Summary of the main results and scientific contributions of assistant prof. Dr. eng. Vladislava Hristova Ivanova, submitted for participation in the competition for assoc. professor of 4.1. Physical Sciences (Condensed matter physics with french language) at UCTM

Assistant Professor Dr. Vladislava Hristova Ivanova's publication activity, as part of her application for the position of associate professor, comprises 19 articles, including 10 in international journals with impact factors (cumulative impact factor Σ=17.426) and 9 in indexed journals without impact factors, with SJR ratings. Among them, 2 publications are in Q1 journals, 7 in Q2 journals, 7 in Q3 journals, and 3 in Q4 journals. Assistant Professor Dr. Vladislava Ivanova is presenting in the competition with 25 citations. Personal contribution to these articles: first author in 3 of them (Г4, Г5, Г6), second author in 9 - (Г1, Г2, Г3, А1, А2, А4, А8, А11, А12, А13), corresponding author - in 7 (А4, А5, А6, А11, А12, Г5, Г6).

All the submitted publications for the competition are in the field of synthesis, characterization, study of properties, and study of correlations structure-property of various materials, as well as the development of new teaching methods for the disciplines of Physics and Materials Science, which are key factors in training skilled professionals in the fields of technical and natural sciences.

Personal contribution to these articles: In 3 of them (Г4, Г5, Г6), I am the first author; in 9 of them, I am the second author (Г1, Г2, Г3, А1, А2, А4, А8, А11, А12, А13); in 7, I am the corresponding author (А4, А5, А6, А11, А12, Г5, Г6).

Furthermore, she has actively participated in 54 international, national, and university scientific forums. Moreover, she has led 8 contracts with the SRC at UCTM and has served as leader in 7 and as participant in 11 contracts with the Embassy of France in Bulgaria, the Agency of Francophone Universities, the Fund for Scientific Research, the Operational Program "Science and Education for Intelligent Growth," the Operational Program and The National Program "European Scientific Networks." Under her guidance during the period 2015-2024, ass. prof. Dr. Vladislava Ivanova successfully supervised the defense of 4 students for the Master's degree. Her research focuses on the synthesis characterization, study of properties and study of correlations between the structure and properties of various materials, as well as development of new teaching methodologies in Physics and Materials Science.

The main topics of the research conducted could be classified in the following three areas:

1. Preparation and study of chalcogenide materials;

2. Research on biosensors and peptide mimetics;

3. Development and implementation of new methods to increase the engagement and interest of engineering students in Physics and Materials Science education.

Topic 1 Preparation and study of chalcogenide materials

1. Synthesis of bulk samples of chalcogenide materials

The main presented results, which presents the synthesis of chalcogenide materials, are presented in publications A2, A4, A5, A8, A13, Г2, Г3, Г4, Г5, Г6, of which the most cited is Г2.

Using melt-quenched technique into a water/ice mixture are synthesized bulk samples of :

- ➢ new tellurium-based chalcogenide materials from the systems $(GeTe_y)_{100-x}In_x$, where y=3, 4, 5; x = 0-20 mol% and $(GeTe_4)_{100-x}Cu_x$, with x = 5-20 mol% (publications A2, A4, A11, A12, Г2, Г3, Г4, Г5, Г6) with a composition that has not been reported so far in the scientific literature;
- ➢ Ge_xSe_{100-x}, x = 14, 17, 20 25 mol. %, and $(GeSe_5)_{100-x}Me_x$, x = 0-20 mol. %, where Me = Ga, In (publications A2, A5);
- ➢ As_2Se_3-Ag_2Te-GeTe in the range of 0-90 mol% GeTe, and in the binary system As_2Se_3-Ag_2Te from 0-50 mol% Ag_2Te (publication A8) and $Bi_2(Se_{1-x}Te_x)_3$ x= 10%, 50% и 100% (publication A13).

