region of the spectrum) , with recording being optically reversible or thermally erasable.

The literature review is written on the basis of 182 sources (out of a total of 232 for the entire dissertation), most of which have been published in recent years. This demonstrates the candidate's excellent awareness and in-depth knowledge of the issues on the topic of the dissertation.

2.3. Research methods in response to the set goals and objectives

To achieve the goals, Blaga Blagoeva has used various approaches: from selecting a suitable method for depositing layers with a smooth surface and high optical quality, to surface analysis and selection of optical set-ups for implementing polarization holographic recording and measuring diffraction efficiency, response time, erasure time and recording of holographic optical elements - all of them very well combined and thought out.

For example, a spin-coating deposition method was used to deposit the layers, and various methods were used to determine the thicknesses of the resulting layers: profilometric, interferometric (based on thin-layer interference) , and spectrophotometric.

For drying of the prepared solutions a method is applied using dynamic speckle analysis, which includes statistical processing on correlated in the time sequences from speckle images (e.g. drop of azopolymeric solution in solvent as water or methanol), formed on the surface of glass. The method is based on the high one sensitivity on speckle to micro-changes on the topography and/ or the refraction index of the studied object. In this way is evaluated the speed of drying of the polymer solution in dependance from the substrate temperature.

Another method is Atomic Force Microscopy (AFM), used for determination of the topography on the surface of the deposited layers, as well as roughness parameters. For determination of mechanical properties (universal hardness, hardness on indentation, module on elasticity and elastic component) the method of sensorics indentation . Analized is also the behavior at slippage on the tested materials and it has been established elastic-plastic behavior for all azopolymers.

To optimize the processes and the stability of the holographic recording, key parameters such as highest value of Δn, high stability over the time, and achieving the fastest response time have been studied by constructing different optical setups. Various wavelengths of laser radiation were used - 355 nm, 442 nm, 491 nm, 514 nm and 532 nm, and variety of the polarization states.

Also, computer modeling is presented, which study the development factors of various holographic optical elements, inducing the diffraction efficiency of surface relief gratings, recorded also in azopolymer PAZO, at different spatial frequencies, profile and height on the relief through computer software GSolver. The resulting theoretical surface analysis is compared with the experimental results .

Here it should also be noted the long years experience and expertise of the scientific supervisors and consultant of the doctoral student from Holography group at the IOMT-BAS, under which leadership Blaga Blagoeva has very successfully achieved the set goals, as well as the very successful cooperation with the colleagues from the University of Chemical Technologies and Metallurgy in Sofia, who assisted in the synthesis of azo dyes CAD-Q and CAD-N , the subject of research in the dissertation work .

2.4. Analysis of the obtained results

The research results in the dissertation are presented in three Chapters, the last of which is dedicated to applications. of the studied azopolymers as optical switches and polarization diffraction elements. Each chapter ends with brief conclusions.

In **the First Chapter** the main groups organic materials (azo compounds, stilbenes and Schiff compounds bases) are presented as well as the mechanisms, which induces linear and circular birefringence under impact on polarized light. It has been discussed the way in which the supramolecular chiral structure can accomplish polarization holographic record. Special attention is paid to the influence of the formed chiral structures on the values of diffraction efficiency, with the main ones presented and discussed factors related to height on the relief of the formed surface gratings for applications like optical switches and polarization diffraction elements.

Second Chapter is dedicated to the characterization and preparation of the thin layers of selected organic materials, of which four azopolymer with azochromophores in the side chain, four azo dyes and two Schiffs bases in polymer matrix, as well as polyimide on the base of stilbene. Different methods of thin film deposition are compared, with special attention paid to the choice on suitable solvent in order to maintain excellent optical qualities and surface quality of the layer. For some of the materials the drying process of azopolymeric solutions is tracked through application of the dynamic speckle analysis method. Moreover, studies on superficial topography, microstructure and micromechanical characteristics are presented.

