Dr hab. Bożena Zgardzińska, prof. UMCS
Department of Materials Science
Institute of Physics
Maria Curie-Sklodowska University in Lublin

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Review Report on the PhD dissertation
MSc Eng. Jakub Szlęzak
„Pnictogen modified Ge-Ga-Se(Te)-based glasses for optoelectronic devices"

The doctoral dissertation presented for review is a research study of a group of chalcogenide glasses (ChG), which, due to their properties, are dedicated to applications for photonics, e.g. as optical devices or elements of semiconductor devices.

The PhD thesis was created as part of Polish-French cooperation between Institute of Physics, College of Natural Sciences, University of Rzeszów and Institute of Chemical Science in Rennes, University of Rennes 1. The results presented in the dissertation were created as a part of the doctoral student's participation in research work carried out in the above-mentioned centers and cooperation with other centers (e.g. AGH Kraków). The dissertation was prepared under the supervision of prof. Bruno Bureau and prof. Józef Cebulski, as well as co-supervisor (*promotor pomocniczy*) dr Yaroslav Shpotyuk.

Topics and thesis of the dissertation

The title of the dissertation "Pnictogen modified Ge-Ga-Se(Te)-based glasses for optoelectronic devices" fully reflects its content. The Author points to the progress in the field of modern photonics, taking into account economic and technological aspects, as justification for the selected topic. Focusing on a selected group of ChG, the Author presents selected aspects of the glass production technology, indicates the direction of modification of these glasses (by changing the composition) leading to obtaining materials with the desired final parameters (hardness, glass transition temperature, viscosity and electrical conductivity, transmission and absorption, optical signal attenuation and others).

The Author presents a very extensive group of results obtained with the use of many experimental techniques (including X-ray diffraction, electron microscopy, Raman spectroscopy, differential scanning calorimetry and others). Author skillfully grouped these results, so that it was possible to conclude about the influence of glass composition on the properties obtained by them. The aim of the dissertation has been presented in a general way already in the summary/introduction to the thesis - the Author sought to produce and modify glasses whose thermodynamic, mechanical, electrical and optical properties would be optimized for their potential applications. MSc Eng. Szlęzak incorporated research hypotheses into the content of the PhD thesis, which were then proved on the basis of the research results, e.g. "... *the basis for this study was to obtain pnictogen-modified glass-ceramic material having inside crystallites of $Bi_2Te_xSe_{3-x}$ solid solutions. The hypothesis was that the TE phase, well distributed in the glassy matrix, could possess more structural defects caused by the formation of chemically and structurally more complex $Bi_2Te_xSe_{3-x}$.*"

The Author focused on the modification of the Ga-Ge-Se-Te system with pnictogens (bismuth, antimony, phosphorus) leading to the obtaining of glass for use in thermoelectric (TE) devices. Structural and resistivity tests were performed. The kinetics of the crystallization process was investigated and the activation energies of the crystallization processes were determined. The influence of bismuth concentration on the optical transparency of the system was assessed. Ultimately, new ChG systems for the production of optical fibers for FEWS sensors and remote light sources were developed and manufactured, and their optical properties were characterized. Attention was paid to the influence of glass purity on the obtained optical parameters.

Summarizing, the Author focused on two fundamental problems in the dissertation: 1) optimization of high purity glass production techniques and 2) selection of the chemical composition of glasses leading to optimization of selected parameters dictated by potential applications of glasses. This subject is the most up-to-date, both from the research point of view and from the point of view of the application of research products.

The subject of the dissertation is up-to-date and - due to the interdisciplinary and application nature of the issue - innovative. The aims of the thesis were presented in a clear manner, unequivocally indicating the scope of the subject.

