OPINION

on the PhD dissertation for awarding the educational and scientific degree "Doctor of Philosophy" in higher education area 4. Natural Sciences, Mathematics and Computing, professional field 4.1. Physical sciences, doctoral program Electrical, magnetic and optical properties of condensed matter

PhD candidate: Blaga Hristova Blagoeva, Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences

Scientific supervisors: Prof. Lian Nedelchev, PhD, and Prof. Dimana Nazarova, PhD

Dissertation title: "**Photoanisotropic media for optical recording sensitive in the visible and ultraviolet spectral regions**"

Member of the scientific jury, appointed by order № RD-15790/21.11.2024 of the Director of IOMT-BAS: Assoc. Prof. Silvia Emilova Angelova, PhD; Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences

I. Biographical information

Blaga Hristova Blagoeva graduated with a Bachelor's and Master's degree from the Faculty of Physics of Sofia University "St. Kliment Ohridski" in 2014 and 2017 respectively. Since 2014 she has been working at IOMT-BAS, Optical Metrology and Holography Department as a technician, after obtaining her Bachelor's degree - as a physicist. From the attached diploma for the Master's degree it can be seen that she graduated with an average grade of 5.93 and an average grade of 6.00 in her thesis on "Thermally and optically reversible anisotropy in azopolymers". She was enrolled as a full-time PhD student at IOMT-BAS in 2018.

II. General description of the dissertation

The dissertation submitted for review on "Photoanisotropic media for optical recording sensitive in the visible and ultraviolet spectral regions" has a total length of 140 pages and is structured as follows: It consists of a list of abbreviations, introduction, literature review (chapter 1), results and discussion (chapters 2 and 3), conclusion, main contributions, list of publications used in the thesis, list of papers presented, list of project contributions, appendix, and bibliography. The dissertation contains 66 figures and illustrations and 12 tables. The bibliography includes 223 references. The literature used is focused on the research problem. The appendices are directly relevant to the material in the thesis and should be considered as part of the thesis. The presentation in the dissertation is well structured and logical, supported by illustrative material and tables of results. The dissertation is accompanied by an abstract of 42 pages, which follows its structure and reproduces its contents with the exception of the literature review, the list of papers presented, the list of project contributions and the appendix.

The literature review introduces the reader to the molecular processes occurring in some organic materials (azo compounds, stilbenes and Schiff bases) under the influence of polarized light. These processes in photoanisotropic materials give rise to linear and circular birefringence. The importance of high values of birefringence for media intended for optical

recording as well as for the development of optical switches and polarization diffractive elements is elucidated.

The aim of the dissertation is to establish the optimal parameters for birefringence induction and for polarization holographic recording in photoanisotropic materials sensitive in the visible and ultraviolet spectral regions. To achieve the aim, the PhD student formulated the following research tasks:

1. Deposition of thin homogeneous layers with good optical quality;
2. Determination of the photoanisotropic parameters of the samples and tracking of the recording and erasure parameters of the birefringence Δn;
3. Investigate the spectral dependence of Δn induced in azo polymer;
4. Preparation of optical elements and devices: polarization diffraction optical elements and optical switch;
5. Computer modeling of diffraction efficiency of surface relief gratings in azopolymer.

Various research techniques and approaches have been successfully applied for the study. These methodological approaches quite accurately meet the research objectives and make the achievement of the goal possible.

III. Main scientific results

The dissertation describes the study of a total of eleven different polarization holographic recording media sensitive in both the visible and ultraviolet spectral regions: four polymers with azo chromophores in the side chain (P_1, P_{1-2}, P_2, PAZO), a stilbene-based polyimide (PI-St), two disperse (DR1, DR13) and two coumarin-based (CAD-Q, CAD-N) azo dyes dispersed in a polymer (PMMA) matrix, two Schiff bases (SB-S, SB-N), also dispersed in PMMA. The dynamic speckle analysis method was applied to follow the drying process of azopolymer solutions. Studies of surface topography, microstructure and micromechanical characteristics of some of them are presented. The photoanisotropic parameters of the materials when irradiated with linearly polarized laser light of wavelengths in the visible and ultraviolet part of the spectrum are investigated and compared.