The photoanisotropic parameters when irradiating the materials with linearly polarized light with a wavelength from the visible and ultraviolet regions of the spectrum were examined and compared. An analysis on the photoanisotropic parameters for application as optical elements has also been made. Special attention is paid to the research

of the possibility for multiple recordings and erasing of the photoinduced birefringence, according to the required maximum birefringence modulation (Δn_{max}), the response time (τ) and the decay time (r) to keep the same values at each consecutive cycle.

Chapter 3 is devoted to the holographic recording of polarization-selective optical elements and structures. It is shown the formation of supramolecular chiral structures operating as optical switch in the azopolymers PAZO, P_1, P_{1-2} and P_2, and the azo dyes DR_1 and DR_{13}. For PAZO and P_{1-2}, the influence of intensity on the laser radiation on the process on formation of chiral structures. The reversibility of the direction on chiral structures through change on the sign on ellipticity on polarization is studied further. The process of holographic recording of polarizing gratings in the azopolymer PAZO is presented in details, as it has been proposed method for improvement the polarization properties of an optical element functioning as circular polarization beam splitter. Presented is computerized modeling on diffraction efficiency on relief grating, recorded in PAZO, at different spatial frequencies, profile and height of the grating. The formation of supramolecular chiral structures operating as optical switchers is shown. The influence of the type of solvent and the thickness of the layer on the properties of an optical element, representing a circular polarization splitter, was examined and a method for improving its polarization properties was proposed.

The experimental results and conclusions presented in the thesis work show that the goals and objectives of the dissertation have been fully achieved.

2.5. Scientific and applied- scientific contributions in the dissertation work

I agree with the formulated contributions of the thesis work, which belongs to **scientific-applied nature** and can be briefly summarized as follows:

- **For the first time** the spectral dependence of the birefringence induced in azopolymer PAZO has been reported at the optimal wavelength of 442 nm. It was obtained the optimal concentration of the azo dye DR1 relative to the PMMA matrix, at which has been achieved higher maximum value on birefringence compared to the reported so far in the literature. Birefringence has also been successfully induced at 355 nm in the polymers PAZO and PI-St, the azo dyes CAD-Q and CAD-N, as well as the Schiff SB-S and SB-N bases. It has been demonstrated the potential of above materials for development on polarizing diffraction elements operating in a wide spectral range .

- **A new, original method** was proposed to improve the polarization properties of an optical element, which is a circular polarization splitter, consisting of applying a transparent adhesive PAZO layer on the surface and placing a microscopic glass, thus successfully suppressing the process of formation of surface relief. Circular polarization beam splitter can be used for construction of spectral polarimeter. I define this achievement as **innovative and original.**

- The influence of the solvents (water or methanol) on the optical quality of the obtained PAZO layers and on the parameters of the recorded surface relief gratings

was determined. Using a methanol solvent, a surface relief grating with a height of 528 nm compared to a 625 nm layer thickness was obtained. The applied dynamic speckle analysis of the drying process confirms that the methanol solution layers are of much better optical quality than those obtained from aqueous solution.

- Supramolecular chiral structures have been successfully formed in the azopolymers PAZO and P1-2, which can be used as an all-optical switch. It has been experimentally shown that the direction of the chiral structure changes when the sign of the ellipticity of the incident light changes. The results presented in the dissertation **are original and reliable.**

3. **Assessment of the PhD student's personal contribution**

I have known Blaga Blagoeva since she started working at IOMT and I am very impressed with her professional progress .

From my personal impressions, I believe that the work carried out on the dissertation thesis is mainly her work. Knowing the ambitious work of the team at which Blaga Blagoeva works and her scientific supervisors and consultant, undoubtedly the results in this dissertation will open new possibilities for applications of azopolymer materials for the development of new, modern holographic optical elements for the next generation polarization optics.

Here I should note that over the years Blaga Blagoeva has also actively participated in various scientific projects at the national and international level - currently 15 in number.

Blaga Blagoeva is the author of a total of 40 publications and has over 52 independent citations, h-index 7. She has participated in over 40 international conferences and scientific forums with a total of 69 invited papers, oral presentations and poster presentations.

