REVIEW

by Prof. Lyubomir Todorov Vlaev, D.Sc., currently retired

Re: Announcement of a procedure for the defense of a dissertation at the Faculty of Natural Sciences at Prof. Dr. Asen Zlatarov University of Burgas by regular doctoral student Georgi Vasilev Rusev for the award of an educational and scientific degree of "Doctor" in the doctoral program "Inorganic Chemistry" in the professional field 4.2.

Position of the reviewer: member of the scientific jury for the defense of a dissertation for the degree of Doctor of Science.

Basis for the review: Decision of the Faculty Council of the Faculty of Natural Sciences (Minutes No. 25 of 18 June 2025) and Order No. RD 235 of 30 June 2025 of the Rector of Prof. Dr. Asen Zlatarov University.

I have known the doctoral student personally since he enrolled in the Department of Chemistry as a regular doctoral student, and I have been following his scientific development, being a doctoral student of my former doctoral student from the same faculty, who worked on a similar topic. I have no joint publications with him and I have no conflict of interest with the doctoral student.

1. Information and data on the doctoral student's professional development.

In 2016, **Georgi Vasilev Rusev** received a bachelor's degree in Organic Chemical Technologies, in 2019 he received a master's degree in Computer Systems and Technologies, and in 2021 - a master's degree in Informatics and Information Technologies in Chemistry and Chemical Education from Prof. Dr. Asen Zlatarov University, Burgas. In January 2025, after passing a competitive examination, he was appointed as a full-time assistant professor in the Department of Chemistry at the same university.

2. Assessment of the doctoral student's research activity.

In my capacity as a reviewer, I have been provided with hard copies and electronic versions of the doctoral student's dissertation, an abstract of the dissertation, and three publications related to the doctoral student's research work in full text. The dissertation submitted by Georgi Rusev meets the requirements of the PPZRASRB and contains an introduction, objectives and tasks, a literature review, an experimental section, results and discussion, conclusions, and a bibliography. The dissertation is written on 159 standard pages, includes 76 figures and 19 tables, and correctly cites 257 literary sources, published mainly after 2000. Five pages of appendices have been added to the dissertation. The abstract is 64 pages long and concludes with Conclusions, Scientific Contributions, and a List of the Methods and Forms of Dissemination of the Scientific Results Obtained.

Three scientific publications related to the dissertation have been presented, all of which are in quartile Q3. Of the three journals in which the scientific papers were published, the one with the highest impact factor (IF = 4.7) is the Journal of Molecular Structure, Reaction Kinetics, Mechanisms and Catalysis (IF = 1.7) and the International Journal of Chemical Kinetics (IF = 1.6). The first publication is 14 pages long, in which the doctoral student is the third co-author out of a total of four. The second is 27 pages long (second co-author out of a total of six), and the third is 9 pages long (first co-author out of a total of four), with the content of all three publications corresponding to the topic of the dissertation. This leads me to conclude that the doctoral student worked in a team, but his own participation in conducting the experiment and interpreting the results is mainly his own work. In addition, the doctoral student participated in FOUR scientific conferences in the country, in all of which he was the first co-author.

3. Essence of the dissertation, goals, and tasks

The topic of the dissertation is "Synthesis, structure, and properties of oxotelurates (IV, VI) of elements from group IV B," and the goal is to obtain titanium, zirconium, and hafnium oxotelurates (IV, VI) based on hydrothermal synthesis, to characterize their structure and properties using physicochemical methods of analysis, to describe the kinetics of their decomposition under non-isothermal heating conditions, and to investigate their catalytic activity in some model reactions.

To achieve the set goal, the following tasks were accomplished:

1. To carry out hydrothermal synthesis of oxotelurates(IV, VI) of the elements from group IVB in the temperature range 100–250°C, characterizing the resulting solid phases using instrumental techniques and methods (XRD, TGA, UV-vis, IR, Raman, XPS, SEM).

2. To determine the type of crystal lattice of the synthesized oxotelurates single crystals and analyze the reactivity and properties of the obtained compounds using theoretical quantum chemical methods.

3. To study the thermal stability and analyze the kinetics of the decomposition of oxotelurates from IVB of the Periodic Table under non-isothermal heating conditions.

