OPINION

by Dr Leniya-Nezaet de Brito Gonsalves
Associate Professor at Burgas State University "Prof. Dr Assen Zlatarov,"
in Higher Education Area 4. Natural Sciences, Mathematics and Informatics,
Professional Field 4.2. Chemical Sciences, scientific specialty Analytical Chemistry

on a dissertation for the award of the educational and scientific degree "Doctor"
in Higher Education Area 4. Natural Sciences, Mathematics and Informatics,
Professional Field 4.2. Chemical Sciences,
Doctoral Program Inorganic Chemistry

Candidate: Georgi Vasilev Rusev
Title: Synthesis, structure and properties of oxotellurates(IV, VI) of elements from IVB group
Scientific Supervisor: Assoc. Prof. Dr Svetlana Zheleva, Burgas State University "Prof. Dr Assen Zlatarov"

1. General Presentation of the Procedure

By Order No. UD-235/30.06.2025 of the Rector of Burgas State University "Prof. Dr Assen Zlatarov," I was appointed as a member of the Scientific Jury to participate in the procedure for the defense of the dissertation entitled "Synthesis, structure and properties of oxotellurates(IV, VI) of elements from IVB group" for the acquisition of the educational and scientific degree "Doctor" in Higher Education Area 4: Natural Sciences, Mathematics and Informatics, Professional Field 4.2: Chemical Sciences, Doctoral Program Inorganic Chemistry. The author of the dissertation is Georgi Vasilev Rusev, a full-time doctoral student at the Department of Chemistry, Faculty of Natural Sciences, Burgas State University, with scientific supervision provided by Assoc. Prof. Svetlana Zheleva, PhD, of Burgas State University "Prof. Dr. Assen Zlatarov."
The set of materials submitted by the doctoral candidate in hard copy is in compliance with Article 43(3) of the Regulations on the Conditions and Procedures for the Acquisition of Academic Degrees and for Occupying Academic Positions at Burgas State University "Prof. Dr. Assen Zlatarov," and includes all required documents.

2. Brief Biographical Data

The doctoral candidate commenced his studies in 2011 at Burgas State University in the specialty Organic Chemical Technologies, where in 2016 he obtained the educational qualification degree of Bachelor with the professional qualification of Chemical Engineer. During the period 2017 – 2019, he continued his education in the master's program Computer Systems and Technologies, graduating with the qualification of Master Engineer. Subsequently, in the period 2019 – 2021, he completed a second master's program in Informatics and Information Technologies in Chemistry and Chemical Education. In 2021, he was enrolled as a full-time doctoral student in Inorganic Chemistry, and in September 2024 he was officially withdrawn with the right to defense. Since January 2025, he has been holding the position of Assistant Professor at the Department of Chemistry, Faculty of Natural Sciences, Burgas State University.

3. Relevance of the Research Topic

The relevance of the dissertation arises from the scarcity of literature data concerning the structure, thermal stability and catalytic properties of oxotellurates of titanium, zirconium and hafnium, combined with the growing interest in the application of these compounds in catalysis, sensor technologies and sustainable materials. The significance of the research lies in the synthesis and detailed characterization of new zirconium and hafnium oxotellurates, whose structure, morphology and decomposition mechanisms have been largely elucidated through a wide range of physicochemical methods and quantum-chemical analysis. These achievements make a fundamental contribution to expanding knowledge in the fields of inorganic chemistry and materials science. The applicability of the work has been demonstrated by the established catalytic activity of some of the synthesized compounds in esterification processes and their proven thermal stability, which outline them as promising heterogeneous catalysts. The results obtained provide a foundation for the rational design of new functional materials with potential applications in catalysis and in the development of chemical and biosensors.

4. Characteristics and Evaluation of the Dissertation

The submitted dissertation fully complies with the requirements of the Regulations for the Application of the Academic Staff Development Act and is structured in a classical academic format. Its total volume is 159 standard pages and includes: Introduction with formulated aims and objectives, Literature Review, Experimental Section, Results and Discussion, Conclusions, Scientific Contributions and References, as well as five pages of Appendices. Within the text, 76 figures, 18 tables, and 18 equations are numbered, with an additional six figures presented in the appendix. It should be noted that some inconsistencies occur in the numbering of figures and equations: figures 44 and 54 are missing, figure 62 appears twice and tables 12, 14, 17 are duplicated. The numbering of equations is sequential up to number 10, after which it restarts from 8. Despite these technical inaccuracies, which do not affect the content of the dissertation, the overall structure and formatting are accurate and well-organized. The bibliography includes 257 references, most of which were published after 2000, ensuring the relevance, contemporaneity, and reliability of the scholarly framework.

