SUMMARY OF THE MAIN RESULTS AND SCIENTIFIC CONTRIBUTIONS
as a part of the application of Dr. Ani Stoilova in the competition for the academic position of "Associate Professor" in 4.1 Physical Sciences (Electrical, magnetic and optical properties of the condensed matter), announced by UCTM in the Government Gazette №14 /18.02.2022

The presented scientific activity includes 21 articles, 13 of them published in impact factor journals (General IF= 23.22) and 8 in referenced and indexed in academic research databases journals without impact factor. They are a result of a team work conducted in the scientific research groups of prof. Plamen Petkov (UCTM) and prof. Dimana Nazarova (IOMT-BAS).

The main topics of the research conducted could be classified in the following two areas:
(1) Development of new polarization-sensitive materials and characterization of their structure and properties
(2) Polarization methods for visualization of morphological changes in biological tissues

The scientific contributions on lines (1) are of fundamental and applied significance in the field of the development of new optical materials based on chalcogenide glasses or azobenzenes. The results obtained on lines (2) have fundamental importance for the accumulation of statistics on the change in the state of the polarized light by its propagation in histological specimens, on which basis new, non-invasive methods for medical diagnosis are being developed. The studies on line (2) are also of applied significance in demonstrating the possibility, after appropriate reconstruction of images obtained with polarized light, to visualize pathomorphological changes in human tissues due to various diseases with better contrast.

Contributions of fundamental significance:

(1) Development of new polarization-sensitive materials and characterization of their structure and properties

- New bulk chalcogenide materials from the systems Ge-Se-In, Ge-Se-B and Ge-Te-Cu have been synthesized [5_6a; 10_6г] with a composition that has not been reported so far in the scientific literature.
- The atomic structure of newly synthesized chalcogenide glasses with the composition $(Ge_{0.2}Se_{0.8})_{85}B_{15}$ and $(Ge_{0.2}Se_{0.8})_{85}In_{15}$ has been studied with X-ray diffraction, Neutron diffraction and Extended X-ray Absorption Spectroscopy. The experimental data were modelled simultaneously with the reverse Monte Carlo simulation method. GeSe4/2 tetrahedra are shown to be the main structural units in the binary and ternary glasses investigated. The excess Se atoms build homonuclear Se-Se bonds. The addition of either In or B atoms results in the formation of Se-In, respectively Se-B bonds, as indium, respectively boron, binds predominantly to selenium atoms from the Se-Se chains [5_6a].
- The structure of new bulk chalcogenide materials from the system Ge-Te-Cu was studied using XRD analysis. The results show that the new materials are crystalline and consist of $GeTe_4$ and $CuTe_4$ tetrahedra and tellurium chains. Basic crystallographic parameters have been determined.
- Thin film materials for application in the optoelectronics have been prepared from newly synthesized chalcogenide bulk samples [1_6г, 6_6г, 9_6г], as well as composite materials based on new azo dyes crosslinked in a polymer matrix [1_6, 6a, 3_6] and on the azo polymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], shortly PAZO, doped with

chalcogenide particles [11_6a, 10_6г] or with particles of new metal complexes [1_6a, 3_6г]. The layers were prepared using different methods - vacuum thermal evaporation, electro-spray deposition, spin-coating.

- The processes of vacuum evaporation and condensation in the Ge-Se-In system were investigated. The determination of the evaporation and condensation energy as a function of the chalcogen content is an important parameter when optimizing the conditions for fabrication thin layers with predefined properties. [9_6г].
- Optical parameters of new chalcogenide thin film materials [7_6a] and of composite layers based on the PAZO azo polymer doped with particles of new chalcogenide materials or new metal complexes were determined [1_6a, 11_6a, 3_6г, 10_6г].
- A new minimization procedure for calculating the complex refractive index of thin layers of azo polymers has been proposed [4_6г].
- It has been studied the kinetics of the photoinduced birefringence in thin film materials based on: New N-phthalimide azo-azomethine dyes [4_6a]; New perylene bis azo-imide dyes [3_6a]; Copolymers with different weight ratios of two monomers which differ in the length of the spacer between the azochromophore and the polymer backbone [8_6г]; The commercially available PAZO polymer doped with chalcogenide particles [10_6г] or with particles of new metal complexes of the hydantoin [5_6г].
- For the first time, results of measuring the kinetics of the photoinduced birefringence in layers based on Schiff bases undergoing tautomeric conversation has been reported [9_6a].
- A relationship has been established between the amount of the photoinduced birefringence (Δn) in the thin film materials listed above and the type and the number of the chromophore groups, the presence of donor or acceptor substituents in the molecule, the crosslinking of the dyes in a polymer matrix or the doping of the azo polymer. An increase in the maximum value of the photoinduced birefringence has been observed for the composite layers crosslinked in a matrix [3_6a] and for those based on the PAZO polymer doped with Cu(II) 3-amino-5,5'-dimethylhydantoin or with Ni(II) 3-amino-5,5'-dimethylhydantoin particles [1_6a, 5_6г] in comparison to the pure PAZO films. By the composite layers based on the newly synthesized perylene bis azo-imide dyes (Fig. 2), a higher value of the maximum induced birefringence was measured for those containing electron donor groups in the phenylazo fragments [3_6a] in comparison to those containing electron-acceptor groups. The presence of electron acceptor substitutes in this case leads to a faster response. The composite layers based on the newly synthesized dyes containing the two chromophore groups –CH = N– and –N = N–, show lower amount of the maximum induced birefringence compared to those prepared from the dyes containing only the –N = N– group [4_6a]. The simultaneously effect of the azo (-N = N-) and azomethine (-CH = N-) groups on the amount of the photoinduced birefringence in anisotropic media has not been reported in the scientific literature to date.
- The diffraction efficiency in thin amorphous chalcogenide layers from the binary system Ge-Se and from the ternary Ge-Se-Ga (In) systems has been measured. It has been established that the addition of a third component to the binary Ge-Se system improves the optical response of the material. It was established that the thin film materials containing indium show higher diffraction efficiency in comparison to those containing gallium [1_6г].

