REVIEW

on PhD thesis for obtaining the educational and scientific degree "Doctor"
in the professional field 4.2. Chemical Sciences" (Inorganic Chemistry)

Author: Asst. Prof. Georgi Vasilev Rusev, Faculty of Natural Sciences, State University "Prof. Dr. Asen Zlatarov", Burgas

PhD Thesis: „Synthesis, Structure and Properties of Oxotellurates(IV,VI) of the Elements of the IVB group"

Reviewer: Prof. Dr. Violeta Georgieva Koleva, Institute of General and Inorganic Chemistry-Bulgarian Academy of Sciences

Pursuant to orders of the Rector of State University "Prof. Dr. Asen Zlatarov", Burgas, № УД – 235/30.06.2025 and № УД – 258/08.07.2025, I have been appointed as a member of the scientific jury and reviewer in the procedure for the defense of a dissertation for obtaining the educational and scientific degree of "Doctor" in the doctoral program "Inorganic Chemistry" in the professional field 4.2. Chemical Sciences. The set of materials submitted by Georgi Rusev includes the following documents: a PhD thesis, Author's Summary in Bulgarian and English, Curriculum Vitae, copies of articles related to the dissertation, and a report on the fulfillment of the minimum national requirements for obtaining the educational and scientific degree of "Doctor".

1. Brief information for Georgi Rusev

Engineer Georgi Rusev graduated from "Prof. Dr. Asen Zlatarov" University in Burgas with a bachelor's degree in Organic Chemical Technologies and two master's degrees: "Computer Systems and Technologies and Informatics" and "Information Technologies in Chemistry and Chemical Education". In February 2021, he was enrolled as a regular doctoral student at the same university under the supervision of Assoc. Prof. Svetlana Zheleva. He is currently an assistant professor in the Department of Chemistry at the same university.

2. Topical relevance

The topic of the dissertation addresses a current problem in inorganic materials science related to the study of new materials with potential applications in various fields. The dissertation is devoted to the study of oxotellurates (IV, VI), which are of interest both from a fundamental point of view for clarifying the diversity of crystal structures and from the point of view of their practical application mainly in optoelectronics, photonics, laser technologies, energy, pharmacy, etc. This is related to a number of important technical characteristics such as nonlinear optical properties, thermoelectric, piezoelectric, semiconductor properties, high ionic and electronic conductivity, biological and catalytic activity and many others. The specific objects of the study are oxotellurate salts of Ti, Zr, and Hf, which are poorly studied, and their specific properties make them valuable for various technological applications.

3. General characteristics of the PhD Thesis

The dissertation by Georgi Rusev submitted to me for review is on a topic that fully corresponds to the scientific specialty of "Inorganic Chemistry." In short, it focuses on the

comprehensive study of a group of new oxotellurates of Ti, Zr, and Hf using a set of analytical methods to determine their physicochemical characteristics and certain properties.

The dissertation is written in accordance with the requirements of the Regulations on the conditions and procedures for acquiring scientific degrees and occupying academic positions at "Prof. Dr. Asen Zlatarov" University. It contains all the necessary sections: Introduction, Literature Review, Experimental Part, Results and Discussion, Conclusions, Scientific Contributions, Declaration of Originality, and Bibliography. The dissertation is 159 pages long, includes 75 figures, 19 tables, and cites 257 references. The proportions between the main components of the dissertation generally correspond to those established in practice, namely: a literature review of 45 pages (about 28%), an experimental part of 9 pages (6%), and results and discussion of 74 pages (47%). I believe that this ratio between these main sections is optimal.

The overview and analysis section includes four main points with 31 figures and is based on 158 refrences that are relevant to the topic and correctly cited.

The first and second points provide general information about oxotellurates in two directions: (1) Detailed description of crystal structures; (2) Synthesis, characterization, and properties. The difference in the crystal chemical characteristics of oxotellurates depending on the degree of Te oxidation is outlined. The enormous variety of crystal structures is demonstrated, especially for oxotellurates(IV), caused by the variable coordination number of Te(IV) in the oxotellurate anion (from 3 to 5) and the presence of a stereochemically active unshared electron pair on Te(IV). A wealth of information on the chemical composition of oxotellurates(IV,VI) of s-, p-, d-, and f-elements is summarized, together with the methods of preparation such as hydrothermal synthesis, precipitation, solid-phase synthesis, and the Czochralski method for single crystal samples. Data on their vibrational characteristics, thermal stability, and phase transformations are provided.