The Introduction provides a concise overview of tellurium and its compounds, highlighting the unique structural and chemical features of the element and the broad diversity of oxotellurate formation. Particular emphasis is placed on the factors determining their properties, as well as on analogies with silicate crystal chemistry, which demonstrates the breadth of scientific perspective. At the same time, potential applications of oxotellurates in key high-tech areas – optoelectronics, photonics, energy, and catalysis – are clearly outlined, which underlines the topicality and significance of the research. Based on this review, the aims and specific objectives of the dissertation are defined. They are formulated clearly and systematically, ranging from the hydrothermal synthesis of new oxotellurates, through their structural, spectroscopic, and theoretical characterization, to the study of thermal stability and catalytic activity. This demonstrates logical consistency and sound scientific justification.

The Literature Review is well-structured and provides comprehensive information on the crystal chemistry, synthesis and properties of oxotellurates(IV, VI). The text offers an in-depth presentation of structural units and their diversity, including the specific features of Te(IV) and

Te(VI) in different coordination environments and their modes of linkage into more complex structures. An important contribution of this section is the detailed description of synthetic methods and the emphasis on their potential for producing new materials. The review demonstrates correlations between structure and properties, illustrated with examples of optical, thermal and electronic characteristics, and provides comparative analyses with related systems such as oxoarsenates and oxoselenates. Alongside these strengths, it highlights areas where research remains limited or absent, thus reinforcing the importance of the chosen topic. From the presented review, it can be concluded that systems involving Te(IV) and those with d- and f-elements remain less thoroughly explored – systematic data on the stability of Te(IV) compounds, the synthesis and structure of most d-element tellurates, and sufficient information on the structural chemistry and functional properties of f-element systems are still lacking.

The Experimental Section, spanning 11 pages, describes the conditions for the hydrothermal synthesis of oxotellurates(IV, VI) of Ti, Zr, and Hf, along with the theoretical and experimental methods employed for their study. Quantum-chemical approaches such as frontier molecular orbital and Hirshfeld surface analyses are included, together with a broad range of physicochemical techniques: X-ray diffraction (powder and single-crystal), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), ultraviolet-visible spectroscopy (UV-Vis) and thermal analysis (TG/DTA, TG/DSC). The mathematical framework for studying decomposition kinetics under non-isothermal heating is presented in detail, including equations linking activation energy (E_a), pre-exponential factor (A) in the Arrhenius equation and rate constant (k), as well as the relationships between Gibbs free energy, enthalpy and entropy in the formation of the activated complex. Finally, the experimental setup for testing catalytic activity is described, with the synthesized oxotellurates employed as heterogeneous catalysts in model reactions.

The Results and Discussion section is distinguished by consistency, depth and breadth of research approach. The doctoral candidate demonstrates that in the hydrothermal synthesis of titanium oxotellurates(IV, VI), the resulting solid phases are amorphous and do not reach a crystalline structure despite variations in temperature – a finding presented with sound reasoning as a basis for comparison with zirconium and hafnium compounds. This demonstrates critical thinking and the ability to argue the significance of negative results. In the zirconium systems, an important achievement is the synthesis and X-ray structural characterization of a new crystalline phase ($ZrTe_2O_6Cl$), while in the hafnium analogues the difficulty of obtaining a well-indexed lattice due to the high thermal stability of HfO_2 is reported – an observation placed in the context of literature data and indicative of scientific maturity.

A strong point of this chapter is the rich analytical toolkit: XRD, FTIR, Raman, XPS, SEM and UV-Vis spectroscopies are employed not merely formally but to confirm phases and reveal structural trends. An integrated approach is applied, which is particularly convincing as it provides both experimental and theoretical validation of the results. Of special significance is the application of thermal analysis (TG/DTA, DSC) combined with kinetic models (Coats-Redfern, Kissinger-Akahira-Sunose, Vyazovkin), through which not only the temperature ranges of decomposition are determined but also specific parameters such as activation energy and pre-exponential factor. A particularly valuable contribution is the first proposed description of thermal decomposition mechanisms, linking structural features to the real stability and reactivity of the materials. The high activation energy for Hf-oxotellurate(IV) and the observed negative entropy

underscore the stability and complexity of the crystalline structure – results of notable contributory value.

Additional weight is given by the catalytic experiments: the synthesized Zr- and Hf-oxotellurates are investigated for the first time as heterogeneous catalysts in esterification reactions for the production of butyl acetate. Although the results are preliminary, the established catalytic activity and the prospect of their further development as acid catalysts in the context of green chemistry and sustainable technologies emphasize the applied potential of the research.

In summary, the Results and Discussion chapter is written with scientific precision and persuasiveness, skillfully combining positive and negative findings, experimental and theoretical approaches, and both fundamental and applied dimensions. It not only fully meets the requirements for a dissertation but exceeds them by presenting new structural data, a reliable kinetic and thermodynamic analysis, and initial steps toward the practical application of these compounds.

