Warsaw, January 26th, 2025

Doctoral Thesis Evaluation Report
Submitted to Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Toruń.

Candidate:	mgr. Abdellah Bachiri
PhD title:	Development of Novel Semiconductor Scintillators
Supervisor:	Prof. dr. hab. Winicjusz Drozdowski
Co-supervisor:	Dr. Marcin E. Witkowski

Introduction and background.

The PhD thesis of mgr. Abdellah Bachiri is devoted to study the properties of semiconductor scintillators from three types of crystals: pure and doped gallium oxide (β-Ga_2O_3), Ga-based spinels ($MgGa_2O_4$ and $ZnGa_2O_4$) and mixed (Zn,Be)Se crystals. Research is aimed at enhancement of the basic scintillation parameters, such as light yield, energy resolution and decay time constants.

Thus, this thesis addresses the highly relevant and vital areas of current scintillator research. This subject is interesting not only from theoretical but also from practical point of view due to wide application of scintillators and the fact that semiconductor scintillators are gaining increasing attention.

General short description of the thesis

The dissertation comprises 177 pages (plus Annex with the scientific outcome of the Author) and is enriched by number of figures (140) and tables (17) and follows the classic structure of a PhD thesis in science. It begins with abstract and Chapter 1 *Introduction* to the subject which includes a list of several main goals of the thesis. There are 9 references for Chapter 1. Each chapter has its own reference list separately at the end of the chapter. The advantage of such a structure is that the chapters, consisting of integral parts, can be read and analyzed separately.

Chapter 2 *Physical bases of the scintillation phenomenon* consists a literature review which has a logical partition and includes the fundamentals of the physical principles behind scintillation process, such as: definition of radiation, interaction of ionizing radiation with matter, solid state classification, types of interactions between energetically charged particles and matter, the phenomenon of scintillation and mechanisms of energy transfer. This part is well referenced (26 references) and a comprehensive bibliography contains all the relevant papers for the discussed field. Chapter 2 is well written and provides a very good background for understanding the rest of the thesis.

Chapter 3 *Present-day scintillator market* presents quite extensive description of various scintillating materials such as transparent crystals, phosphors, plastics, or organic liquids as well as scintillating gases. The main parameters and features of scintillators are described together with their applications, historical overview and future trends. This part presents an interesting overview of some new trends in scintillator development. Chapter 3 has 72 references. The literature used in this part of the doctoral dissertation is correctly selected, showing the topical issues.

Chapter 4 *Materials and experiment* presents a concise overview of the current state of art of the diverse growth techniques employed for the fabrication of bulk single crystals of transparent semiconducting oxides and introduces details (growing conditions, crystal structure, band structure) of the studied materials: gallium oxide (β-Ga_2O_3), Ga-based spinels: $ZnGa_2O_4$, $MgGa_2O_4$. Experimental setups accessible in the Scintillator and Phosphor Materials Spectroscopy Group in the Faculty of Physics, Astronomy and Informatics in Toruń and in the National Centre for Nuclear Research in Świerk, together with the measurement techniques are described in detail in subchapter 4.3. This part contains extensive bibliography (178 positions) which shows that mgr. Abdellah Bachiri has a broad overview of the subject literature.

In my opinion chapters 1, 2 and 3 are well written and provide a very good background for understanding the rest of the thesis. However, this part appears to me to be too long, too wide. It should be more concise and focus on relevant content, avoiding any unnecessary or redundant information. It is better to mention only those aspects that are needed to contextualize the problem that the study is solving.

The main part of the thesis consists of Chapter 5 *Results of conducted research with discussion* which I will describe later in this review.

In the final section, Chapter 6 *Summary and conclusions* the general conclusions of the work are presented. The results from these studies are categorized into three groups. The first category involves the measurement of scintillation and luminescent properties of gallium oxide crystals, Ga-based spinels, ZnSe, and (Zn,Be)Se. The second category includes temperature-dependent relative light yield measurements for all crystals. The third category explores the thermal properties of (Zn,Be)Se crystals. The conclusions confirm that the formed objectives of the work were successfully obtained.