(2) Polarization methods for visualization of morphological changes in biological tissues

- Statistical data has been accumulated on the changes of parameters of the polarized light by its propagation within histological specimens of lung and liver tissues characterized by morphological changes due to various diseases [8_6a, 10_6a].

II. Contributions from applied significance

(1) Development of new polarization-sensitive materials and characterization of their structure and properties

- Multiple optical recording was performed in thin film materials based on new azo dyes [3_6a, 4_6a; 9_6a].
- Diffraction gratings were recorded in composite layers based on the PAZO azo polymer doped with Cu(II) 3-amino-5,5'-dimethylhydantoin or with Ni(II) 3-amino-5,5'-dimethylhydantoin particles [1_6a]. Highest relief was observed for the composite materials containing particles at the concentration of which the maximum birefringence was measured. Along with the anisotropic grating in the volume of the media, surface relief is also formed.

(2) Polarization methods for visualization of morphological changes in biological tissues

- Orthogonal polarization images of human lung and liver histological specimens were obtained. The images show improved contrast in comparison to the images obtained with unpolarized light or before a reconstruction aiming to limit the contribution of the photons scattered from the depth of the biological samples to the final image. [8_6a, 10_6a].

SUMMARY OF THE MAIN RESULTS

[1_6a] Stoilova, G. Mateev, D. Nazarova, L. Nedelchev, E. Stoykova, B. Blagoeva, N. Berberova, S. Georgieva, P. Todorov, Polarization holographic gratings in PAZO polymer films doped with particles of biometals" Journal of Photochemistry and Photobiology A: Chemistry", 411, 2021, 113196, IF=3.982

Thin films based on the commercially available azo polymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]) doped with particles of the transition biometals nickel and copper complexed by aminohydantoin ligands, Cu(II) 3-amino-5,5′-dimethylhydantoin (CLP) and Ni(II) 3-amino-5,5′-dimethylhydantoin (NLP), were spin coated. In the so prepared composite films were recorded, using a He-Cd gas laser with wavelength 442 nm, stable in the time polarization holographic gratings and their diffraction efficiency was studied. The influence of the dopants composition and concentration on the parameters of the recorded in the composite films gratings has been discussed. Significant enhancement in the value of the surface relief height and of the diffraction efficiency has been observed for the hybrid materials in comparison to the pure PAZO polymer film. Diffraction efficiency of 33.0 % and profile height of 586 nm have been achieved for the composite film doped with 1 wt.% particles of the Ni(II) 3-amino-5,5′-dimethylhydantoin. Among the samples from the series doped with particles of the Cu(II) 3-amino-5,5′-dimethylhydantoin highest diffrac-tion efficiency, $\eta+1$ =31.1 %, and highest profile height, h =586 nm, shows the composite film doped with 2 wt.% CLP.

[2_6a] A. Georgiev, A. Stoilova, D. Dimov, D. Yordanov, I. Zhivkov, M. Weiter, Synthesis and photochromic properties of some N-phthalimide azo-azomethine dyes. A DFT quantum mechanical calculations on imine-enamine tautomerism and trans-cis

photoisomerization, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 210, 2019, 230-244, IF=4.098

Three new N-phthalimide azo-azomethine dyes exhibiting tautomeric transformations with proton transfer to the azomethine group (-CH=N-) and E → Z photoisomerization of the azo group (-N = N-) (Fig. 1) have been synthesized. A laser-induced trans-cis-trans photoisomerization experiment in DMF solution and at room temperature was performed to evaluate the degree of photoisomerization and the photostationary state of the newly synthesized dyes, in view of the possibilities for their application as optical elements. The dye containing -NO_2 and -CH groups shows highest degree of isomerization, approximately 80% at λ_{max} = 624 nm, reached after 60 min time of irradiation.

