REVIEW

by

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Member of the scientific jury, approved by order No. 583/19.12.2025 of the Rector of the University "Prof. Dr. Asen Zlatarov", Burgas.

of a dissertation on the topic "**Structure and functional properties of oxoselenates (IV, VI)**" by Prof. Dr. Rumyana Zlatinova Yankova-Avramova for the award of the scientific degree "Doctor of Sciences", in the field of higher education: 4. Natural Sciences, Mathematics and Informatics; professional field 4.2. Chemical Sciences; scientific specialty "Inorganic Chemistry".

The set of documents and publications of Prof. Dr. Yankova meet the requirements of the LDASRB (Law of Development of Academic Staff of Republic of Bulgaria), the regulations for its implementation and the regulations for the conditions and procedure for acquiring scientific degrees and occupying academic positions at the University "Prof. Dr. Asen Zlatarov" – Burgas.

My review will be based on the following scientific criteria:

1) relevance of the topic of the dissertation;

2) scientific framework of the research;

3) main scientific results;

4) contribution of the dissertation to the field of inorganic chemistry;

5) scientific-metric indicators;

6) overall quality of the dissertation with a view to a convincing and adequate presentation of the dissertation work.

1. Relevance of the topic of the dissertation

The topic of the structure and functional properties of oxoselenates is extremely relevant in modern solid-state chemistry and materials science. Its importance stems from the unique crystallochemical characteristics of selenium and the potential for creating high-tech materials. Here are the main aspects that determine its modern significance:

1. Stereochemical activity of the lone electron pair:

In selenates(IV), also known as selenites, Se^{4+} possesses an unshared electron pair ($4s^2$). This pair is stereo-chemically active and induces a strong asymmetry in the crystal lattice. Why it is important: This asymmetry is a "recipe" for creating materials without a center of symmetry, which are critical for laser technologies. This finds application in the development of materials for nonlinear optics (NLO), which can change the frequency of light.

2. Multifunctional materials

Selenates(VI) and oxoselenates are often studied in combination with transition or rare earth metals. This allows the combination of several physical properties in one substance:

- Ferroelectricity and pyroelectricity: Due to polar structures.
- Magnetism: Study of low-dimensional magnetic systems (chains, layers), where selenate groups serve as "bridges" between magnetic ions.

3. Ecological aspect and geochemistry

Understanding the structure of these compounds is key to environmental protection. Selenium is a dual element – an essential trace element, but highly toxic in higher concentrations.

Mobility in nature: The solubility and migration of selenium in soils and waters depend directly on whether it is in the form of selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}).
Purification: The synthesis of new oxoselenates helps to develop methods for immobilizing toxic selenium in stable crystalline phases.

2. Scientific framework of the study

In view of the great importance of selenium compounds in modern materials science, the main goal of this work is the synthesis of new selenites and selenates, experimental and theoretical study of their crystal lattice and physical and chemical properties in order to find their possible application.

To achieve the set goal, the following main tasks have been formulated:

1. Synthesis of oxoselenates (IV, VI);

2. Determination of the structure of their crystal lattice;

3. Study of their UV, IR spectrum and thermal stability;

4. Quantum chemical study of the newly obtained oxoselenates with a view to their more complete characterization at the molecular level and finding a connection with the structure of the crystal lattice and its properties;

5. Finding potential applications of the newly obtained oxoselenates;

This scientific framework is actually standard for any innovative research task in materials science – synthesis, proof of the molecular structure, study of the structure of the crystal lattice and its chemical and physical properties, as well as quantum-chemical study of the molecule for a better understanding of its properties and relationship with the macro-properties of matter.

3. Main scientific results

1. 14 oxoselenates have been synthesized:

$Sm_2(OH)_2(SeO_3)(HSeO_3)_2(H_2O)_2$, $[Hf(SeO_3)_2(H_2O)_4]\cdot 2H_2O$, $Al_2(SeO_3)_3\cdot 6H_2O$, $Rb_2Co(SeO_3)_2$, Ag_2SeO_4, Rb_2SeO_4, $[Co(H_2O)_4]SeO_4\cdot H2O$, $Hf(SeO_4)_2(H_2O)_4$, $Rb_2[Cu(H_2O)_6](SeO_4)_2$, $Cs_2Ni(SeO_4)_2\cdot 4H_2O$, $Hf(SeO_3)(SeO_4)(H_2O)_4$, $Na_2Fe(SeO_4)_2\cdot 2H_2O$ и $Na_2Co(SeO_4)_2\cdot 2H_2O$.