2. Thin films preparation

For a complete characterization of the materials and the analysis of a number of properties, it is necessary to prepare thin films from newly synthesized chalcogenide bulk samples. In scientific publications A5, A6, A7, A13, Г2, Г4, Г5, Г6, results of analyses of thin films deposited by the vacuum-thermal evaporation method have been published.

Thin films were prepared:

➢ on glass substrates with different compositions of the chalcogenide systems $(GeTe_y)_{100-x}In_x$, where y=3, 4, 5; x = 0-20 mol.%, Ge_xSe_{100-x}, x = 14, 17, 20 25 mol. %, and $(GeSe_5)_{100-x}Me_x$, x = 5-20 mol.%, where Me = Ga, In (publications A5, A11, Г2, Г4, Г5) and $Bi_2(Se_{1-x}Te_x)_3$ x= 10%, 50% и 100% (publication A13);

➢ on silicon substrates and silicon micro-machined cantilevers, from chalcogenide systems $(GeTe_y)_{100-x}In_x$, where y=3, 4; x = 0 - 20 mol% (publications Г5, Г6);

➢ using the doctor blade technique with composition $Cu_{0.9}(In_{0.7}Ga_{0.3})Se_2$ (CIGS) for a photovoltaic solar cell absorber (publication A7), with different film thicknesses as a result of collaborative work with colleagues from the Department of Inorganic and Organic Chemistry, Jaume I University, Av. Sos Baynat, Castellón de la Plana, Spain;

➢ using electro-spray deposition as composite materials based on the azo polymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], shortly PAZO, doped with chalcogenide particles from the system $(GeTe_4)_{100-x}Cu_x$, where x = 5-20 mol % (publication A6).

3. Characterization of chalcogenide materials (A1, A2, A4, A5, A6, A7, A8, A9, A10, A11, A12, Г2, Г3, Г4, Г5, Г6).

3.1. Structural studies have been carried out using X-ray diffraction of samples from the Ge-Te-In, As_2Se_3-Ag_2Te-GeTe, CIGS and $Bi_2(Se_{1-x}Te_x)_3$ systems (publications A7, A8,

A13) and using atomic models containing up to 300 atoms, through ab initio molecular dynamics (AIMD) for the Ge-Te-In system (publications A1, A12).

➢ The structure of As_2Se_3-Ag_2Te-GeTe, $Bi_2(Se_{1-x}Te_x)_3$ and CIGS layers was studied by X-ray diffraction (XRD) (publications A7, A8, A13). In the analyses of the diffraction spectra of CIGS films (publication A7), some of the diffraction peaks were assigned to the crystalline phase $Cu(In_{0.7}Ga_{0.3})Se_2$ (CIGS). It can be emphasized that in one thin film, which contains 2 layers, a single CIGS crystalline phase is detected, while in the second film, which contains three layers, some secondary phases are also detected, which can be related to the formation of $Cu_{1.8}Se$ during the thermal selenization. By the visual and XRD analyses, the state of samples from the As_2Se_3-Ag_2Te-GeTe system (publication A8) was proven, and the glass formation region in the system was established. Chalcogenide glasses have been obtained in the As_2Se_3-GeTe system in the range of 0 to 90 mol% GeTe, while in the binary As_2Se_3-Ag_2Te-GeTe system, from 0 to 50 mol% Ag_2Te;

➢ The structure of chalcogenide glasses with the composition $(GeTe_y)_{100-x}In_x$, where y=4, 5; x = 0-20 mol%, has been investigated using atomic models containing up to 300 atoms, through ab initio molecular dynamics (AIMD) and density functional theory (DFT) (publications A1, A12). Ring statistics investigation of amorphous $(GeTe_4)_{100-x}In_x$ (publication A1) suggest that structure of $(GeTe_4)_{100-x}In_x$ with x = 0-20 mol% have a significant number of 4-fold rings which responsible to the rapid crystal growth in crystal-amorphous transition. Results of time evolution of 4-fold rings investigation show that crystallization of samples with 80–100 atoms occur in hundreds of picoseconds making them suitable candidates of phase change materials.