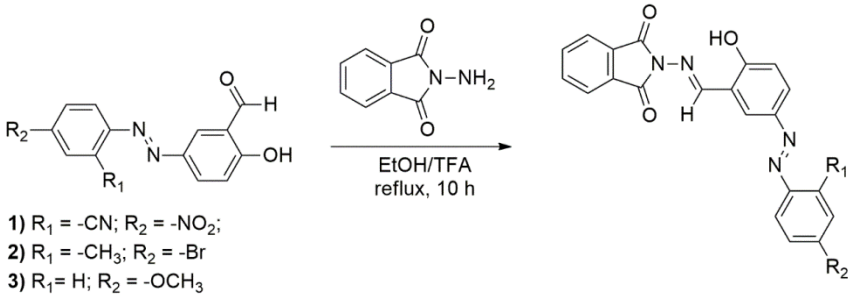
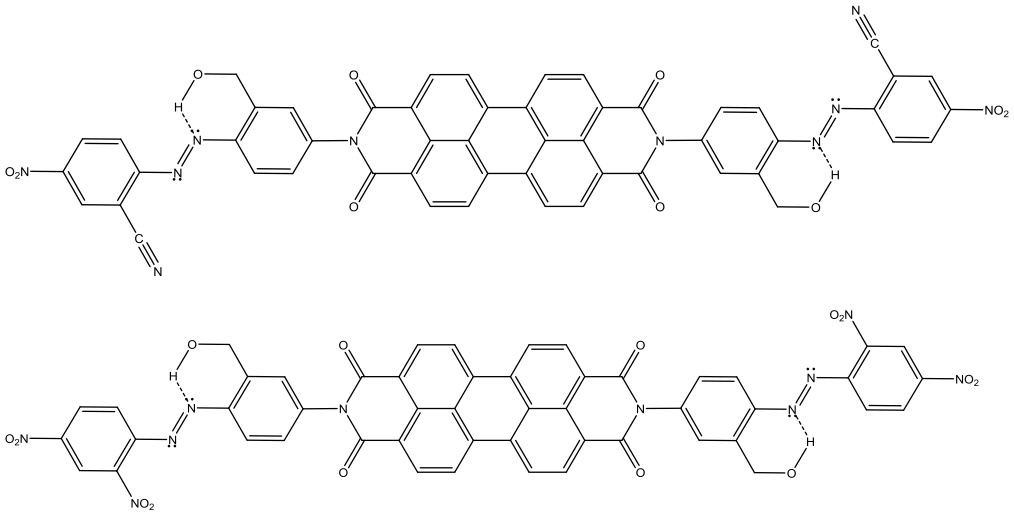


Fig. 1: Stricture of the new N-phthalimide azo-azomethine dyes.

[3_6a] A. Georgiev, D. Dimov, A. Stoilova, F. Markova, D. Nazarova, Vapour deposited nanocomposite films of perylene bis azo-imides with improved photoresponsiveness by visible light, Optical Materials 89, 2019, 5-**13 2.779**

The paper presents the preparation of composite thin films of three newly synthesized perylene bis azo-imides (PAD) in polyimide matrix (PI) (fig.2) and of single films of the same dyes by vapour deposition, results of DFT quantum chemical calculations, UV-VIS and fluorescence spectroscopy study of the thin films in order to investigate the nature of the electron transitions and donor-acceptor interactions between the phenylazo fragments and the perylene core as well as photoinduced birefringence measurements. A comparison between the photoresponsiveness of the single PAD dye films and of the composite films has been done. The results show an improved optical activity in the "host-guest" systems, whereby the increases of the dye concentration in the PI matrix favors the effect. The possibility for multiple cycles of photoswitching by visible light has been also demonstrated in the polyimide composite films.



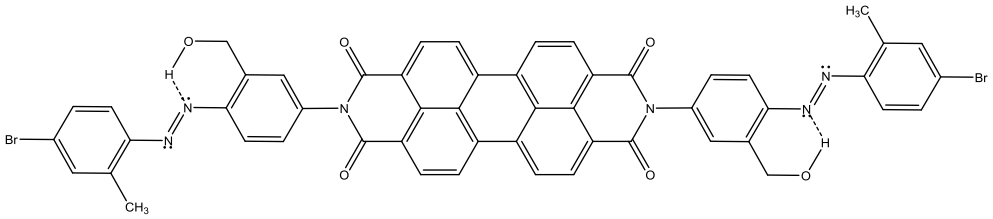


Fig. 2: Structure of the new PAD dyes.

