OPINION

by **Dr. Nina Dimitrova Dimcheva, Assoc. Prof.**

Department of Physical Chemistry, Plovdiv University "Paisii Hilendarski"

Regarding the Award of the Educational and Scientific Degree of "Doctor of Phylosophy, Ph.D." in the Field of Higher Education 4. Natural Sciences, Mathematics, and Informatics, Professional Direction 4.2 Chemical Sciences, Doctoral Program "Inorganic Chemistry"

Candidate: **Georgi Vasilev Rusev**

Topic: "**Synthesis, Structure, and Properties of Oxotellurates (IV, VI) of the Elements from Group IVB**"

Scientific Supervisor: **Assoc. Prof. Dr. Svetlana Zheleva**, Burgas State University "Prof. Dr. Assen Zlatarov" – Burgas

1. General Overview of the Procedure

I have been appointed as a member of the scientific jury in connection with the defense of the dissertation of Ph.D. student Georgi Vasilev Rusev by order of the Rector of Burgas State University "Prof. Dr. Assen Zlatarov" No. УД – 235/30.06.2025. The set of documents submitted by the PhD candidate Georgi Rusev, both in paper and electronic form, complies with the requirements of the Law for the Career Development of the Academic Staff of the Republic of Bulgaria, as well as Article 43, Paragraph 3 of the Regulations for the Conditions and Procedure for Acquiring Scientific Degrees and Holding Academic Positions at Burgas State University "Prof. Dr. Assen Zlatarov" – Burgas.

Georgi V. Rusev was enrolled as a regular doctoral student in the Department of Chemistry in February 2021 and was discharged with the right to defend his dissertation on 14.09.2024.

2. Brief Autobiographical Data

According to the provided biography, Mr. Georgi Rusev received a Bachelor's degree in 2016 with a major in "Organic Chemical Technologies" at the University "Prof. Dr. Assen Zlatarov" – Burgas. He completed a Master's degree in 2019 with a specialization in "Computer Systems and Technologies" and a Master's degree in "Informatics and Information Technologies in Chemistry and Chemical Education" in 2021 at the same university. Since January 2025, he has been appointed as an assistant professor at the University. His previous work experience was in the field of arts.

3. Relevance of the Topic

The rapid development of microelectronics poses new challenges to Materials Science, particularly the search for novel semiconductor materials as alternatives to silicon chips, which would allow further miniaturization of electronic components while reducing their energy consumption. Such intentions are focused on selenides of Zr and Hf, which meet both requirements, but it is highly likely that the oxotellurates examined in this Dissertation may provide an even better opportunity in this direction. Additionally, the theoretical and experimental

investigation of the catalytic properties of the synthesized compounds in esterification processes is of exceptional interest for finding new technological solutions in biofuel production. In this regard, I consider the current research, dedicated to the synthesis and characterization of the structure and properties of oxotellurates of the two elements from Group IVB of the periodic table, to be highly relevant.

4. Characteristics and Evaluation of the Dissertation

The Dissertation is structured as a monograph, organized into the following classic sections: Introduction; Literature Review; Experimental Part; Results and Discussion; Conclusions; Scientific Contributions; Dissemination of Results; and References.

The dissertation comprises 161 pages, with the obtained results illustrated by 76 figures and 19 tables. The attached bibliography includes 257 literature sources from the period from 1962 to 2025, ¼ of which are sources published during the last five years, and more than half of the references are from the last 10 years.

The goal of the Dissertation, as defined in the introduction, is related to the synthesis and physicochemical characterization of titanium, zirconium, and hafnium oxotellurates (IV, VI), investigating the kinetics of decomposition of oxotellurates under non-isothermal conditions and describing their catalytic activity in the esterification reaction. Achieving this goal is tied to the completion of specific research tasks and the obtaining of solid results. The research methods, including experimental and theoretical approaches, are outlined.

The literature review provides a detailed overview of the structure and properties of oxotellurates, with the specifics of oxo-compounds where tellurium is in the IV or VI oxidation state presented at the very beginning. Special attention is paid to the methods of synthesis of oxotellurates of d-elements, their structure and properties, with an emphasis on the known data to date on oxotellurates of chemical elements from Group IVB. The conclusions from the detailed literature review show that the planned research covers an area of scientific knowledge where information is either lacking or very scarce.

In the experimental part, both the methods for the synthesis of the target compounds and the numerous methods for their characterization are explained in detail: X-ray, spectroscopic, microscopic, thermal analysis, and kinetic studies.

The section "Results and Discussion" follows a similar arrangement of presentation. The oxotellurates of zirconium and hafnium synthesized by the hydrothermal method were subjected to X-ray diffraction, which clarified the phase composition of the samples and proposed a hypothesis regarding the size of the crystallites. The surface morphology of the obtained oxotellurates was visualized using electron microscopy, and the presence of crystallization water was proven by infrared spectroscopy.