3.2. The structure, morphology, topology and composition of thin layers have been studied A6, A7, Г5, Г6.

➢ The morphology of composite films based on the azo polymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], doped with chalcogenide particles from the system $(GeTe_4)_{100-x}Cu_x$, where x = 5-20 mol %, obtained by electro-spray deposition (publication A6) was studied using polarization microscopy. The study shows a highly developed surface morphology, as the addition of chalcogenide particles leads to the formation of a porous microstructure, which makes them suitable media for application in chemical sensor devices. The crystal structure of the prepared chalcogenide particles was confirmed by TEM.

➢ Using scanning electron microscopy, it was confirmed that the doctor blade technique allows the preparation of homogeneous CIGS thin films without three-dimensional defects such as pores. The chemical composition, analyzed by EDX, corresponds to an initial stoichiometry (Cu/In/Ga = 1:0.78:0.33) (publication A7).

➢ In order to establish the possibility of performing a phase transition at low temperature for potential application as an active element in phase change memory devices, the morphology, topology and structure of tellurium-based thin films of the systems $(GeTe_y)_{100-x}In_x$, where y=3, 4; x = 0-20 mol% (publications Г5, Г6) were investigated using atomic force microscopy and scanning electron microscopy, and their composition - with EDS. The EDS results show that the thin films are homogenous by composition, which is identical to that of the initial bulk samples (publications Г5, Г6). The thin films are homogeneous in thickness and relatively smooth, making them suitable for applications in optics and optoelectronics. The surface of the thin films with the composition $(GeTe_3)_{100-x}In_x$ is glassy, while that of the thin films $(GeTe_4)_{100-x}In_x$ is characterized by a uniform distribution of aggregation areas, whose number increases

with increasing In content. The results referring to the cross-section of the thin films show that a microcrystallization process occurs in depth of these films (publication Г5);

➢ To clarify the correlation between the stress, composition and structure of freshly deposited films of the systems $(GeTe_3)_{100-x}In_x$, x=0-20 mol% and $(GeTe_4)_{100-x}In_x$ x= 0-10 mol%, structural analyses were performed using the X-ray diffraction method (publication Г6), which showed that the resulting films are amorphous.

3.3. Mechanical properties of samples from the Ge-Te-In system (publication Г6) and As_2Se_3-Ag_2Te-GeTe (publication A8) were investigated.

➢ The correlation between the stress, composition and structure of freshly deposited thin films of the systems $(GeTe_3)_{100-x}In_x$ x = 0-20 mol% and $(GeTe_4)_{100-x}In_x$, x = 0-10 mol%, and its relaxation after 30 days was studied (publication Г6). The effect of the addition of In on some mechanical characteristics of Te-containing thin films was studied. As a result of the studies, it was found that for all studied chalcogenide films the stress decreases, but does not change in type with time. For both studied sections of the Ge-Te-In system the stress type is compressive. This gives us reason to assume that the cause of the mechanical stress in the Ge-Te-In system is structural and the structural units that make up the glass remain stable over time. The obtained results give us reason to assume that the relaxation of mechanical stress is related to the rearrangement of structural units, and the nonlinear dependence of stress on composition corresponds to the theory of Philips and Thorpe.

➢ New experimental data on Vickers microhardness and modulus of elasticity have been obtained for the As_2Se_3-Ag_2Te-GeTe system (publication A8). The influence of the composition on these properties has been investigated, showing that the introduction of GeTe leads to a densification of the structure and an increase in the microhardness values, while the addition of silver telluride results in a decrease in microhardness.

3.4. The physicochemical properties have been studied to obtain useful information about the real structure of the glasses (publications A2, A4, A8, A10, Г3, Г6).