[4_6a] A. Stoilova, A. Georgiev, L. Nedelchev, D. Nazarova, D. Dimov, Structure-property relationship and photoinduced birefringence of the azo and azo-azomethine dyes thin films in PMMA matrix, Optical Materials 87, 2019, 16-23, IF= 2.779

Thin "host-guest" films based on three newly synthesized by us 4-aminazobenzen and three new azo-azomethine dyes (fig. 3), containing different electron withdrawing and electron donating on o- and p- position in respect to the chromophore group, have been prepared through spin coating. PMMA was used as a polymer matrix. The photoinduced at 355 nm и 422 nm birefringence in the composite films was measured. Maximum value of the photoinduced birefringence was measured for the composite film containing Azo-3, respectively $\Delta n_{max}=4.11\times10^{-3}$ at λ=355 nm and $\Delta nmax=5.43\times10^{-3}$ at λ=442 nm. A relation between the structure of the dyes and the values of the maximum induced in the composite films birefringence was made in dependence on the type of the chromophore groups presenting in the dyes molecules. The thin layers containing azo-azomethine dyes show lower birefringence values compared to the layers based on the dyes containing only the –N = N– group. The samples containing two photosensitive functional groups, namely -CH=N– and -N=N–, show also lower saturation values of the induced birefringence in comparison to the thin layers based on the 4-aminazobenzen dyes.

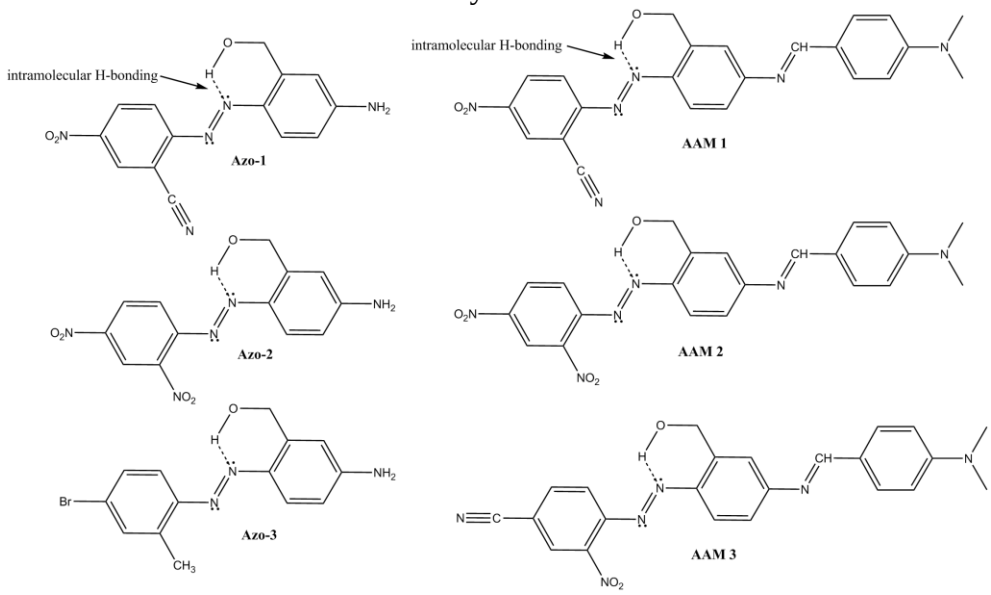


Fig. 3: Structure of the 4-aminoazobenzene (Azo-1, Azo-2 and Azo-3) and azo-azomethine dyes (AAM 1, AAM 2 and AAM 3).

[5_6a] Kaban I., P. Jóvári, T. Petkova, P. Petkov, A. Stoilova, B. Beuneu, W. Hoyer, Atomic Structure of (Ge0.2Se0.8)85B15 and (Ge0.2Se0.8)85In15 Glasses, Nanotechnological Basis for Advanced Sensors, 195-202, 2009

Chalcogenide bulk samples with composition (Ge0.2Se0.8) 85B15 and (Ge0.2Se0.8) 85In15 have been prepared in evacuated and sealed quartz ampoules by conventional

synthesis in a rotary furnace. The structure of the newly synthesized materials was studied using Extended X-Ray Absorption Fine Structure (EXAFS), synchrotron X-ray diffraction and neutronography (ND). The experimental data were compared with the theoretical ones obtained using the Reverse Monte Carlo simulation method, and an atomic structure model of the newly synthesized materials is proposed, according to which: GeSe4/2 tetrahedra are the main structural units of all the glasses studied; The excess Se atoms build homonuclear Se-Se bonds. Addition of either In or B atoms results in the formation ot Se-In, respectively Se-B bonds.