The possibility of multiple cycles of induction and optical erasure of birefringence in P_{1-2}, PAZO, CAD-Q, CAD-N and SB-N is demonstrated. It has been found that for the induction of birefringence in the so-called in this dissertation "guest-host" systems (polymer matrices doped with dye), both the parameters of the pumped radiation and various characteristics of the sample, such as e.g. type of polymer matrix and azo dye concentration, play an important role. The PAZO polymer has been identified as the most suitable for experiments involving polarization holographic recording. The conditions for obtaining PAZO thin films for polarization holographic recording, namely solvent type and specimen thickness, were optimized. A method for improving the polarization properties of an optical element representing a circularly polarizing light splitter is proposed. Data from computer modeling of the diffraction efficiency of surface relief gratings in PAZO are presented.

IV. Contributions and significance of research

The research described in this dissertation is in a cutting-edge area that is particularly relevant nowadays - the field of optical technology. The results reveal the role of individual factors in the induction of birefringence and in polarization holographic recording in different types of photoanisotropic media. Optimization of the conditions at each stage of the

development of optical elements based on these media, from layer deposition processes to element recording, is of great importance for their high efficiency and reliability. The dissertation contains scientific results that are fundamental in nature and contribute to the understanding of the properties of matter and specific phenomena. At the same time, the results have practical significance - there is a possibility of using them to improve materials and technologies used in practice.

The main contributions formulated in the dissertation accurately reflect the scientific results:

- The spectral dependence of birefringence induced in the PAZO azopolymer is reported for the first time. It is shown that this azopolymer can be used to record polarization diffraction elements operating over a wide spectral range. The birefringence parameters in some of the investigated photoanisotropic media have been optimized.
- A method for improving the polarization properties of an optical element representing a circularly polarizing light splitter is proposed.
- The influence of the type of solvent (water and methanol) on the optical quality of the PAZO layers obtained from the solutions and on the parameters of surface relief gratings recorded in this azopolymer is established.
- Supramolecular chiral structures were observed in the PAZO and $P_{1\text{-}2}$ azopolymers, which can act as an all-optical switch.

V. Assessment of publications and personal contribution of the candidate

The research on the topic of the dissertation has been published in full or in part in 9 scientific papers in full text. There are 14 citations of 2 publications related to the dissertation. Of the publications included in the dissertation, 1 is in a Q1 journal, 2 in a Q2 journal. Blaga Blagoeva is first author in 5 of the 9 publications, second author in the other 2, which is a clear indicator of her contribution to the research.

VI. Critical remarks and recommendations

The PhD student has a very clear writing style, which helps make the material presented in the dissertation understandable. A description is made of the chemical structure of the main groups of compounds investigated, of phenomena such as isomerism (stereoisomerism and prototropic isomerism), but there are small inaccuracies in the expression, such as the statement on page 19 that "Schiff bases have not only spatial isomeric (*trans-cis*) forms, but also enol-keto tautomers (a type of structural isomerism)". This leaves the impression that it applies to all Schiff bases (which is not true), not just to the structures shown in Fig. I.6. Furthermore, keto-enol tautomerism is observed in many other compounds, including azo dyes in the presence of groups where proton migration can take place.

I recommend the use of the accepted terms *keto-enol* tautomerism and *host-guest* systems instead of *enol-keto* tautomerism and *guest-host* systems.

The remarks and recommendations made do not diminish the value of this dissertation.

VII. Conclusion

The dissertation of Blaga Blagoeva represents a focused, well-planned (and qualitatively executed) study of photoanisotropic materials for optical recording, sensitive in the visible and ultraviolet spectral regions. The achieved results and the way they are presented

in publications and in the dissertation give me reason to give a high evaluation. A large amount of research work has been carried out at a high level, and the PhD student has used a wide range of methods.

The dissertation fully meets the requirements for the award of the PhD degree. On the basis of the scientific contributions and the significance of the dissertation work, I express my positive opinion and propose the members of the esteemed scientific jury to award the educational and scientific degree "Doctor of Philosophy" in the professional field 4.1. Physical Sciences to Blaga Hristova Blagoeva.

Sofia
26.12.2024 г.

/Assoc. Prof. Silvia Angelova, PhD/