

ABSTRACT

Dissertation for the degree of Doctor of Philosophy (PhD) in the educational program «8D05301 – Chemistry»

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«Synthesis and Physicochemical Properties of Tellurium Derivatives of Some Rare Earth Elements»

General characteristics of the work. The dissertation is aimed at the synthesis of novel tellurium polyoxo-compounds based on rare earth element (REE) oxides, tellurium, and alkaline earth metals, as well as at a comprehensive investigation of their physicochemical properties. The synthesis of tellurites by means of ceramic technology and their characterization using elemental analysis, X-ray diffraction, quantum chemical calculations, IR spectroscopy, calorimetry, and electrophysical methods enabled the study of the X-ray diffraction characteristics, thermodynamic properties, and electrophysical properties of the newly obtained compounds and the identification of their valuable physicochemical characteristics.

Relevance of the work. Studies of the physicochemical properties of complex oxides with perovskite structure based on rare earth elements, alkali and alkaline earth metals have demonstrated that these materials possess unique magnetic and electrical properties, as well as considerable electrochemical and catalytic activity. Complex oxides with perovskite structure are widely used as electrode materials for solid oxide fuel cells, for the production of pure oxygen from air, in ceramic membrane fabrication, and in emerging fields of science and technology, including spintronics devices. Systematic investigations of materials with electrical properties have shown that the electrical parameters of complex oxides are determined not only by their complex chemical composition, but also by the phase composition and crystal lattice structure.

The targeted synthesis of complex rare earth oxides doped with tellurium, alkaline earth metals, and d-metals is aimed at reducing their production cost, ensuring relative availability and environmental safety, and imparting valuable properties to the compounds, such as semiconducting and ferroelectric properties. These factors determine the relevance of the present study and underscore its considerable scientific and practical significance.

Research objective: to study the synthesis and physicochemical properties of binary and ternary tellurites formed in the systems $[\text{Gd}_2\text{O}_3; \text{Nd}_2\text{O}_3; \text{Sm}_2\text{O}_3] - \text{TeO}_2 - \text{MeCO}_3$ and $\text{Lu}_2\text{O}_3 - \text{TeO}_2 - \text{Fe}_2\text{O}_3 - \text{MeCO}_3$ (Me – Mg, Ca, Sr, Ba).

Research objectives:

1. Synthesis of novel tellurium derivatives of rare earth elements in the specified systems by means of high-temperature solid-state reaction;
2. Identification of compound composition by X-ray diffraction phase analysis;
3. Calorimetric investigation of the temperature dependence of heat capacity

of the resulting phases and calculation of thermodynamic functions;

4. Study of the electrophysical properties of the compounds;

5. Determination of the valuable physicochemical properties of the novel tellurium derivatives of rare earth elements and development of recommendations regarding their potential applications.

Research methods:

To achieve the objectives of the dissertation, a set of complementary experimental and theoretical methods was employed. A total of sixteen novel tellurites were synthesized by high-temperature solid-state synthesis.

X-ray diffraction patterns of the synthesized compounds were obtained using an Empyrean powder diffractometer (PANalytical). The obtained diffraction patterns were processed using the X'Pert HighScore Plus software, which enables quantitative phase analysis, and the phases were identified. The Crystallography Open Database and the PDF-2 database were used for phase composition determination. Indexing of powder X-ray diffraction patterns was carried out by the homology method.

The surface morphology of the tellurites was examined by scanning electron microscopy using a Mira 3 instrument (TESCAN). The elemental composition of the tellurite microcomponents was determined using an EDS detector. Geometric structural models of the tellurites were proposed using quantum chemical calculations and IR spectroscopy.

For the first time, the standard heat capacities of binary neodymium tellurites and ternary lutetium ferrotellurites were determined by the dynamic calorimetry method.

For the first time, the electrophysical properties, namely temperature dependences of dielectric permittivity and electrical resistance of binary and ternary tellurites were investigated using an LCR-800 measuring system (Taiwan).

The combination of methods employed enabled a comprehensive investigation of the composition, structure, X-ray diffraction characteristics, thermochemical, and electrophysical properties of the synthesized tellurites.

Main propositions submitted for defense:

1. Sixteen novel polyoxotellurites of compositions $\text{GdMeTeO}_{4.5}$, $\text{NdMeTeO}_{4.5}$, $\text{SmMeTeO}_{4.5}$ and LuMeFeTeO_6 (Me – Mg, Ca, Sr, Ba) were synthesized by high-temperature solid-state synthesis. Their crystal systems, unit cell parameters, unit cell volume, number of formula units, X-ray and pycnometric densities were determined. A secondary periodic phenomenon was observed upon variation of the unit cell volume ($V_{\text{unit cell}}^0$) of LuMeFeTeO_6 ferrotellurites in the Ca – Sr – Ba series. It was established that the crystal lattice parameters of binary tellurites of neodymium and samarium, and ternary lutetium ferrotellurites, including X-ray densities and unit cell volumes, correspond with high accuracy to the unit cell volumes calculated from $V_{\text{unit cell}}^0$ of the constituent oxides. X-ray data showed that the synthesized binary and ternary tellurites crystallize in the perovskite structural type, which was confirmed by determination of the “tolerance factor” t for the synthesized tellurites ($t = 0.88\text{--}0.96$). Quantum chemical calculations enabled the proposal of geometric structural models for binary tellurites and ternary

ferrotellurites. SEM studies showed that the tellurites can be classified as nanostructured nanoclusters.