[6_6a] I. Mitov, A. Stoilova, B.Yordanov, D. Krastev, Technological research on converting iron ore tailings into a marketable product, Journal of the Southern African Institute of Mining and Metallurgy, 121 (5), 2021, 181–186, IF=0.69

We present three technological scenarios for the recovery of valuable components from gangue, stored in the tailings dam at Kremikovtzi metallurgical plant in Bulgaria, into marketable iron-containing pellets. In the first approach the iron concentrate was recovered through a two-stage flotation process, desliming, and magnetic separation. In the second proposed process, the iron concentrate was subjected to four sequential stages of magnetic separation coupled with selective magnetic flocculation. The third route entails the not very common practice of magnetizing roasting, followed by selective magnetic flocculation, desliming, and magnetic separation. The iron concentrate was pelletized in a laboratory-scale pelletizer. The main mineral constituents of the iron ore tailings, were determined using XRD. Each technology has been assessed with regard to the mass yield of iron concentrate, the iron recover and the iron, lead, and zinc content in order to identify the most effective route.

[7_6a] P. Petkov, A. Stoilova, Y. Nedeva, E. Petkov, Optical behaviors of thin indium-containing chalcogenide films, Surface and Interface Analysis 42 (6-7), 2010, 1235-1238, IF=1.374

The optical behavior of vacuum thermal evaporated thin layers from the system $(GeSe5)_{1-x}In_x$, where x = 0; 5; 15 and 20 mol.%, was studied. The thin films transmission and reflection spectra were measured in the range between 400 and 2500 nm. It was calculated the refractive index (using the Swanepoel method), the extinction coefficient, the absorption coefficient and the optical band gap of the deposited layers before and after annealing below the glass transition temperature. The results show, that the values of the refractive index and the extinction coefficient decrease with increasing the wavelength, as the addition of indium leads to a slight increase in the values of the refractive index. The optical band gap of the thin layers decreases by increasing the concentration of the indium as well as after the thermal annealing.

[8_6a] Stoilova, B. Blagoeva, D. Nazarova, E. Stoykova, N. Berberova-Buhova, L. Nedelchev, A. Machikhin, Visualization of pathologic changes in liver tissue via polarized light, accepted for publication in Optica Applicata, IF=0.673

Experimental studies on the change in the polarization state of the light by its propagation within histological human liver samples with different diagnosis were carried out. The results have shown that the azimuth and the light power could be used to discriminate among healthy and unhealthy tissue as well as among liver tissue pathologies from different origin. By the use of an optical system proposed by Jacques and Lee [Jacques et al. 1998], constituted of a light source, a polarizer, a sample and an analyzer placed in front of a CCD camera that rotates to allow acquiring of images with light polarized in planes parallel (Ppar) and perpendicular (Pper) to the polarization plane of the incident light, and after

reconstruction by the formula Ppol = (Ppar - Pper) / (Ppar + Pper), images of the above mentioned histological specimens, which provide better contrast compared to the nonreconstructed images, were obtained.

[9_6a] B. Blagoeva, A. Stoilova, D. Dimov, D. Yordanov, D. Nazarova, A. Georgiev, L. Antonov, Tautomeric influence on the photoinduced birefringence of 4-substituted phthalimide 2-hydroxy Schiff bases in PMMA matrix, Photochemical & Photobiological Sciences (2021) 20:687–697, IF=3.982

Composite films based on two novel 4-substituted phthalimide 2-hydroxy Schiff bases (Fig. 4a and 4b) embedded into PMMA matrix has been prepared through spin coating. Theoretical DFT calculations have been carried out to provide a simplified model of ground and excited state enol/keto tautomerization and Z/E isomerization energy landscape. The photoinduced birefringence at appropriate wavelength and by varying the laser power was measured in the composite films. Highest value of the photoinduced birefringence was measured for the sample containing the Shiff bases (b) on fig. 4, $\Delta n_{max}= 2.8 \times 10^{-3}$, at λ=442 nm and P=170 mW. Highest stability of the recorded birefringence, $r_{after\ 3\ min}$ =99%, was reached by the same composite film but by irradiating at 355 nm and laser power 8.7 mW. The composite film containing the Shiff base (a) from fig. 3, shows maximum value of the photoinduced birefringence at 355 nm and laser power 13.5 mW, respectively $\Delta n_{max}= 1.3 \times 10^{-3}$. The results have been interpreted as a function of the switching ability of the newly synthesized Shiff bases in solid state.