The third point is devoted to oxotellurates of Ti, Zr, and Hf, with a very comprehensive review, again based on the oxidation states of Te. For Ti(IV) and for all three elements, threetellurates(IV) are known, MTe_3O_8 where M = Ti, Zr, Hf, whose crystal structures have been determined. The threetellurates of Ti and Zr are isostructural and form a continuous series of solid solutions over the entire range of compositions.

Among the double oxotellurates, the tellurium-tungstates of K, Rb, Cs, lithium metal tellurites $Li_3MTe_4O_{11}$ (where M = Al, Ga, and Fe), vanadium oxotellurates(IV) of Sr and Cd, as well as those of lanthanide and actinide elements are considered. There is relatively little literature data, often contradictory, on oxotellurates of Te(VI). They have a complex chemical composition, not always well defined, in most cases contain water and are in an amorphous state, which further complicates their correct identification. Double oxotellurates with various structures are considered, such as: $Na_2M_2TeO_6$ (where M = Ni, Co, Zn, Mg) with a brucite-type structure, those with a perovskite-type structure such as Pb_2CaTeO_6, as well as those with a layered structure - $A_2Ni_2TeO_6$ (A = H, Rb, Cs, Cu, Ag, Au). Examples are given for a number of compounds with mixed degrees of Te oxidation. I will mention only some of them, such as: $Cs_2Te_2O_5$, $Cs_2Te_4O_{12}$, $ACuTe_2O_7$ ($A = Sr^{2+}$, Ba^{2+}, Pb^{2+}), $Th_2Te_3O_{11}$ etc. In addition to a detailed description of the crystal structures, the methods of synthesis, their vibrational characteristics, and physical properties are discussed. In my opinion,

however, the place of double oxotellurates is in the first point, not in the third, which, according to its title, focuses on oxotellurates of Ti, Zr, and Hf.

Based on the literature review, three conclusions were drawn, rather than five as stated in the thesis, since the last two conclusions essentially repeat what was already stated in the first conclusion. In my opinion, this is where the aim and the tasks to be solved, which follow from the literature review, should be placed, but in the dissertation they are formulated at the end of the "Introduction" section. The aim of the dissertation is to synthesize and characterize titanium, zirconium, and hafnium oxotellurates (IV, VI), to determine their crystal structure, and to study their decomposition kinetics and catalytic activity. Accordingly, tasks have been set out that are adequate to the stated objective.

The experimental part describes in detail the hydrothermal method of oxotellurates synthesis, the reagents used, and the experimental conditions. A wide range of experimental and theoretical methods of analysis are applied, which, in my opinion, exceeds the requirements for this type of dissertation. The experimental methods include powder X-ray diffraction and single crystal diffraction, IR spectroscopy (incorrectly classified as a surface analysis method), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and thermal analysis (TG/DTA, TG/DSC). The theoretical methods applied include density functional theory with calculation of molecular electrostatic potential and analysis of frontier molecular orbitals, as well as Hirschfeld surface analysis for the evaluation of intermolecular interactions. The kinetics of decomposition under non-isothermal conditions was tracked using an integral method, and the catalytic activity was investigated for the synthesis of butyl acetate.

The results and discussion are presented in two main points and several sub-points. In summary, the research conducted and the most important results can be summarized as follows:

1) New poorly crystallized phases of hydrated zirconium hydrogentellurate ($ZrO(HTeO_4)_2 \cdot 4H_2O$) and hafnium hydrogentellurate ($Hf(HTeO_4)_4 \cdot 8H_2O$) were obtained by hydrothermal synthesis.

2) Using the molecular electrostatic potential method, information was obtained about the electronic structure and, consequently, the chemical reactivity of the synthesized $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$. It was found that the nucleophilic reactivity of zirconyl hydrogentellurate is determined by the positive charge of the hydrogen atoms belonging to the $HTeO_4$ ion, while in Hf-salt the highest positive charge is recorded for the hydrogens of the water molecule. Te atoms in hafnium hydrogentellurate have a more pronounced positive potential than those in zirconium hydrogentellurate. These data are used further in the interpretation of the mechanism of the esterification reaction using these two salts as heterogeneous catalysts.