4. To investigate the catalytic activity of oxotellurates in the model esterification reaction and to study the kinetics of heterogeneous processes

4. Literature review:

The literature review provides a detailed overview of the synthesis, structure, and properties of oxotellurates (IV, VI) of Ti, Zr, and Hf. On 38 pages, including 31 figures and 3 tables, the actual situation on the issue is described, and the relevant critical conclusions are drawn, which show the following:

a) There is little data available on the crystal structure and properties of oxotelurates(IV, VI) of titanium, zirconium, and hafnium, and there is no data at all on thermal stability, decomposition kinetics, or catalytic activity.

b) Researchers' keen interest in studying this exotic class of compounds is dictated by the unusual crystal structures of oxotelurates(IV) and the emerging new direction of application of telurite glasses in the development of oxotelurates(IV) for biomedical purposes.

c) There is a lack of data on the thermal stability and kinetics of thermal decomposition of oxotelurates(IV, VI) of titanium, zirconium, and hafnium upon heating, as well as on the catalytic activity of oxotelurates(IV, VI) and the kinetics of model heterogeneous catalytic reactions.

Based on these findings, the prerequisites that motivated the aim and objectives of this dissertation have been outlined.

5. Experimental section

The experimental section, on page 10, describes the conditions of hydrothermal synthesis of tellurates, the theoretical (Frontier Molecular Orbital (FMO) analysis and Hirschfeld surface analysis) and experimental (X-ray diffraction methods, infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), ultraviolet spectroscopy (UV-Vis) and thermal analysis (TG/DTA, TG/DSC)) physicochemical methods of analysis. The mathematical apparatus used to study the kinetics of decomposition during non-isothermal heating of the oxotellurates studied is described in detail. Added to this are the equations relating the activation energy EA, the pre-exponential factor A in the Arrhenius equation and the rate constant k of the reaction, as well as the relationships between the thermodynamic state functions of Gibbs energy change, enthalpy, and entropy during the formation of the activated complex of the reagent. In addition, the kinetic experiment with the selected model reactions involving the obtained oxotellurates as heterogeneous catalysts is described.

6. Results and discussion

The main section, "Results and discussion," is presented on 71 pages and contains 37 figures and 13 tables. The graphs are accurately executed, appropriately dimensioned, and clearly outline the course of the respective dependencies. Many of the figures are in color, which makes the different curves easily distinguishable and easier to interpret. I believe that the experimental results have been adequately interpreted by the doctoral student, as evidenced by the volume and level of scientific papers published in the relevant specialized journals.

According to the doctoral student's own conclusion, the most important conclusions from his scientific research can be summarized in the following THREE groups of results:

I. Synthesis, structural characterization, thermal stability, and catalytic activity of zirconium and hafnium oxotelurates(VI).

* New zirconium and hafnium oxotelurates(VI) were synthesized under hydrothermal conditions, defined as zirconyl hydrogen telurate tetrahydrate, $ZrO(HTeO4)2{\cdot}4H2O$, and hafnium hydrogen telurate octahydrate, $Hf(HTeO4)4{\cdot}8H2O$. The obtained crystal phases

possess the necessary phase purity and clearly defined crystallographic parameters. Spectroscopic studies (FTIR and Raman) reveal characteristic vibrations of the Te–O and M–O bonds and confirm the formation of stable coordination environments.

** A theoretical approach was used to characterize the electronic structure and chemical reactivity of the newly synthesized phases of zirconium and hafnium oxotelurates(VI). It has been established that the nucleophilic reactivity of zirconyl hydrogen teluride is determined by the positive charge of the hydrogen atoms. The Te atoms in hafnium hydrogen teluride have a more pronounced positive potential than those in zirconyl hydrogen telluride.

*** The thermal stability of $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ was studied up to 1000°C, and for the first time a decomposition mechanism was proposed and the kinetic parameters of the processes were determined using various computational procedures. $ZrO(HTeO_4)_2 \cdot 4H_2O$ dehydrates faster than $Hf(HTeO_4)_4 \cdot 8H_2O$, which is explained by weaker hydrogen bonds and lower activation energy.

**** Synthetic hydrogen telurates were first studied as acid catalytic systems in the esterification process. It was found that the highly acidic hydrogen atom (H26) in the form of HTeO4– fragments determines the nucleophilic reactivity of zirconyl hydrogen telurate. In the hafnium sample, hydrogen atoms (H33 and H44) with lower positive potential are identified as the most electrophilic centers. XPS analysis proves that $HTeO_4^-$ fragments are most superficially distributed.

II. Synthesis, structural characterization, and properties of zirconium chloroxotelurate(IV)

* A new phase, zirconium chloroxotelurate(IV) with the composition $ZrTe_2O_6Cl$, was synthesized under hydrothermal conditions. A single crystal was successfully isolated from the obtained crystal phase and structurally characterized. Zirconium chlorine oxotelurate(IV) belongs to the monoclinic centrosymmetric crystal system with space group C2/m.