2. For the first time, the isobaric heat capacity of binary neodymium tellurites and ternary lutetium ferrotellurites was determined by dynamic calorimetry in the temperature range 298.15–673 K. Equations for the temperature dependence of heat capacity of the compounds were derived. Anomalous deviations observed in the $C_p^0 \sim f(T)$ curves of the investigated tellurites, associated with a second-order phase transition, indicate that the compounds under study may possess unique electrophysical properties. It was demonstrated that the experimental values of the standard molar heat capacities of the investigated tellurites are in excellent agreement with values calculated by well-known thermodynamic methods (Kumok, Landiya, and the Neumann-Kopp rule).

3. For the first time, the temperature dependences of dielectric permittivity and electrical resistance of binary tellurites of samarium, gadolinium, and neodymium, and ternary lutetium ferrotellurites were studied using an LCR-800 system in the temperature range 293–483 K. The maxima and minima observed on the $\lg R \sim f(T)$ and $\lg E \sim f(T)$ curves are explained by λ -like effects corresponding to a second-order phase transition. The temperature coefficients of electrical resistance and the band gap ($\Delta E = 1.04\text{--}2.64$ eV) of the synthesized compounds were determined. The data obtained are of interest for electronics and capacitor technology, since the investigated tellurites exhibit semiconducting and ferroelectric properties.

Summary of main research results. As a result of the study, 16 novel tellurium derivatives based on rare earth element (REE) oxides, tellurium, and alkaline earth metals were synthesized for the first time. The composition, crystal system, and crystal lattice parameters of the synthesized binary tellurites and ternary REE ferrotellurites were determined. X-ray data showed that the synthesized binary and ternary tellurites crystallize in perovskite structural form, which was confirmed by determination of the “tolerance factor” (t) for the synthesized tellurites. Geometric structural models of the tellurites were proposed using quantum chemical calculations.

For the first time, the isobaric heat capacities of the tellurites were determined by dynamic calorimetry in the range 298.15–673 K. Anomalous deviations in the $C_p^0 \sim f(T)$ curves of the investigated tellurites, attributed to a second-order phase transition, indicate that the compounds under study may possess unique electrophysical properties. It was demonstrated that the experimental values of the standard molar heat capacities of the investigated compounds are in excellent agreement with values calculated by well-known thermodynamic methods. Temperature dependences of thermodynamic functions $C_p^0(T)$, $S^0(T)$, $H^0(T) - H^0(298.15)$, $\Phi^{xx}(T)$ were calculated over the specified temperature range.

For the first time, the temperature dependences of dielectric permittivity and electrical resistance of the synthesized tellurites were studied in the temperature range 293–483 K. Second-order phase transition effects were observed on the $\lg R \sim f(T)$ and $\lg E \sim f(T)$ curves. Based on the band gaps of the compounds, they were classified as semiconductors.

Overall, the results obtained provide a deeper understanding of the structure–

property relationships of tellurites and form a scientific basis for the targeted synthesis of new functional materials.

Scientific novelty of the work:

1. A total of sixteen compounds of compositions $\text{GdMeTeO}_{4.5}$, $\text{NdMeTeO}_{4.5}$, $\text{SmMeTeO}_{4.5}$, LuMeFeTeO_6 (Me - Mg, Ca, Sr, Ba) were synthesized for the first time;

2. The crystal system and unit cell parameters of the investigated compounds were established, and the X-ray and pycnometric densities were determined. Calculated tolerance factor (t) values demonstrated that the tellurites possess perovskite structure;

3. For the first time, the heat capacities of tellurites in the temperature range 298.15–673 K were investigated by dynamic calorimetry;

4. For the first time, using binary neodymium tellurites as an example, λ -shaped effects observed during second-order phase transitions in the range 298.15–673 K on the $C_p^\circ - f(T)$ curves were identified, and heat capacity equations in polynomial form accounting for phase transition temperatures were derived;

5. Temperature dependences of thermodynamic functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$ and $\Phi^{\text{xx}}(T)$ in the range 298.15–673 K were calculated on the basis of experimental heat capacity values and standard entropy values determined by the ionic increment method;

6. Investigation of the electrophysical properties of tellurites (dielectric permittivity, electrical resistance) in the range 293–483 K showed that the synthesized compounds possess semiconducting and ferroelectric properties.