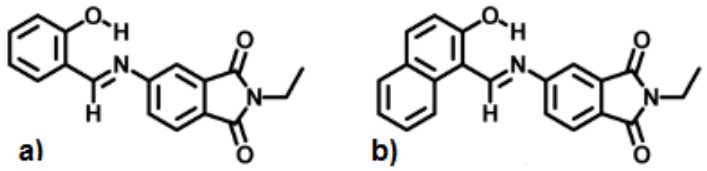


Fig. 4: Structures of the 4-substituted phthalimide 2-hydroxy Schiff bases 4 and 5

[10_6a] A. Stoilova, D. Nazarova, B. Blagoeva, V. Strijkova, P. Petkov, Polarized light for detection of pathological changes within biological tissues, Nanoscience and Nanotechnology in Security and Protection against CBRN Threats, 2020

Images of human lung specimens with different histological diagnosis were acquired using a polarization microscope and reconstructed in accordance to the method proposed by Jacques and Lee [Lasers in surgery: advanced characterization, therapeutics, and systems VIII: polarized video imaging of skin. In: SPIE. BiOS '98 international biomedical optics symposium, vol 3245, San Jose, CA, USA, 1998; https://doi.org/10.1117/12.312307]. The obtained images have shown an enhanced contrast and clear boundaries distinction of the studied pathology in comparison to the images taken with "white" unpolarized light or before the reconstruction. Tissue polarimetry has been also applied to study the histological samples. The outcome of this measurement reveals that the angle of ellipticity, the azimuth, the illuminating power and the degree of polarization could be used to discriminate among different lung tissue pathologies.

[11_6a] A. Stoilova, V. Lilova, V. Ivanova, Y. Trifonova, D. Dimov, Optical properties of electrospray deposited PAZO polymer films doped with $GeTe_4$-Cu chalcogenide particles, Journal of Chemical Technology and Metallurgy, 57, 1, 2022, 126-131

Composite films based on the azo polymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]) doped with 1 wt.% crystal particles of the previously synthesized by us new tellurium containing chalcogenide system (GeTe4)100-xCux, where x = 5, 10, 15 and 20 mol.%, have been prepared by

electrospray deposition. The polarization microscopy study of the prepared films shows highly developed surface morphology as the addition of chalcogenide particles leads to the formation of porous microstructure. The transmittance coefficient, the reflectance coefficient, the refractive index, the extinction coefficient, the optical absorption coefficient and the optical band gap of the electrospray deposited PAZO polymer composite films have been determined. It was found that the absorption of these novel composite film materials arises from indirect allowed transitions (r = 2) and occurs at photon energy in the range between 1.37 and 1.72 eV, depending on the cooper concentration in the chalcogenide particles.

[1_6г] Y. Trifonova, A. Stoilova, V. Ivanova, V. Lilova, P. Petkov, Se-based chalcogenide glasses as holographic media, Journal of Chemical Technology and Metallurgy 55 (4), 2020, 810-813

Bulk chalcogenide glasses from the binary system Ge-Se and from the ternary system Ge-Se-M (M = Ga, In) were synthesized by the melt-quenching technique. Using vacuum-thermal evaporation thin layers with a thickness of 500 nm ± 5% were deposited from the synthesized bulk samples. The dependence of the diffraction efficiency of the thin films on the recording time and the power of the laser beam was investigated. The results show that the addition of gallium or indium to the binary system Ge-Se leads to a significant increase in the diffraction efficiency. The maximum diffraction efficiency reached (at λ=448 nm) in the thin layers of pure selenium was $\eta_{max} = 0.45.10^{-4}$ % by laser beam power P=5.0 kW/m^2 and after 30 minutes time of irradiation. In layers based on the binary system Ge-Se, it was reached a maximum diffraction efficiency of $0{,}7.10^{-2}$%, by P= 3.5 kW/m^2 and time of irradiation ≈15 min. By the layers doped with gallium maximum diffraction efficiency was measured for the sample with the composition $Ge_{14}Se_{71}Ga_{15}$, η_{max} = 0.61% (P = 3.5 kW/m^2, after 20 minutes time of irradiation), and by the layers doped with indium, maximum diffraction efficiency was obtained for the sample with the composition $Ge_{14}Se_{71}In_{15}$, respectively η_{max} = 0.74% by P = 3.5 kW/m^2 and after 20 minutes time of irradiation.

[2_6г] A. Stoilova, A. Georgiev, D. Nazarova, L. Nedelchev, D. Dimov, P. Petkov, Development of Nanostructured Materials with CBRN Agents Sensing Properties, Advanced Nanotechnologies for Detection and Defence against CBRN Agents, 2018, 499-507

The paper presents a brief overview of the nanomaterials applicability for detection of category A biological agents, as well as development of azobenzene based sensors used for detection of neurotoxins, plant viruses and other biological molecules.