Assessment of the editorial side of the PhD thesis

The PhD thesis consists of 200 pages and includes a short summary in English and Polish, an extended abstract in French and 165 pages of the substantive part in English. This last part of the dissertation has been divided into 3 main chapters. Each chapter is a compendium of knowledge for one of the three stages of the project. The 1st Chapter (45 pages) provides a summary of the properties of the investigated glasses and an overview of the experimental techniques used to study them. This chapter is also a summarizing of selected aspects of the ChG production procedure. Chapter 2 (55 pages) focuses on a selected group of glasses dedicated to thermoelectric applications. The results for these systems were divided into three groups due to the composition of the systems. Within each group, the results were summarized. The last chapter of the dissertation (49 pages) summarizes the current state of knowledge in the area of glass application in the production of optical fibers and presents the results of selected parameters important for optical fiber technology.

The layout of the thesis is not classic, but it is justified by the substantive division of the discussed content and therefore it is absolutely correct. The structure and proportions of the dissertation are appropriate. The result and discussion part is included in each of the main chapters - in the first chapter, a detailed reference to the technology of glass production can be considered as such, in the next two chapters - the presentation and analysis of the results performed for the samples. The editorial side of the thesis is correct, and consistency in numbering (chapters, drawings, formulas, references to literature) makes it easier to navigate the text.

Each of the three chapters ends with a reference list: 57, 56 and 58 items, respectively. The literature contains correct choice of the relevant papers for the discussed field. The PhD thesis contains 21 tables (2 in chapter 1, 10 in chapter 2 and 9 in chapter 3) and rich graphic material included in 93 figures (25 in chapter 1, 34 in chapter 2 and 34 in chapter 3), although in fact their number is greater because under one figure number there are often several figures/photos/charts.

There are few editorial flaws in the thesis, but they do not affect the overall positive perception of the dissertation. For example, on page 64 the author writes "... *waveguide under two restrictions*" and then lists three factors; in several places of thesis, there are quantities described by symbols, the meaning of which is not explained and the reader can only guess what the Author meant (e.g. T_M on p. 59). Editorial flaws are very rare and do not deserve to be shown.

The value of the dissertation could be increased by greater care for the graphic side of the thesis. The quality of some figures is low, which affects the comfort of reading and makes it difficult to understand some issues and descriptions, some figures have an illegible, very small font (e.g. Fig. 1.7), others contain unjustified markings (e.g. exclamation marks in Fig. 1.6), and some of the figures do not carry information to which the dissertation text refers (e.g. in Fig. 1.16 one cannot see the dotted lines, the finding of which is suggested by the description referring to the figure). There are also repetitions, e.g. inset b) in Fig. 1.7 is the same as the Fig. 1.10. The quality of some figures is so low, that it does not allow for conclusions on their basis, nor for assessing whether the Author puts forward correct conclusions (e.g. Fig. 2.8.a, Fig. 2.24.b, 2.27.b). In the case of figures from DSC (e.g. Figs. 2.9, 2.10.), the scales of the vertical axes are usually indicated, giving heat flow in units of mass (W/g), often normalized. Are the data in Figure 2.9 normalized? It can be assumed that some of these flaws will be marginal in the electronic version of dissertation (higher quality of graphics), but the effect of font size maladjustment will remain. Taking into account the above remarks, it should be noted that some of the illegible drawings do not contribute to the thesis and could be replaced with a description of the conclusion drawn on their basis.

The above remarks should be treated by the Author as hints and suggestions for further work, because, in the opinion of the reviewer, **the dissertation was prepared with due diligence in terms of editing, and the layout of the work is well thought out and correct**.

Specific comments to the main part of the dissertation

The first chapter of the thesis describes the general properties of ChG taking into account the properties of their structure depending on the chemical composition. In this chapter, the Author introduces a number of concepts (e.g. the definition of glass, the range of ordering), to which he refers in later parts of the dissertation, interpreting the results. The Author has devoted a large part of this chapter to the procedures for the preparation of glasses, including the stage of their purification. Fig. 1.10 shows changes in temperature as a function of time, but a comment is needed: how the temperature jump from 700°C down to temperature close to T_g is realized immediately - how the control and stabilization of such a process looks like? An interesting approach to the topic, in the context of the planned applications of the studied materials, would be to present how the process of crystallization of glass at room temperature takes place on a far extended time scale (e.g. decades).