The thesis is prepared in good editing standard. All the figures are carefully prepared and clearly presented. The language is comprehensive and coherent while errors and inaccuracies are relatively rare (my minor editorial comments are listed on a separate page). However, in my opinion a small disadvantage appears, in that some portions of information found in the introduction, literature and experimental sections (Chapters 1 – 5) are repeated. Also, because each chapter is separately referenced, which might be convenient because smaller files are easier to scroll through, references are multiplied (for example: the work: Z. Galazka et al., "$MgGa_2O_4$ as a new wide bandgap transparent semiconducting oxide: growth and properties of bulk single crystals" Physical Status Solidi A., 212 (2015) 1455-2015, is repeated in the references six times, like many others).

Detailed substantive evaluation of the dissertation

The results and discussions are presented in the fifth chapter (pages 102-168). Subchapters 5.1. 5.2, 5.3 and 5.4 are devoted to present results on the investigation of β-Ga_2O_3 pure and doped with silicon, $MgGa_2O_4$ and $ZnGa_2O_4$ single crystals, ZnSe and (Zn,Be)Se crystals and thermal properties of $Zn_{1-x}Be_xSe$ crystals, respectively. For each group of materials pulse height spectra, scintillation time profiles, radioluminescence, thermoluminescence and temperature dependence results are presented and discussed. Chapter 5 has 20 references.

Gallium oxide crystals β-Ga_2O_3, both pure and doped with silicon were presented and analyzed in subchapter 5.1. Several samples were tested but only samples with the highest efficiency were chosen for presentation. It was shown for Ga_2O_3 that for obtaining relatively high scintillation yields and shorter mean decay times a concentration of free carriers around 10^{17} cm^{-3} is needed. Si doping resulted in shorter decay times and influenced the scintillation decay rate and efficiency. It was concluded that doping gallium oxide crystals with silicon significantly decreases scintillation efficiency. This was related to the fact that β-Ga_2O_3:Si crystals are characterized by a higher concentration of free carriers compared to pure crystals. Thus, probability of the Auger effect occurrence, which is parasitic effect relative to scintillation and is proportional to the third power of n_e, increases. These studies underscore the importance of material purity in optimizing scintillation performance.

To ensure accurate analysis Candidate developed a new method for analyzing scintillation decay curves by recording both the sample and apparatus responses, which were deconvolved and fitted with multi-exponential decay functions.

It was observed that the radio-luminescence (RL) efficiency at room temperature is significantly lower than at the cryogenic temperatures. This was more pronounced for pure samples and smaller for samples with silicon. This implies that scintillation efficiency based on pulse height spectra at low temperatures, would be higher on the order of tens of thousands of ph/MeV. This indicates a significant potential in β-Ga_2O_3, which could be utilized in the future, if a way to reduce thermal damping is found.

Results of the thermoluminescence experiments of β-Ga_2O_3 and β-Ga_2O_3:Si led to the conclusion that there is only a sole trap present in each sample which determines the luminescence characteristics of the material.

Lowering in scintillation yield with temperature was attributed to the decrease in free electron concentration at lower temperatures. It was proposed that other quenching mechanisms, linked to the thermal activation of non-radiative recombination processes at Fe impurities, along with contributions from Auger quenching, may also be active.

In section 5.2 an analysis of the fundamental scintillation characteristics observed for $MgGa_2O_4$ and $ZnGa_2O_4$ crystals were presented. It was shown that scintillation yields reach levels of approximately 2,500 ph/MeV. By examination of scintillation time profiles, an inverse correlation between scintillation yields and decay rates were reported. Observations

suggested that the radioluminescence of both $MgGa_2O_4$ and $ZnGa_2O_4$ was notably more pronounced at lower temperatures, indicating the presence of important thermal quenching mechanisms.
In Table 5.8 very strong differences in the behavior of investigated crystals, prepared by Czochralski and Vercal Gradient Freeze (VGF) methods could be observed, which perhaps deserves more detailed explanation.