Of all these compounds, 4 have been studied in detail: $[Hf(SeO_3)_2(H_2O)_4]\cdot 2H_2O$, $Al_2(SeO_3)_3\cdot 6H_2O$, $Sm_2(OH)_2(SeO_3)(HSeO_3)_2(H_2O)_2$ и $Rb_2Co(SeO_3)_2$ and two of them are synthesized for the first time – $[Hf(SeO_3)_2(H_2O)_4]\cdot 2H_2O$ и $Sm_2(OH)_2(SeO_3)(HSeO_3)_2(H_2O)_2$;

2. The atomic coordinates, the symmetry of the crystal lattice, the interatomic distances and the spatial packing in the crystals of the above-mentioned compounds were determined by XRD;

3. The IR and UV spectra of the above-mentioned compounds were obtained. The characteristic vibrational frequencies in them were established;

4. Their thermal stability was studied by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. They established a specific dehydration temperature of each crystal hydrate and a general thermal stability up to about 1100 K. The mechanism of thermal decomposition was established.

5. A comprehensive quantum chemical study of the oxoselenates was carried out for a better understanding of their molecular properties and their reactivity.

3. Contribution of the dissertation work to the field of inorganic chemistry

1. Synthesis of new selenite compounds: $[Hf(SeO_3)_2(H_2O)_4]\cdot 2H_2O$ and $Sm_2(OH)_2(SeO_3)(HSeO_3)_2(H_2O)_2$;

2. Geometrical, electronic and thermodynamic parameters, HOMO–LUMO energies, electrostatic potential and hyperconjugative interactions between atoms, leading to more stable complexes, were determined through quantum-chemical calculations

3. Hydrogen bonds in the samarium compound were described for the first time.

4. Selenites with different metal coordination were identified with characteristic electronic structure and thermal stability for each.

5. A new nonlinear-optical selenite was discovered – $Rb_2Co(SeO_3)_2$.

6. A Newton interpolation scheme for calculating standard enthalpies of formation of selenites with high accuracy has been introduced and validated.

5. Scientific metrics

The materials presented by Prof. Yankova proving her scientific merits fully comply with the requirements of the Law of Development of Academic Staff of Republic of Bulgaria and the related regulations at the national and university level. The declared points by groups of scientometric indicators are:

Indicators A: Dissertation for awarding the ONS "Doctor" - 50 points.

Indicators B: Dissertation for awarding the scientific degree "Doctor of Sciences" - 100 points.

Indicators D: Scientific publications in refereed journals in Scopus/Web of Science, a list of 20 publications is presented - 311 points.

Of these, 4 are in quartile Q2, 13 in quartile Q3 and 3 in quartile Q4 and meet the official requirements of the documentation.

Indicators E: Citations in scientific publications in Scopus/Web of Science - 96 citations – 192 points.

Indicators E: Nine participations in a national scientific or educational project, leader of 3 national projects, 3 university textbooks published – 168.4 points.

In total, this makes 821.4 points, which significantly exceeds the national minimum requirements (350 points), and the university minimum requirements of the University "Prof. Dr. A. Zlatarov" (700 points).

6. Overall quality of the dissertation with a view to a convincing and adequate presentation of the dissertation work.

The dissertation contains 391 pages, 75 tables and 117 figures. The bibliography includes 339 literary sources. The literature review includes a significant literature review on quantum chemical methods for studying molecules, spectroscopic characteristics of selenates and related physical and chemical properties and much more information on the relationship between the molecular structure and properties of substances. All indicates the enormous theoretical training of Prof. Yankova and therefore I can say that she is an expert in inorganic chemistry. The dissertation and the abstract are presented in a coherent and logical manner. In other words: the work was done professionally. There is nothing more to add.

In view of all this, I fully support the candidacy of Prof. Yankova for the scientific degree "Doctor of Sciences" in the professional field: 4.2. Chemical Sciences, scientific specialty: "Inorganic Chemistry".

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/prof. Dr. Stoyan Karakashev/