[3_6г] V. Lilova, Y. Trifonova, A. Stoilova, S. Georgieva, P. Todorov, Optical properties of PAZO polymer composite films doped with particles of a novel copper hydantoin complex, accepted for publication in The Journal of Chemical Technology and Metallurgy, 2021

The transmittance coefficient (T), the reflectance coefficient (R), the refractive index (n), the extinction coefficient (k), the optical absorption coefficient (α) and the optical band gap (E_g) of spin coated PAZO azo polymer composite films with embedded particles of the Cu(II) 3-amino-5,5'-dimethylhydantoin metal complex, have been determined. The values of T, R, n, k, α and E_g obtained for the samples studied are close as with increased particles concentration a slight decrease in the obtained values is observed. It was found that the absorption of these novel composite thin film materials arises from indirect allowed transitions (r = 2) and occurs at photon energy in the range 2.57 to 2.46 eV, depending on the composition.

[4_6г] N. Berberova, P. Sharlandjiev, A. Stoilova, L. Nedelchev, D. Nazarova, Optical constants of azopolymer PAZO thin films in the spectral range 320–800 nm, Journal of Physics: Conference Series 992 (1), 2018, 012019, IF= 0.55

The complex refractive index of a PAZO layer was evaluated from transmission and reflection spectrophotometric data at normal incidence between 320 nm and 800 nm. For determination of the spectral dependence of the refractive index of azopolymer thin films, we proposed a minimization procedure based on solving a set of two nonlinear equations with two unknowns – the real and imaginary parts of the refractive index on a wavelength-by-wavelength basis. A solution of the inverse optical problem was obtained by the socalled "trust-region-dogleg" algorithm. The leading idea of this method is to define a region in the parametric N-K space (trust-region), where the optical response can be approximated by a simpler function.

[5_6г] G. Mateev, A. Stoilova, D. Nazarova, L. Nedelchev, P. Todorov, S.Georgieva, Y. Trifonova, V. Lilova, Photoinduced birefringence in pazo polymer nanocomposite films with embedded particles of biologically active metal complexes, Journal of Chemical Technology and Metallurgy, 54, 6, 2019, 1123-1127

Composite layers based on the PAZO polymer doped with particles of the metal complexes Cu(II) 3-amino-5,5'-dimethylhydantoin (CLP) or Ni(II) 3-amino-5,5'-dimethylhydantoin (NLP) at three different concentrations, namely 1 wt.% weight, 2 wt.% and 5 wt.%, have been deposited through spin-coating. The photoinduced birefringence was measured by a classical polarimetric setup. As pump laser was used a vertically polarized He-Cd laser (Kimmon Koha) emitting at λ = 442 nm (P_{442} = 108 mW before the sample). To measure the photoinduced birefringence, a linearly polarized at 45° laser beam was used from a DPSS laser (B&W TEK) emitting at λ = 635 nm (P_{635} = 2 mW before the sample), referred to as the probe beam. It was observed an increase in the value of the photoinduced birefringence with increasing the concentration of the dopant, as at a concentration of 5 wt. % of the dopant Δn decreases. The samples show relatively high values of the residual birefringence (above 91%) and relatively short response time.

[6_6г] P. Petkov, A. Stoilova, T. Petkova, Nanoscaled chalcogenide films for optical applications, Dielectric Materials and Applications: ISyDMA'2016 1, 119, 2016

The paper presents a comparative examination on the optical properties of thin amorphous films from the systems $[Ge(Se/Te)\ 5]_{1-x}In_x$, x = 5; 10; 15; 20; 25 mol.%, prepared by vacuum-thermal evaporation. The influence of the indium content and the thermal annealing on the density, the molar volume, the absorption coefficient, the refractive index, the band gap and the oscillation energy of the thin layers is discussed. The variations in the density and the molar volume show an almost lienar increase with indium introduction with small deviation from the trend in samples with 10 mol.% In (Nco = 3). By increasing the concentration of the indium, the absorption edge shifts to the longer wavelength of the spectrum, the refractive index and the absorption coefficient increase, and the value of the optical band gap decreases. After temperature treatment the films show higher refractive index and the dispersion in the average energy gap values becomes smaller.

[7_6г] Y. Trifonova, V. Ivanova, A. Stoilova, V. Lilova, Comparative analysis of some physico-chemical properties of the glassy systems (GeSe5)(100-x) In-x and (GeTe5)(100-x) In-x, Bulgarian Chemical Communications 48 (4), 2016, 624-627, IF=0.4

In this paper some physico-chemical properties, such as density, compactness, molar volume, number of constraints per atom and overall mean bond energy, of the glassy systems $(GeSe_5)_{100-x}In_x$ and $(GeTe_5)_{100-x}In_x$, x= 0 and 5 mol.%, were studied. The bulk sample

containing Te shows higher value of the density compared to this one containing Se. The addition of In to the selenium ot tellurium based system leads to variation of the density, in the first one the density increases and in the second one the value of the density decreases by addition of indium. The compositional dependence of the molar volume repeats the compositional dependence of the density. The overall mean bond energy of the glassy alloys containing Te (Z_{glassy} = 2.37) is higher than the overall mean bond energy of the glassy alloys containing Se (Z_{glassy} = 2.37). By In addition the bonds between the atoms of the glass components become more stable. The correlations between the composition and the properties of the glasses were discussed in terms of the supposed structural changes that occur in the investigated chalcogenide materials.