The Author clearly presented the physical basics of optical spectroscopy and optical properties of glasses. A particularly valuable fragment of the thesis (from the point of view of familiarizing researchers with techniques commercially used to assess the quality of optical parameters of the produced materials) is the fragment devoted to the fibber attenuation study. In the "1.5.2.2 *Length reduction approach for fiber attenuation study*" a description of the optical fiber qualitative test technique is briefly presented. However, the knowledge about selected details of cutback method is still lacking, e.g. how the cutting process proceeds and does the obtained shear surface of the optical fiber (e.g. its smoothness, shear angle) affect the measured value of I? Graphical visualization of shortening the length of the fiber (Fig. 1.13) does not allow to imagine the length scale - are they meters or millimeters, what are (even approximately) the limit values of L_1 and L_4? This is important in later chapters - some of this information can be obtained indirectly from the figures in chapter 3. Does the obtained value of α depend on the thickness of the optical fiber? as well as in the context of the contraction (tapering) of the optical fibers? Are the fibers optically isolated from the environment during the measurements?

The first chapter also provides an introduction to structural research techniques. The Author has presented here, inter alia, description of the use of the XRD technique for research on amorphous systems, Oliver-Pharr's approach, research on the chemical composition of glasses. In chapter 1.6.3, the Author indicates that EDS allows to test the purity of glasses, while pointing out (and rightly) that "*... possible error in chemical composition measurement exceeds ± 1-2%.*" Is it justified to use these data to assess the purity of the chemical composition of the glasses in the context of the low content of selected elements already at the stage of glass production, or in the context of a significant impact on the glasses properties the trace amounts of impurities?

The next fragment of the dissertation is a brief introduction to the differential scanning calorimetry method used to determine the phase transitions temperatures. This technique is described in more detail in the second chapter. Next we find a brief reference to viscosity and electrical conductivity. In section 1.7.3. the idea of electrical conductivity measurement was presented. However, it was not indicated whether analogous measurements had already been made for the glasses and what the measurement looks like, what values are obtained. This information would be useful for the reader in assessing the validity of using the technique in glass research.

The Chapter 2 conducts briefly through up to date research advances in TE materials. Author presents the current state of knowledge in the field of Bi and Sb modified Ge-Te-Se glasses research in the context of their applications for TE. The ChG and glass-ceramics have low thermal conductivity and high electrical conductivity for a glassy phase, and for this reason the Author decided to check structural and electrical parameters of glasses divided into three groups (because of chemical composition). The experimental part demonstrates research results including 1) characterization of phase multiplicity of complex ChG and glass-ceramics alloys from $Bi_xGa_5(Ge_{0.2}Se_{0.8})(Ge_{0.2}Te_{0.8})$, $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$, as well as $Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$ systems by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and Raman scattering techniques; 2) study of the thermodynamic properties of the aforementioned alloys, proposition of the fitting model for deconvolution of exothermic crystalline peaks gathered with DSC technique; 3) preparatory experimentation for the assessment of changes in electrical conductivity and Seebeck coefficient for chosen thermally modified Bi-containing alloy and 4) investigation of nanomechanical surface response as a valuable tool to study elastic deformation leading to structural predictions using nanoindentation technique.

With regard to the presented DSC results, there is a doubt as to how the selection of a different rate of temperature affects the results and whether the different measurement regime proposed in the study is justified - Table 2.2 presents T_g and T_x for rate 10 K/min, while Fig. 2.10 presents the analysis of spectra collected with rate 5 K/min.

The thesis presents results of optical transmission. The found correlation of this parameter with the composition of the samples and their thickness is a very interesting result. In the context of these, as well as the results discussed later, the question arises about the spectrum of the light source itself - whether its shape is known to the Author and the presented results have been related to the spectrum of the light source?