➢ New experimental data have been obtained on the density of chalcogenide materials from the systems $(GeTey)_{100-x}Me_x$, where Me = In, Cu; y = 3, 4, 5; x = 0–20 mol %, and As_2Se_3-Ag_2Te-GeTe and $Bi_2(Se_{1-x}Te_x)_3$ (publications A2, A4, A8, A10, A13, Г3, Г6). Based on the results, some physico-chemical properties such as compactness, molar and free volume, as well as the coordination number, number of constraints per atom and overall mean bond energy for glassy samples, have been determined. The correlations between the composition and the properties have been established. The results of the density and molar volume show that the introduction of indium into the binary Ge-Te system stabilizes the glassy system. It has been found that for glassy samples with a coordination number Zglass=2.40–2.43, for systems with In, there is a nonlinear dependence in density, molar volume, and compactness, which aligns with Thorpe's theory. The study of the As2Se3-Ag2Te-GeTe system (publication A8) revealed that the introduction of GeTe leads to structural densification and an increase in density values.

➢ For the first time, a comparative analysis of the physico-chemical properties of bulk samples from the systems $(GeSe_5)_{100-x}In_x$ and $(GeTe_5)_{100-x}In_x$ was performed. The studies showed that the density values of compositions containing Te are higher than those of compositions containing Se (publication A2). Increasing the In content provokes a different change in density in Ge-Se-In and Ge-Te-In systems. Due to lower compactness, more structural changes are expected in the compositions containing Te. The dependence of molar volume on composition repeats that of density. The increase in the number of degrees of freedom with the addition of

In leads to enhanced stability of the glassy system. The overall average bond energy of the compositions containing Te is higher than that of the compositions containing Se. As a result of the study, it was established that the addition of indium makes the bonds between the glass atoms more stable.

➢ The limitations of well-known approaches for verification of methods of measurements of chemical and physical characteristics of specific samples have been discussed, due to the wide variety of activities and corresponding tasks in a research laboratory (publication A10).

3.5. Electronic properties have been studied (publication A12).

➢ For the first time using density functional theory (DFT) and molecular dynamics, the electronic properties of ternary chalcogenide systems $(GeTe_4)_{1-x}In_x$ and $(GeTe_5)_{1-x}In_x$ with compositions x=0–20 mol% were investigated (publication A12). The pair correlation function, static structure factor, electronic density of states, and electronic band gap energy were analyzed using the local density approximation within the framework of first-principles calculations. The results revealed a significant decrease in the energy bandgap of the binary germanium-tellurium system with the inclusion of indium atoms. The incorporation of indium atoms causes a substantial change in the electronic structure.

3.6. Thermal properties have been studied (publications Г3, A8, A11, A12, A13).

➢ Thermal properties of chalcogenide glasses from the systems $Bi_2(Se_{1-x}Te_x)_3$ (publication A13), $(GeTe_4)_{1-x}In_x$ and $(GeTe_5)_{1-x}In_x$, where x=0–20 mol% (publication Г3), and As_2Se_3-Ag_2Te-GeTe (publication A8) were studied, and their glass-forming ability was determined. The stability of the glasses was confirmed through the investigation of their thermal properties. Thermal characteristics such as glass transition temperature (T_g), crystallization temperature (T_{cr}), and melting temperature (T_m) were determined for some samples, and the influence of composition on these properties was analyzed. Thermos-effects of crystallization and melting were not observed in some of the samples from the As_2Se_3-Ag_2Te-GeTe system (publication A8). Data analysis indicated that introducing Ag_2Te into the system increases the metallic component of the chemical bond in the chalcogenide glasses, and as its content increases (at z=const), the softening temperature decreases. Conversely, as the GeTe content increases (at m=const), Tg increases. Contrary to expectations, the addition of GeTe to As_2Se_3 (at m=const) does not lower Tg instead, the opposite effect is observed. Increasing concentrations of Ag_2Te (at z=const), the crystallization temperature decreases. The study of the thermal behaviours of the glasses in the Ge-Te-In system was performed using Linseis Thermal Analysis Simultaneous Thermal Analysis (STA) by simultaneous measurement of differential scanning calorimetry and thermogravimetry under the same conditions. The results demonstrated that the introduction of indium into the binary Ge-Te system stabilizes the glassy system. The composition of binary $GeTe_5$ is definitely closer to the eutectic than $GeTe_4$; however, the results show that $GeTe_4$ glass is more stable than $GeTe_5$ glass.