4. Dissertation publications

The dissertation is written based on 9 publications in journals such as *Photochemical and Photobiological Sciences ; Journal of Photochemistry & Photobiology A: Chemistry ; Thin Solid Films* etc., of 3 which have an impact factor. It should be noted here that Blaga Blagoeva is the first author in five of the publications submitted to the competition.

There are 14 citations on the topic of the dissertation, 5 of which are to the publication "Tautomeric influence on the photoinduced birefringence of 4-substituted phthalimide 2-hydroxy Schiff bases in PMMA matrix", in *Photoch. Photobio. Sci* from 2021, in which Blagoeva is the first author and 9 citations of the article *"Optical anisotropy induced at five different wavelengths in azopolymer thin films: Kinetics and spectral dependence"* in *Journal of Photochemistry & Photobiology A: Chemistry* from 2019

The results of the dissertation have also been presented in the form of reports or poster presentations at 14 scientific forums.

The high publication activity of the doctoral student, as well as the number of citations noted, are an excellent indicator of the relevance of the scientific problem and the significance of the results.

5. Evaluation of the Abstract booklet

The Abstract booklet is very well-structured and meets the requirements for volume and content. The main activities, obtained results and contributions of the dissertation work are listed.

6. Critical notes and questions

I have no critical comments on the dissertation.

I have the following questions and comments:

- On Page 41, Fig. II.6 the dependences of the absorption coefficient of thin layers at different concentrations of azo dye DR1 relative to the polymer matrix PMMA are presented. What is the thickness of the layers under this study and what accounts for the variation in the absorption coefficient from the percentage content (for example, at 500 nm)?
- What is the reason for the increase in Δn during the relaxation process of P2 (Figure II.26 b, p. 61) after irradiation with 444 nm ?
- On Page 60, Fig . II.25 the dependences of Δn for azopolymer PAZO at irradiation with different wavelengths and on wavelengths: 355 nm, 442 nm, 491 nm, 514 nm and 532 nm are subsequently summarized in Table II.6. What are the considerations for choosing precisely these values for the thicknesses ?
- I congratulate the doctoral student and the supervising team for the proposed method for applying a transparent adhesive on a PAZO layer in order to suppress the formation of a surface relief grating, which, as can be seen from Fig . III.17, has a very significant contribution to the diffraction efficiency. Are there other ways to increase the $+1^{st}$ order diffraction efficiency of the recorded polarization holographic grating?

7. Reasoned and clearly formulated conclusion.

The presented dissertation work is original. The contributions in the dissertation are substantial and have a scientific-applied nature. The work done on the dissertation is enormous, a very large number of experiments have been done and many results have been summarized and analyzed.

Important results have been achieved, published in prestigious journals such as *Photochemical and Photobiological Sciences; Journal of Photochemistry & Photobiology A: Chemistry; Thin Solid Films, etc.* (quartiles Q1 and Q2) and others. In 5 of the mentioned articles on the dissertation, Blaga Blagoeva is the first author. Some of the results have also been presented at scientific forums.

So far, 14 citations have been noted, which proves the relevance of the topic being developed. Undoubtedly, Blaga Blagoeva's contribution is significant.

The dissertation submitted to me for review and the scientometric data of Blaga Blagoeva meet and even exceed the national requirements for awarding the ONS "doctor" in according to the Law on the Development of the Scientific Staff in the Republic of Bulgaria, as well as the requirements for the defense of a dissertation work in the Terms and Conditions Regulations for acquiring scientific degrees and for occupying academic positions at IOMT-BAS.

In conclusion, I express my agreement and recommend to the respected Scientific Jury to award the educational and scientific degree "doctor" in professional direction 4.1 Physical sciences, specialty "Electrical, magnetic and optical properties of condensed matter" to Blaga Hristova Blagoeva.

08.01.2025

Reviewer:

/Prof. DSc. Vera Marinova/