In the 2.3.9. Author writes that measurement *has been carried out using self-made apparatus equipped with a thermally-isolated sample compartment keeping a through soldering approach of electrical contacts enabling for ΔV/K and resistivity measurements.* However, there is no more detailed information about this self-assembled system.

The Chapter 3 referees state-of-the-art in the RE-doped FEWS sensors and encompasses an explanation of the selected physical phenomena on which optical sensors operate, as well as the selected details and aspects of fiber optic technology. The Author assumed that the chosen glass is an effective host matrix for the RE dopants and presents experimental results concerning ChG-based single-index fibers. In this chapter, we can distinguish sections devoted to: 1) synthesis and characterization (mechanical, thermodynamic and optical parameters) of multi-component Ge and/or As-based selenium glasses, such as $Ga_5Ge_{20}As_{10}Se_{65}$, $Te_{20}As_{30}Se_{50}$, or As_2Se_3 modified with Ga and Sb to increase the RE solubility and maintain stability of the amorphous state; 2) optimization of optical properties employing different purification and distillation processes and characterization of ChG-based single-core fibers of diameters ranging from -drawn waveguides.

MSc Eng. J. Szlęzak is a co-author of 9 papers (source: Web of Science, March 2021), selected elements of which, were included in the dissertation. Fragments of the dissertation (e.g. Figures 2.16, 2.17, 2.18, 2.19, 2.21, 2.22, Table 2.5) come directly from the papers (listed here come from article [23] quoted in chapter 2) in which the student is a co-author - also in such a situation it is required placing a reference to literature in the figure caption, what the Author did not do.

A certain difficulty is the credible assessment of the doctoral student's contribution to the implementation of individual tasks in the assessed thesis. For example, the extensive description of samples preparation does not indicate whether the Author himself prepared the samples, participated/assisted in the process of their production, or whether he presents this part of the dissertation for information purposes only, as the introduction of information relevant for the subsequent interpretation of the obtained results. In the Author's favor, it can be assumed that his participation in the project was significant, and among the arguments confirming this approach, it should be emphasized that the set of results contained in the dissertation is more extensive than that presented in the publications, and at the same time not all information (research results) presented in the publications were included in PhD thesis.

Deserving distinction is the graphical and descriptive method of indicating the area of research interests adopted by the Author (e.g. Fig. 2.4, Fig. 3.9), with a clear indication what elements of research paths are implemented by the Author, and what are the paths currently developed in other groups. This way of presenting the topic proves the Author's good orientation in the current state of knowledge and clearly defined research priorities.

The presented results seems to be reliable and well documented, the interpretation and the results discussion are thoughtful and well presented. In the opinion of the reviewer, **the subject of the dissertation prepared by MSc Eng. Jakub Szlęzak is new, interesting and has application potential. In addition, the subject matter is topical among the issues of modern materials engineering and fiber optic technology. The results of the work have the potential for practical use.**

Concluding remarks

The PhD thesis contains extensive experimental material, in my opinion the dissertation is undoubtedly an original contribution to the development of science, it was prepared with due diligence and deserves a positive overall assessment. The Author shows both the skills and predispositions required to formulate and solve scientific problems using a variety of measurement techniques. The whole proves the PhD student's readiness to undertake independent research work.

The Jakub Szlęzak PhD thesis entitled "Pnictogen modified Ge-Ga-Se(Te)-based glasses for optoelectronic devices " meets the conditions for doctoral dissertations in accordance with the Act of March 14, 2003 on scientific degrees and scientific title as well as degrees and title in the field of art (Journal of Laws of 2003, No. 65, item 595), as amended (PL: *Ustawa z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz stopniach i tytule w zakresie sztuki (Dz. U. Nr 65 poz. 595) z późniejszymi zmianami*), and I hereby request admission to further stages of the doctoral dissertation.

Considering the very extensive scientific achievements, supported by co-authorship in publications in renowned scientific journals, extensive and generally very well prepared doctoral dissertation, I am applying for a distinction of the dissertation by MSc Eng. J. Szlęzak.