➢ The evaporation kinetics during physical vapor deposition technique of thin chalcogenide films from the $GeTe_4$ and $GeTe_5$ systems doped with In were analyzed (publication A11). This study revealed a significant and exponential increase in the evaporation rate of $GeTe_4$ and $GeTe_5$ with the introduction of indium, which was particularly noticeable at higher temperatures. It was found that the addition of indium affects the evaporation rate and elevates the energy requirements for the evaporation process, providing new insights into the thermal dynamics of these materials. The newly obtained data from this study significantly contribute

to understanding deposition processes, enabling the optimization of thin film manufacturing techniques, which could lead to more efficient and higher-performing optoelectronic devices and memory storage solutions.

3.6. The optical properties of samples with the compositions $(GeTe_4)_{1-x}In_x$ (publication Γ2), $(GeTe_5)_{1-x}In_x$ (publication Γ4), with x=0–20 mol.%, Ge_xSe_{100-x}, x=14, 17, 20, 25 mol.%, and $(GeSe_5)_{100-x}Me_x$, x=5–20 mol.%, where Me=Ga, In (publication A5), $Cu_{0.9}(In_{0.7}Ga_{0.3})Se_2$ (CIGS) layers (publication A7), PAZO films doped with $GeTe_4$-Cu chalcogenide particles (publication A6) and $Bi_2(Se_{1-x}Te_x)_3$ (publication A13), have been studied.

The investigation of the optical properties of thin films provides insights into whether they could be used in optoelectronics as an optical storage media, in infrared optics, and other applications.

Among the presented scientific works on optical properties, publication Γ2 has the highest number of citations, totaling 8, of which 5 are in scientific articles published in journals indexed in Scopus or Web of Science. This publication has been submitted as part of the competition for the academic position of "Associate Professor."

➢ The transmission and reflection spectra of thin films from the chalcogenide systems $Bi_2(Se_{1-x}Te_x)_3$ (publication A13) and $(GeTe_4)_{1-x}In_x$ with compositions x=0–20 mol% were studied, and the transparency region was determined (publication Γ2). Using the Swanepoel method, the main optical constants, the refractive index and extinction coefficient, were determined, revealing that the refractive index exhibits high values. The absorption coefficient was also calculated, and the optical bandgap was determined using the Tauc's procedure, along with its dependence on the composition. The data showed that the optical band gap decreases with the addition of indium.

➢ Optical parameters such as transmittance coefficient, reflectance coefficient, refractive index, extinction coefficient, optical absorption coefficient, and optical bandgap were determined for composite films based on the azopolymer poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt], doped with chalcogenide particles from the $(GeTe_4)_{100-x}Cu_x$ system, where x=5–20 mol%, prepared through electrospray deposition (publication A6). A significant change in the optical properties of the composite films in comparison to the non-doped azo polymer film has been observed.

➢ Photoinduced changes were studied (publication Γ4) in thin films from the $(GeTe_5)_{1-x}In_x$ system with various compositions x=0–20 mol%. A red shift of the transmission of the films was observed with the addition of In to the glassy matrix. The thin film's nonuniform thickness was accounted for to accurately determine the optical constants. The optical constants were determined by two methods: using a fitting procedure based on the Swanepoel method and using Pointwise Unconstrained Minimization Approach (PUMA). The refractive index, absorption coefficient, and optical band gap of the thin layers were determined both before and after irradiation. The analysis revealed that the introduction of In reduces the refractive index and the extinction coefficient. A regular increase in the absorption coefficient values before and after treatment is discovered. It was established that the optical band gap decreases in samples with higher In content. The dependencies of the fundamental optical constants on the composition were obtained.