At the conclusion of the dissertation, the scientific and applied contributions of the study are presented, which stand out for their originality and novelty. For the first time, new phases of zirconium and hafnium oxotellurates(IV, VI) have been synthesized and thoroughly characterized, and by combining experimental and quantum-chemical methods, an in-depth understanding of their coordination environment, morphology and electronic features has been achieved. The determination of kinetic and thermodynamic parameters of decomposition contributes to a better understanding of the stability and reactivity of these materials and enriches knowledge in the field of crystal chemistry. From an applied perspective, the proven catalytic activity of zirconium and hafnium hydrogentellurates in esterification processes, combined with their good thermal stability, highlights their potential as efficient heterogeneous catalysts for high-temperature processes. The established relationship between structure and catalytic activity provides a basis for the rational design of new functional oxide catalysts, while the potential for application in sensor technologies broadens the practical dimensions of the research. The contributions presented are a clear indicator of the high scientific and applied value of the dissertation.

5. Assessment of the Publications and the Doctoral Candidate's Personal Contribution

The required indicators of the candidate, pursuant to the Academic Staff Development Act and Article 43, paragraph 3 of the Regulations on the Conditions and Procedures for the Acquisition of Academic Degrees and for Occupying Academic Positions at Burgas State University "Prof. Dr. Assen Zlatarov," are as follows:

Indicator A1

Indicator A1. Dissertation for the educational and scientific degree "Doctor" – completed dissertation on the topic "Experimental and Theoretical Studies of Selenate Systems" in Professional Field 4.2 Chemical Sciences – 50 points.

Indicator G7

Indicator G7. Scientific publications in journals that are peer-reviewed and indexed in internationally recognized databases of scientific information (Web of Science and Scopus), excluding the habilitation thesis – 2 publications are attached, both in Q3 quartile, i.e. 30 points:

- Tankov I., Rusev G., Yankova R., Georgieva V., Kolev H., Genieva S. Zirconyl and hafnium hydrogen tellurates as catalysts for esterification (2024) Reaction Kinetics, Mechanisms and Catalysis, 137 (4), pp. 2105–2131, DOI: 10.1007/s11144-024-02655-5;
- Rusev G., Georgieva V., Genieva S., Tankov I. Non-Isothermal Decomposition Kinetics of Hafnium and Zirconyl Hydrogentellurates (2025) International Journal of Chemical Kinetics (ISSN 0538-8066, EISSN 1097-4601), 57 (4), pp. 254–262, DOI: 10.1002/kin.21773.

A total of 80 points for all groups of indicators

The submitted report demonstrates that the candidate meets the minimum national requirements under the Academic Staff Development Act and the Regulations on the Conditions and Procedures for the Acquisition of Academic Degrees and for Occupying Academic Positions at Burgas State University "Prof. Dr. Assen Zlatarov." With regard to the candidate's personal contribution, this may be inferred from his position in the authorship of the presented publications – he is listed second in the first article and first in the second. In addition to the two publications indicated in the report, the candidate has also published another article related to the dissertation topic in an impact factor journal, which further attests to his scientific activity.

6. Author's Abstract

The author's abstract of Georgi Rusev adequately reflects the main results and contributions of the dissertation. The key novel compounds, the methods employed for their structural characterization, as well as the calculated kinetic and thermodynamic parameters are presented clearly and concisely. The results concerning catalytic activity are summarized with specific values for yields and rate constants, which reinforces their persuasiveness. The abstract provides a synthesized and accurate account of the principal achievements and contributions, while consistently maintaining an academic style and well-grounded argumentation.

7. Critical Remarks and Recommendations

The dissertation is written in sound scientific language. The figures and tables are neatly prepared and present the information clearly, allowing for quick and accurate interpretation of the results. Technical inconsistencies and typographical errors are negligible, mainly related to inaccuracies in the numbering of tables and figures. In some instances, the temperature is presented in degrees Celsius, while in the majority of the text absolute thermodynamic temperature (Kelvin) is used, which disrupts the consistency and uniformity of the exposition. These remarks, however, are purely technical in nature and do not affect the content or the scientific value of the dissertation. I have no principal objections to the material presented.

Conclusion

I have been acquainted with PhD candidate Georgi Rusev since his enrollment in the master's program "Informatics and Information Technologies in Chemistry and Chemical Education", and I have had the opportunity to observe first-hand his determination, diligence, sense of

responsibility and consistency in his work. The comprehensive execution and presentation of this dissertation convincingly reaffirm the presence of the qualities and competencies required for the independent pursuit of scientific research.

In view of the presented scientific publications, the results achieved, their precise interpretation and the scientific and applied contributions derived therefrom, I express a positive evaluation of the dissertation entitled "Synthesis, structure and properties of oxotellurates(IV, VI) of elements from IVB group." I respectfully recommend that the esteemed Scientific Jury confer upon Eng. Georgi Vasilev Rusev the educational and scientific degree of Doctor in Higher Education Area 4: Natural Sciences, Mathematics and Informatics, Professional Field 4.2: Chemical Sciences, in the scientific specialty Inorganic Chemistry.

Подпис заличен
Чл.2 от ЗЗЛД

19.08.2025 г. Chair of the Scientific Jury:

(Assoc. Prod. Dr Lenia Gonsalvesh)