OPINION

By Daniela Georgieva Kovacheva, Professor, PhD at the Institute of General and Inorganic Chemistry-BAS, on the dissertation for the acquisition of the educational and scientific degree "Doctor" in the scientific field 4.2 Chemical Sciences (Inorganic Chemistry)

Author of the dissertation: Georgi Vassilev Rusev**Title of the dissertation**: "Synthesis, structure and properties of" Oxotellurates (IV, VI) of elements from group IVB"

1. Fulfillment of the minimum requirements according to the Regulations for the acquisition of scientific degrees and holding academic positions at Burgas State University "Prof. Dr. Asen Zlatarov".

Georgi Rusev obtained a bachelor's degree in 2016 from the University "Prof. Dr. Asen Zlatarov", Burgas, in the specialty Organic Chemical Technologies. In 2019, he obtained 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 the University "Prof. Dr. Asen Zlatarov", Burgas. From February 2021 to February 2024, he was a full-time doctoral student at the University "Prof. Dr. Asen Zlatarov", Burgas, in the field 4.2. "Chemical Sciences" - Inorganic Chemistry. The submitted documents show that Eng. Rusev has successfully passed all the exams required by the doctoral program. There are three publications on the topic of the dissertation and 4 participations in scientific forums. The submitted documents show that all the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDASRB) and the Regulations for Acquiring Scientific Degrees and Holding Academic Positions at the University "Prof. Dr. Asen Zlatarov", Burgas have been met.

2. Relevance of the topic of the dissertation.

Tellurates and tellurites, although less widely used than other metal salts, find specialized applications in materials science and electronics. Tellurite glasses are valuable optical materials with high refraction and low phonon energy, suitable for fiber and nonlinear optics, IR technologies, and electroceramics. Oxotellurates (IV, VI) impress with flexible crystal structures and properties such as photoconductivity, piezoelectricity, and ionic conductivity, used in optoelectronics, photonics, and catalysis. Despite their potential, zirconium and hafnium oxotellurates have been poorly studied, especially in terms of thermal stability and catalytic activity. This emphasizes the relevance of the topic of the dissertation.

3. Type of research.

The dissertation is written on 161 pages, contains 70 figures, and 18 tables. 247 sources are cited. It follows the traditional format of presenting scientific research. The dissertation contains an introductory part, in which the research interest in tellurite materials is justified, which allows the formulation of the goals and objectives of the dissertation. In a literature review of 158 sources, the methods for obtaining tellurium-containing materials are examined in detail, with particular emphasis on their structural features. The experimental part describes the synthetic procedures and

methods for physicochemical characterization of the obtained oxotellurates. The methods are adequately selected, and the results of the analyses are critically summarized to clarify the synthesis-structure-properties relationship. Particular attention is paid to theoretical approaches for predicting and explaining the properties of the studied materials. The results of the research are presented in a way that each of the methods contributes to a full characterization of the structure and properties of the objects, with the overall picture being formed by combining the contributions of the different techniques. The conclusions logically follow from the presented data.

4. Research objectives and obtained results.

The goals of the dissertation of Eng. Georgi Rusev is to obtain new titanium, zirconium, and hafnium oxotellurates(IV,VI) and their detailed structural and physicochemical characterization. The goals also include studying the kinetics of decomposition of oxotellurates under non-isothermal conditions and studying their catalytic activity. I believe that the goals of the dissertation are clearly formulated. The specific tasks for achieving them are appropriately selected and aim at the mastery by the doctoral student of many experimental methods for characterizing materials, as well as theoretical approaches for predicting and evaluating properties.

The dissertation presents the synthesis and studies of new zirconium and hafnium oxotellurates(IV,VI). The compounds $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ were synthesized with high phase purity and clearly defined crystal structures, confirmed by spectroscopic methods (FTIR, Raman). Theoretical analysis revealed differences in electronic structure and reactivity – the zirconium compound shows more pronounced nucleophilicity, while the hafnium compound – electrophilicity. The thermal stability of both phases up to 1000°C was studied, and a decomposition mechanism and certain kinetic parameters were established. Studies on new compounds are also included: zirconium chlorooxotellurate(IV) ($ZrTe_2O_6Cl$) and hafnium oxotellurate(IV) ($Hf_3Te_3O_{12} \cdot 1.5H_2O$), with a proven crystal structure and high thermal stability up to 1200°C. A complex three-step decomposition mechanism with high activation energy and a stable crystal lattice has been established for hafnium oxotellurate. For the first time, the synthesized hydrogentellurates have been applied as heterogeneous acid catalysts in esterification reactions. XPS analysis shows surface enrichment with $HTeO4^-$ fragments, which determines their catalytic activity. The calculated thermodynamic functions further confirm the stability and applicability of the compounds. The obtained results demonstrate the potential of the new materials for application in green chemistry and sustainable technologies. The presented results show that the tasks of the dissertation have been successfully accomplished and the objectives were fulfilled.

5. Contributions of the dissertation work.

The contributions of the dissertation work can be classified as scientific with potential for practical application in at least two areas. They relate to obtaining new data and expanding existing knowledge about tellurium materials. For the first time, oxotellurates(IV, VI) of zirconium and hafnium with compositions: $ZrO(HTeO_4)_2 \cdot 4H_2O$, $Hf(HTeO_4)_4 \cdot 8H_2O$, $ZrTe_2O_6Cl$ and $Hf_3Te_3O_{12} \cdot 1.5H_2O$ were synthesized. Their structure and morphology were characterized by quantum chemical calculations and various physicochemical methods. Kinetic and thermodynamic parameters for the thermal decomposition were calculated, providing insight into their stability

and reactivity. Catalytic activity of the zirconium and hafnium hydrogen tellurates in esterification reactions was demonstrated, proving their potential as effective, high-temperature stable heterogeneous acid catalysts. A relationship between structure and catalytic activity has been outlined, creating a basis for rational design of new oxide catalysts. A methodological framework for the application of metal oxotellurates(VI) in catalysis and sensor technologies has been presented. The dissertation is based on 3 scientific papers (one of which is in a journal with Q2 and two with Q3). Four reports have been presented on the topic of the dissertation at national and international scientific events. The doctoral student is the first author in one of the presented articles and the second and third author in the other two articles included in the dissertation. In my opinion, the doctoral candidate was actively involved in the synthesis, processing, and critical analysis of the results obtained by various characterization methods.

6. Remarks.

The dissertation and the abstract exhibit a number of inaccuracies, especially in the Bulgarian rendering of some terminology used in describing the employed methods. This gives an impression of some carelessness in the final formatting. The abstract accurately and comprehensively reflects the dissertation content, but it appears overly lengthy.

7. Conclusion.

Based on the analysis conducted, I consider that in terms of the scope of the research and the results achieved, the dissertation fully meets the requirements of the LDASRB and the Regulations for acquiring scientific degrees and holding academic positions at the University "Prof. Dr. Asen Zlatarov", Burgas. **My assessment of the dissertation is positive. Therefore, I recommend that the esteemed academic committee award the educational and scientific degree "Doctor" in the scientific field 4.2 Chemical Sciences (Inorganic Chemistry) to Eng. Georgi Vasilev Rusev.**

Sofia 12.08.2025

Signed:

Подпис заличен
чл.2 от ЗЗЛД

(Prof. Dr Daniela Kovacheva)