[8_6г] L. Nedelchev, D. Nazarova, V. Dragostinova, P. Petkov, A. Stoilova, Photoinduced anisotropy in a series of azobenzene copolymers, Bulgarian Chemical Communications 45, 2013, 145-148, IF=0.4

In order to optimize the parameters of the photoinduced birefringence in azopolymers, we have synthesized and studied copolymers with different weight ratios of two monomers (fig. 5) which differ in the length of spacer between the azochromophore and the polymer backbone. The polymer P1 based only on the first monomer is amorphous, and the polymer P2 which contains only the second monomer is liquid-crystalline. In addition to the homopolymers P1 and P2, five copolymers were synthesized, described by the general formula P1(100 – *x*)P2(*x*), where *x* gives the percent weight ratio of the second monomer in the final copolymer and x = 0, 25, 40, 50, 60, 75, 100. As a result the following seven polymers were obtained – P1, P1(75)P2(25), P1(60)P2(40), P1(50)P2(50), P1(40)P2(60), P1(25)P2(75), P2. From the new azo polymers thin films were prepared through spin coating. Birefringence was induced in the samples by a vertically polarized beam from a DPSS laser at 473 nm (I = 400 mW/cm2). Birefringence was induced in the samples by a vertically polarized beam from a DPSS laser at 473 nm (I = 400 mW/cm2), inside the absorption band of the azochromophores. The main parameters of the photoinduced birefringence in these polymers, such as maximal value, response time and time stability, have been measured and compared. The highest birefringence is obtained in the homopolymer P2 (Δnmax = 0,102) and the copolymer P1(75)P2(25) has shortest response time – 6 s.

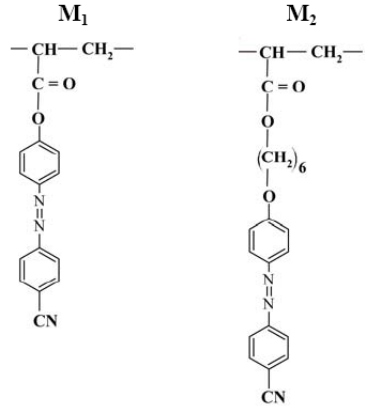


Fig. 5: Structure of the monomers used.

[9_6г] A. Stoilova, P. Petkov, Y. Nedeva, B. Monchev, Kinetics of Ge-Se-In Film Growth, AIP Conference Proceedings 1203 (1), 2010, 398-402, IF=0.4

The processes of vacuum evaporation and condensation in the glassy systems $(GeSe_y)_{1-x}In_x$, where x=0, 5, 10, 15, 20 and y=4, 5 and 6, were investigated. The evaporation (Q_e) and condensation (Q_c) energies were determined. The addition of indium leads to

increase of the Q_e and Q_c, respectively do decrease of the evaporation and condensation velocity. With increasing Se content of the samples from the binary system Ge-Se the values of Qe decrease and the values of Qc increase. By the samples from the ternary system, the higher selenium content facilitates the condensation process.

[10_6r] A. Stoilova, D. Dimov, Y. Trifonova, V. Lilova, B. Blagoeva, D. Nazarova, L. Nedelchev, Preparation, structural investigation and optical properties determination of composite films based on PAZO polymer doped with GeTe4-Cu chalcogenide particles, The European Physical Journal AP, 2021, 95, 30301, IF=0.993

Composite films based on the azo polymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2- ethanediyl, sodium salt]) doped with 1 wt.% particles of the previously synthesized by us new tellurium containing chalcogenide system $(GeTe4)_{100-x}Cu_x$, where x = 5, 10, 15 and 20 mol.%, have been successfully prepared by spin coating. The XRD analysis of the synthesized bulk chalcogenide materials shows that they are crystalline and consist of tetrahedral $GeTe_4$ and $CuTe_4$ units and tellurium chains. The composite films have microscopically similar morphology as the chalcogenide particles are distributed in the form of large clusters. The calculated values of the refractive index, the extinction coefficient, the optical absorption coefficient and the optical band gap are close for all the samples studied. It was found that the absorption of these novel composite thin film materials arises from indirect allowed transitions (r = 2) and occurs at photon energy in the range 2.54 to 2.56 eV, depending on the composition. An increase in the amount of the photoinduced birefringence in comparison to the pure PAZO film ($\Delta n_{max} \approx 0.07$) has been observed for the sample doped with $(GeTe_4)_{85}Cu_{15}$ particles ($\Delta n_{max} \approx 0.09$) by illuminating with linearly polarized light (λ=442 nm).