➢ The effect of the addition of IIIA metal (Ga or In) to Se-based chalcogenide thin films on the diffraction efficiency was studied (publication A5). The relationship between diffraction efficiency, the composition of the glassy system, and the exposure time at constant laser beam intensity was investigated. The results showed that the diffraction efficiency of the films with compositions $(GeSe_5)_{85}Ga_{15}$ and $(GeSe_5)_{85}In_{15}$ possess four orders of magnitude higher diffraction efficiency than the one of the pure Se films and two orders of magnitude as compared to the films of the binary Ge-Se system with analogous Ge concentration.

➢ The transmission and reflection spectra of thin $Cu_{0.9}(In_{0.7}Ga_{0.3})Se_2$ (CIGS) films for photovoltaic solar cell absorbers were studied (publication A7). For the first time, the optical properties of the thin layers with this composition, obtained using the doctor blade technique, were investigated. The value of the transmission coefficient reached 7.46%, and that of the reflection coefficient - up to 2.05%, which makes them suitable for use as absorbers in solar cells. The analyses revealed that the greater the film thickness, the smaller the value of the refractive index. For all thin layers, the refractive index increases with increasing wavelength (abnormal dispersion). It was found that smaller the thickness, the greater the absorption coefficient, and the end of optical absorption for the thicker films occurs at lower energies. Using Tauc's procedure, the optical band gap of the CIGS thin layers was determined, showing that thicker layers have a smaller optical band gap, i.e., they will more easily and quickly transform the solar energy. To improve the optical parameters, one can work in two directions: increasing the thickness of thin films and reducing the amount of added gallium.

Topic 2 Research on Biosensors and Peptide Mimetics

One of my primary goals over the years has been to establish multidisciplinary collaborations with colleagues from other departments at UCTM. This has been achieved through our work in building European and national scientific networks, as well as my participation in various scientific projects (Appendix П-ДД-4.3). This began with an in-depth review of the development of biosensors for lactate determination, which have gained an increased research interest because of their wide application in clinical analysis and control of fermentation processes in the food industry (publication A3). Lactate biosensors with enzyme modified modules are a perspective alternative to the conventional methods in clinical analysis for their fast response, applicability to continuous mode of analysis, low cost and easy automation. Food and beverage industry can also benefit from the advantages of lactate biosensors for monitoring of fermentation processes or control of foods labeled as "low lactate content". The main contribution of this review lies in discussing enzymatic methods for lactate determination and summarizing recent advances in the development of lactate biosensors. It was found that simple, an easy and a low cost analysis, easy maintenance and reduced costs of the analytical instruments, possibility of small devices incorporation in portable instruments become increasingly important.

As a result of my participation in the working group for the National Program "European Scientific Networks" project DRUG-MOLECULE, I initiated joint research with colleagues on specially designed peptide mimetics, which offer higher selectivity regarding their toxicity to mammalian cells. The aim is to clarify the effect of the model peptide KLAKLAK-NH_2 on important physico-chemical parameters of lipid membrane models (publication A9).

Topic 3 Development and implementation of new methods to increase the engagement and interest of engineering students in Physics and Materials Science education

Over the years, through in-depth research and analysis of various issues in Physics and Materials Science education for engineering students, it has been established that creating a more interactive learning environment significantly increases students' engagement and interest in the learning process. The integration of new digital technologies to modernize the education at UCTM aims to enhance students' creativity and involvement. The use of a web camera, not merely as a monitoring device but as a tool for active participation and support in the educational process, has led to the creation of new exercises. The article *"Web camera as a measuring tool in the undergraduate physics laboratory"* (publication Г1) is the most cited work, with 12 citations, 6 of which are in journals indexed in Scopus or Web of Science, and is submitted in the competition for the academic position of Associate Professor.

➢ Three new laboratory exercises have been developed for measuring position and light intensity using an inexpensive web camera connected to a personal computer without additional hardware: ink diffusion in water, pendulum damped oscillations and light diffraction. The measurements are done online, and the results are observed on the computer screen in real time. The configuration is simple and cheap, suitable for demonstrations and laboratory exercises.