Subchapter 5.3 explores the scintillation properties of ZnSe and (Zn,Be)Se. Initially, investigations focused on the scintillation properties of pure ZnSe and mixed (Zn,Be)Se crystals. However, ZnS showed limited scintillation efficiency in its as-grown state, yielding only a few thousand ph/MeV. It was shown, that annealing in zinc vapor increased the scintillation yield to 26,200 ph/MeV for ZnSe and 15,100 ph/MeV for (Zn,Be)Se.
This research was extended to include (Zn,Be)Se samples with varying Be concentrations from 2% to 20% and to investigate how annealing affects their performances. Additionally, measurements were done to understand the energy gap and electronic properties dependence on beryllium concentration, which impacts the scintillation and thermal properties of (Zn,Be)Se crystals. The annealed ZnSe sample showed a yield of 26,000 ph/MeV, while the (Zn,Be)Se sample yielded 15,400 ph/MeV. Thus, significant enhancement in scintillation light output due to annealing in a zinc atmosphere was proved. Presented results underscore the crucial roles of annealing and Be content in optimizing the defect structure, electronic and thermal properties as well as scintillation decay profiles of (Zn,Be)Se materials for specific applications. This knowledge is important not only for understanding the physics of II-VI semiconductors, but also for developing more efficient scintillation materials for various applications.

Thermal properties of $Zn_{1-x}Be_xSe$ crystals are described in subchapter 5.4. The band gap energies for $Zn_{1-x}Be_xSe$ mixed crystals were calculated. Thermal diffusivity values were extracted from experimental data, and thermal conductivity was calculated and discussed in the framework of Abeles phenomenological model. The effect of Be concentration on the optical and thermal properties of $Zn_{1-x}Be_xSe$ crystals was analyzed and discussed.

Specific comments:
- As all presented results underscore the importance of material quality for optimizing its scintillation performance I will expect to present in the document comprehensive description showing the relation between the investigated crystals quality/purity and its basic electrical, optical or scintillating properties.
- On page 55 it is stated that "some crystals have been grown at Nicolaus Copernicus University in Toruń by the author of this thesis", I would like to get more details on that activity.
- I am missing in Chapter 6 a comparison between results obtained in this study and results published by other authors.

Overall, the thesis contains a large number of significant new results and is clearly sufficient for granting a PhD degree. I would like to emphasize that the studies concern a broad area of research and their main value consists in the detailed description of the obtained results. The research results of this PhD thesis contributes significantly to the knowledge and understanding of the important and highly relevant topic.

Final conclusions and evaluation statement

The results of the Candidate significantly improve the knowledge in the field of semiconductor scintillating materials in the discipline of physical sciences. The results are well presented and the interpretation is at high scientific level. Moreover Mr. Abdellah Bachiri, who is a young researcher, is able to critically approach the research methodology he uses. Mr. Abdellah Bachiri work resulted in total in seven peer-reviewed publications over the last five years, which is quite an achievement for a PhD student, and in one of the papers Mr. Bachiri is the first author. Thus, in my opinion the presented doctoral dissertation meets all the requirements i.e.:

- demonstrates the general theoretical knowledge of the candidate in the discipline of physical sciences,
- confirms the candidate's ability to conduct independent research, his familiarity with the relevant research techniques and methods,
- it is an original solution to a scientific problem, which is the prediction of the scintillating properties of several semiconducting materials.

Summarizing, the presented thesis of mgr. Abdellah Bachiri *Development of Novel Semiconductor Scintillators* fulfills all the formal (art. 187 ustawy *Prawo o szkolnictwie wyższym i nauce* z dnia 20 lipca 2018 r. z późn. zm.) and customary requirements, and I recommend to proceed to further steps required to award mgr Abdellah Bachiri the PhD title.

Michał Malinowski

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Minor remarks:

- Page 12 Fig. 2.4. Energy band level diagram of ~~insulator~~ conductor.
- Page 15 Specifically, shorter wavelengths correspond to the emission of electrons with higher kinetic energy ~~levels~~ (?)
- Page 18 the specific luminescent centers present in the material and can extend beyond 10^{-10} seconds.
- Page 77 These crucial metrics can be determined by appropriately adjusting the parameters of a shape function, such as a Gaussian function, to accurately replicate the recorded peak (fitting in Fig. 4.4). Should be: (fitting in Fig. 4.13)
- Page 119 This difference is more pronounced for pure samples and those containing silicon, and smaller but still visible for samples with silicon.

This is not clear, please explain.