The chemical reactivity of the synthesized oxotellurates was evaluated based on the electron density distribution in ZrOHTe and HfHTe, for which the surface method of molecular electrostatic potential (MEP) was used, and their net atomic charges were calculated. Computational methods were widely employed in the dissertation, both for determining the HOMO/LUMO energies and for obtaining kinetic information from the differential thermal

analysis of the samples. An experimental study of the catalytic activity of the synthesized oxotellurates in the process of interaction between organic acids and alcohols in the absence of solvents was also conducted. Rate constants, equilibrium constants of the processes were determined, and the activation functions—activation entropy, activation enthalpy, and the standard Gibbs free energy of activation—were calculated using the Eyring's equation derived in the Transition State Theory. This fact highlights the interdisciplinary nature of the work and the serious theoretical knowledge of the doctoral candidate.

The analysis and interpretation of the obtained results were carried out in depth and are described explicitly. Overall, the Dissertation is a well-structured and comprehensive work that makes a significant contribution to the field of Inorganic Chemistry, particularly in the study of oxotellurates. It demonstrates the candidate's deep understanding of the subject, methodological rigor, and ability to conduct independent research.

The conclusions fully correspond to the defined research tasks and are supported by the results discussed in the work. The Dissertation contains scientific and applied contributions that build upon the known knowledge in the field of Inorganic Chemistry, particularly the synthesis and characterization of catalysts for organic synthesis, and meets all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB).

5. Evaluation of Publications and Personal Contribution of the Doctoral Candidate

The candidate's measurable indicators, according to LDASRB and Article 43, Paragraph 3 of the Regulations for the Conditions and Procedure for Acquiring Academic Degrees and Holding Academic Positions at "Prof. Dr. Assen Zlatarov" University – Burgas, are as follows:

Group A of Indicators

Indicator A1 Ph.D. Thesis – prepared Dissertation titled: "Synthesis, structure and properties of oxotellurates (IV, VI) of the IVB group elements" in the professional field 4.2 Chemical Sciences – 50 points;

Group G of Indicators

Indicator G7: Scientific publications in journals that are refereed and indexed in globally recognized scientific databases (Web of Science and Scopus) – 2 publications in journals with impact factor in quartile Q3, namely in *Reaction Kinetics, Mechanisms and Catalysis* in 2024 and in the *International Journal of Chemical Kinetics* in 2025 –30 points;

Total for all groups of indicators 80 points

From the presented report, it is evident that the candidate meets the minimal National requirements under LDASRB and the Regulations for the Conditions and Procedure for Acquiring Academic Degrees and Holding Academic Positions at "Prof. Dr. Assen Zlatarov" University – Burgas.

Regarding the personal contribution of the candidate, it can be judged by their position in the authorship of the publications. In both declared articles, the candidate is in the first position, which testifies to their significant contribution both in conducting the experiments and in preparing the publications.

The doctoral candidate has reported part of the obtained results at 4 scientific forums with a total of 4 participations – 3 National scientific forums and one International.

In addition to the publications presented in the report, the candidate has one more article published in refereed and indexed journals. The relevance and significance of the candidate's publications can be judged by the fact that, as of now, there is already 1 citation of an article published in 2024 (Hirsch index h = 1).

6. Abstract

The abstract adequately reflects the content of the Dissertation.

I accept the formulated scientific and applied contributions.

7. Recommendations

The Dissertation is written in clear and precise language and the terminology is used competently. I recommend, however, that instead of the term thermodynamic functions, which are used to refer to enthalpy, entropy and standard Gibbs energy of activation defined by the Theory of the Activated Complex, the term activation parameters should be used, since during the formation of a transition state, the thermodynamic equilibrium between reactants and an activated complex is only assumed.

Conclusion

I do not know the Ph.D. candidate personally and have no firsthand impressions of his work, but the overall accomplishment of the current research has firmly convinced me of his qualities and abilities to independently conduct scientific research.

Based on the scientific publications provided, the results achieved, their precise interpretation, and the declared scientific and applied contributions, I give a positive evaluation to the dissertation on the topic "Synthesis, Structure, and Properties of Oxotellurates (IV, VI) of Group IVB Elements." I propose to the esteemed Scientific Committee to award the educational and scientific degree of "Doctor" to Georgi Rusev in the field of higher education 4. Natural Sciences, Mathematics, and Informatics, professional direction 4.2 Chemical Sciences, scientific specialty "Inorganic Chemistry."

Date: August, 10, 2025

Подпис заличен
Чл.2 от ЗЗЛД

Member of the scientific jury:

/Dr. Nina Dimcheva, assoc. prof./