** The crystal structure of $ZrTe_2O_6Cl$ was analyzed using a theoretical approach. The calculated bond lengths and valence angles show values close to those determined by the experimental method. Hirschfeld surface analysis and two-dimensional fingerprint diagrams were applied for a more in-depth analysis of the crystal structure.

*** The thermal stability of $ZrTe_2O_6Cl$ up to 1200°C has been investigated. The compound decomposes in three stages of mass loss: the first due to the release of physically adsorbed water, and the other two due to phase decomposition.

III. Synthesis, structural characterization, and thermal stability of hafnium oxotelurate(IV).

* A new phase, hafnium oxotelurate(IV) with a stoichiometric composition of $Hf_3Te_3O_{12} \cdot 1.5H_2O$, was synthesized under hydrothermal conditions. XRD analysis confirmed phase purity and a clearly defined crystal structure.

** The thermal stability of the obtained hafnium oxotellurate(IV) was investigated up to 1200°C. The analysis revealed a clear three-stage decomposition process involving dehydration, partial destruction of the oxotellurate structure, and complete decomposition to oxides.

*** Computational procedures were applied to determine the kinetic parameters of the decomposition processes of $Hf_3Te_3O_{12}\cdot1.5H_2O$, and it was found that each of the stages demonstrates a unique mechanism, emphasizing the complexity and multistage nature of the overall decomposition process. The main stage proceeds with an activation energy of 231.9 kJ/mol, which indicates a stable and strongly bonded crystal structure. The process is endothermic, with negative entropy ($\Delta S < 0$), indicating a transition from an ordered crystal to a more chaotic intermediate state.

**** The calculated thermodynamic functions (ΔH, ΔS, ΔG) confirm the complexity and stability of the decomposition.

7. Contributions and significance of the work for science and practice

* Scientific contributions include the fact that oxotelurates(IV, VI) of zirconium and hafnium with stoichiometric composition were synthesized for the first time: $ZrO(HTeO_4)_2\cdot4H_2O$, $Hf(HTeO_4)_4\cdot8H_2O$, $ZrTe_2O_6Cl$ and $Hf_3Te_3O_{12}\cdot1.5H_2O$.

** A comprehensive structural characterization of the obtained compounds was performed using a theoretical quantum chemical approach and experimental methods of analysis, including XRD, FTIR, Raman, UV-Vis, XPS, and SEM, allowing for an in-depth understanding of their coordination environment and morphology.

*** Kinetic and thermodynamic parameters of thermal decomposition were calculated, contributing to our knowledge of the stability and reactivity of new ocotellurate materials.

* The results of esterification processes and the established catalytic activity and properties of the synthesized zirconyl hydrogen teluride and hafnium hydrogen teluride, which outline the possibility of their application as effective heterogeneous catalysts, can be attributed to scientific and applied contributions. Their established good thermal stability makes them suitable for catalytic processes at elevated temperatures.

** The relationship between the structure and catalytic activity of materials has been outlined, which is a prerequisite for creating a basis for the rational design of new functional oxide catalysts.

*** A methodological framework for the application of metal oxotellurates(VI) in catalysis and their future potential in sensor technologies is provided.

8. Critical remarks and recommendations

The dissertation is written in good scientific language, and technical inconsistencies and typographical errors are negligible. For example, there are two different tables numbered 12 (on pages 95 and 98). In some places in the dissertation, degrees Celsius are used for temperature, while in most cases the absolute thermodynamic temperature, Kelvin, is used. The figures and tables are presented accurately and allow for quick reading of the information. I have no fundamental objections to the material presented in the dissertation.

My personal impressions of the doctoral student are very good, given that he regularly teaches classes in physical chemistry. I would therefore like to express my satisfaction that he handles complex mathematical apparatus well (see Table 5 and equations 4-10), He correctly handles the physical chemistry parameters and interprets the relevant dependencies well.

9. Conclusion

The dissertation contains scientific and applied scientific results that represent an independent and original contribution to science and practice and meet all the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria (ZRASRB), the Regulations for the Implementation of ZRASRB at BSU "Prof. Dr. Asen Zlatarov."

The dissertation shows that doctoral student Georgi Vasilev Rusev possesses in-depth theoretical knowledge and professional skills in the scientific field of "Inorganic Chemistry," demonstrating qualities and skills for independently conducting and assigning scientific research.

In view of the above, I am confident in giving my positive assessment of the research conducted and the results obtained, and I propose that the distinguished scientific jury award Georgi Vasilev Rusev the educational and scientific degree of "Doctor" in the field of higher education "Inorganic Chemistry" in the professional field 4.2. Chemical Sciences, area of higher education 4. Natural Sciences, Mathematics, and Informatics

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REVIEWER:

Burgas

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