3) For the first time, the temperature behavior of $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ up to 1000 °C has been studied. It has been established that the thermal decomposition processes of both salts up to 1000 °C are associated with the sequential release of water, oxygen, and tellurium oxides. The kinetics of thermal decomposition under non-isothermal conditions were also studied, and the equations best describing the processes were determined by the integral method, and the kinetic parameters (activation energy and pre-exponential factor in the Arrhenius equation) were calculated in different temperature ranges. The thermodynamic parameters of the transition states

were also determined. Based on the calculated activation energies, it was shown that Hf-salt is thermally more stable than Zr-salt. The lowest activation energy is found for the dehydration of the salts, which occurs at around 200 °C, while the highest value is for the decomposition stage between 800 and 1000 °C, with both processes having a chemically controlled mechanism.

4) The catalytic activity of $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ was tested in the esterification reaction of acetic acid with 1-butanol for the synthesis of butylacetate. It was found that the Zr-salt has significantly higher catalytic activity, with a yield of up to 47.4% when used, compared to 16.5% when using the Hf-salt. The difference in the catalytic behavior of the two salts is in good agreement with the data from the calculations using the molecular electrostatic potential method. For Zr-salt, the influence of the amount of catalyst and temperature was studied, and the rate constant, enthalpy, and entropy of the process were determined. A mechanism for the esterification reaction has been proposed, in which the acid hydrogen atom in the $HTeO_4$ anion plays an important role as a center for nucleophilic attack by butylethanol.

5) $ZrTeO_4$ and $HfTeO_4$ were obtained in crystalline form by hydrothermal synthesis. It was found that they crystallize in the monoclinic space group C/m, with similar lattice parameters. Subsequently, the formula of $HfTeO_4$ was corrected to include hydrated water in the composition ($HfTeO_4 \cdot 0.5H_2O$), and the process of thermal decomposition was studied in detail. Data on the kinetics of decomposition under non-isothermal conditions were provided, and in addition, verification was performed using the isothermal method.

6) Zirconium tellurium oxychloride $ZrTe_2O_6Cl$ was obtained as a single crystal by hydrothermal synthesis. Its crystal structure was determined by X-ray diffraction, but the contribution to this was made by colleagues from the Institute of Mineralogy and Crystallography - BAS, although this is not mentioned in the dissertation. In order to obtain more detailed information about the nature of the interactions, density functional theory was applied and a Hirschfeld surface analysis was performed. The calculated theoretical UV-vis, IR, and Raman spectra were compared with the experimental ones. The calculated absorption bands in the UV-vis spectrum show a systematic shift towards higher wavelengths. In the IR and Raman spectra, in my opinion, the deviations between the theoretical and experimental spectra are greater. According to the thermal analysis performed, this compound decomposes above 200 °C with the sequential release of chlorine and TeO_2, forming $ZrTeO_4$ at 1200 °C.

4. Contributions

Overall, the main scientific contribution of the dissertation is the acquisition of new data in the field of inorganic chemistry, which complements and enriches the knowledge on oxotellurates.

5. Scientometric data

The dissertation is based on three publications, two of which are in journals with quartile Q3, and the third (J. Mol. Str.) – with quartile Q2 (not Q1 as stated). The articles have 4-5 authors, with G. Rusev being the first author in one of them. However, I cannot explain why only the first two articles (30 points) are included in the report on the scientometric indicators of Asst. Prof. Rusev. In my opinion, this is not correct. In any case, the minimum national requirements for the degree "Doctor" have been met. The results of the dissertation have been reported at four scientific forums in Bulgaria.

6. Author's summary

The author's summary reflects the content of the dissertation, but lacks summaries of the results and is considerably longer than the generally accepted length of around 40 pages.

7. Critical remarks, comments, and recommendations

1) Section 1.4 of "Results and Discussion" is not written clearly enough. First, it is a gross error in X-ray photoelectron spectroscopy to refer to "nuclear levels" (obviously direct translation from English of the term "core level"). This demonstrates a lack of understanding of the essence of the method, which provides information about the oxidation state of the elements, not about nuclei. Figures 37 and 38 are not "XPS profiles" but they are XPS spectra in the binding energy regions of the respective atoms. From the way these five pages of text are written, it is not even clear what the oxidation states of the elements Te, Zr, and Hf are, and this is the very purpose using this method.

2) On page 61, it is concluded that "the nucleophilic reactivity of zirconyl hydrogentellurate is determined by the positive charge of the hydrogen atoms." However, it is not specified which hydrogen atoms these are—from the water molecule or from the $HTeO_4$ anion. At the same time, the hydrogen and oxygen atoms with the corresponding numbers cannot be found in Fig. 36, and Fig. 44, discussed on page 62, is missing from the dissertation.

3) I have serious doubts about the claim that the mass loss (3.89%) of $Hf_3Te_3O_{12}•1.5H_2O$ in the temperature range of 605-810 °C is related to water release —this is an extremely high temperature for a dehydration process. If, however, we assume that this is the correct interpretation, then in the IR spectrum the band of the stretching vibrations of the hydrate water should be shifted to a much lower wavenumbers, e.g. below 3200 cm^{-1}, due to the presumed strong binding of this water. But this is not observed. I recommend re-analyzing the data in this section and conducting a TG/DTA study combined with mass spectrometry to make a correct interpretation of the thermal data, which will also help to clarify the chemical formula of this salt - whether it is an anhydrous salt or a hydrate. The fact that there are bands at 3406 and 1627 cm^{-1} in the IR spectrum does not necessarily mean that a hydrate has formed - such bands will almost always be seen in the spectra of anhydrous salts and oxides, and even in the spectrum of a KBr tablet. These bands could be due to surface-adsorbed water, which is confirmed by the observed initial mass loss of 0.8%.

4) Conclusion 1 states: "The crystal phases obtained possess the necessary phase purity and clearly defined crystallographic parameters of $ZrO(HTeO_4)_2•4H_2O$ and $Hf(HTeO_4)_4•8H_2O$," which does not correspond to the actual results obtained on pages 57-59. The X-ray diffraction patterns show broad peaks of poorly crystallized phases, so there can be no talk of phase purity, and naturally, it is impossible to calculate even the unit cell parameters. At the same time, on page 58 it is written that "Detailed analysis has established that peaks expressing the specific zirconyl hydrogentellurate phase are not observed in the X-ray diffraction pattern of ZrOHTe."

5) In my opinion, the section "Dissemination of results" should be at the end of the dissertation, not before the references, as is currently the case.

6) There are errors in some terms and expressions that are literal translations from English. I will mention just a few of them. When examining IR spectra, terms such as "razstjagashti and oguvashti" are used instead of stretching and bending vibrations. I find expressions in the text such

as "three-dimensional framework structures," "angular shared (Al/Te)O6 octahedra," the mineral "brookite" instead of brucite, "non-isothermen regime," and many others. Some of the references are cited incompletely and unclearly (e.g., 36, 48, 49, 257, and others).

8. Questions

I have the following questions:

1) The literature review contains numerous figures of crystal structures without citing the source, and it is unclear whether the structures are taken from literature or they are additionally visualized using software such as VESTA.

2) How was the chemical composition of the poorly crystallized phases $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ determined, for which exact formulas are given? I could not find any data on this issue.

3) No information is provided on how the input geometric structure of $ZrO(HTeO_4)_2 \cdot 4H_2O$ and $Hf(HTeO_4)_4 \cdot 8H_2O$ (Fig. 36), used to calculate the electron density distribution in them, was selected. What is the criterion in this case that the selected geometric model is appropriate and describes the systems well, given that there is no comparison of experimental and theoretical data? Have calculations been made for the bidentate bonding of the $HTeO_4$ ion?

4) What is the degree of oxidation of Te, Zr, and Hf in zirconyl hydrogentellurate ($ZrO(HTeO_4)_2 \cdot 4H_2O$) and hafnium hydrogentellurate ($Hf(HTeO_4)_4 \cdot 8H_2O$) compounds according to XPS data, rather than the proposed formula?

5) Which program was used to determine the lattice parameters $ZrTeO_4$ and $HfTeO_4$?

6) When optimizing the molecular structure of zirconium tellurium oxychloride ($ZrTe_2O_6Cl$), wasn't a rather small fragment of the already determined crystal structure selected (Fig. 62)?

7) Considering the fact that the PhD candidate had no prior experience in the field of chemistry before the start of the doctoral program, and given that the duration of the training is only three years, I express serious doubts regarding the extent of his participation in the analysis and interpretation of the data, especially in light of the large volume of data presented from such a wide range of experimental and theoretical methods. In this regard, my question is: Among all the activities and applied analytical methods, in which areas does Asst. Prof. Georgi Rusev feel most competent and has participated to the highest degree in the research?

9. Conclusion

Despite the considerable remarks on the dissertation, based on the obtained results and fulfillment of the minimum national requirements, I generally evaluate positively the dissertation of Georgi Rusev and recommend that the Scientific Jury to award him the educational and scientific degree of "Doctor".

Подпис заличен
Чл.2 от ЗЗЛД

Reviewer:

18.08.2025 /Prof. Dr. Violeta Koleva/