Significance of the research results.

The results obtained in the dissertation are of considerable scientific and applied importance for the development of inorganic chemistry and materials science.

The scientific significance of the work is characterized by the synthesis of novel tellurites based on REE oxides, tellurium, and alkaline earth metals, and by the elucidation of the relationship between their crystal structure and physicochemical properties. The data obtained enrich the chemistry of tellurites and broaden knowledge of the structural features of compounds of this class.

The results of the thermodynamic and electrophysical investigations provide a scientific basis for predicting the properties of the studied compounds and for conducting targeted synthesis. This, in turn, is an important prerequisite for the design of new materials.

The practical significance of the work is determined by the possibility of using the synthesized tellurites as functional materials. In particular, their dielectric and electrical properties make them suitable for applications in electronics, optoelectronics, sensor technology, and energy-efficient technologies.

Furthermore, the results obtained can be used in teaching inorganic chemistry, materials science, and physical chemistry at higher educational institutions, as well as in further scientific research.

Thus, the research results not only complement fundamental scientific knowledge, but also serve as a basis for the development of new materials for use in

contemporary technological fields.

Connection of the work with research projects and state scientific programs: The dissertation was carried out in accordance with the plan of fundamental research on the topic “Synthesis and Properties of Polyfunctional Inorganic Compounds (Materials)” at the Department of Inorganic and Technical Chemistry of Karaganda National Research University named after Academician Ye.A. Buketov. Experiments on the electrophysical properties of the compounds were conducted at the Laboratory of Thermochemical Processes of the Zh. Abishev Chemical and Metallurgical Institute.

Personal contribution of the author consists in formulating the research objectives, direct participation in conducting the experiments, and in the analysis and generalization of the research results obtained.

The doctoral candidate’s contribution to the preparation of each scientific publication includes conducting the literature review, selecting the scientific journal, preparing and formatting the article, interpreting the results obtained, as well as correspondence with journal editors and reviewers. The works have been published in the following scientific articles:

1. «Synthesis and properties of $\text{NdMe}^{\text{II}}\text{TeO}_{4.5}(\text{Me}^{\text{II}} - \text{Ca, Ba})$ tellurites» https://doi.org/10.59957/jctm.v5_9.i1.2024.18 - the aim of this work was the synthesis and study of X-ray and electrophysical properties of binary neodymium tellurites, in particular new phases.

2. «Synthesis and physicochemical properties of new triple lutetium tellurites» <https://doi.org/10.59957/jctm.v60.i5.2025.5> - novel ternary lutetium tellurites, namely LuMeFeTeO_6 (Me - Sr, Ba) were synthesized by ceramic technology from Lu_2O_3 , TeO_2 , and Fe_2O_3 oxides, as well as SrCO_3 and BaCO_3 carbonates. The phases were identified by X-ray diffraction phase analysis; the crystal systems, unit cell parameters, and X-ray and pycnometric densities of the compounds were determined. It was confirmed that the tellurites crystallize in the tetragonal system in a distorted perovskite structural form. The isobaric heat capacities of the tellurites were studied by dynamic calorimetry in the temperature range 298.15–673 K, and equations for the $C_p(T)$ dependence were derived. The standard heat capacities of the novel tellurites were determined, enabling the establishment of a fundamental constant and confirming their agreement with calculated values. The results of the study demonstrated that ternary tellurites are of significance for inorganic and physical chemistry, as well as for the materials science of inorganic materials.

3. «Synthesis, X-ray Diffraction, and Thermodynamic Properties of Ferrotellurite LuCaFeTeO_6 » <https://doi.org/10.1134/S0036024425700025> - a novel ferrotellurite LuCaFeTeO_6 was synthesized by ceramic technology. The crystal system and unit cell parameters were determined by X-ray diffraction phase analysis, and the elemental composition was established by energy-dispersive spectroscopy (EDS). The isobaric heat capacity of the compound in the temperature range 298.15–673 K was studied for the first time by dynamic calorimetry, and an equation for its temperature dependence was derived.

4. «Synthesis and properties of double gadolinium tellurites»

<https://doi.org/10.31489/2021Ch3/67-73> - binary gadolinium tellurites of composition $\text{GdM}^{\text{II}}\text{TeO}_{4.5}$ (M^{II} - Sr, Ba) were synthesized for the first time by solid-state synthesis. X-ray diffraction phase analysis revealed that $\text{GdSrTeO}_{4.5}$ and $\text{GdBaTeO}_{4.5}$ crystallize in the monoclinic crystal system, and their structural parameters were determined. Using the Landiya method, their standard thermodynamic characteristics were estimated and the temperature dependences of their heat capacities were calculated in the range 298–850 K.

5. «New Samarium Oxotellurites: Synthesis and Characteristic» <https://doi.org/10.31489/2959-0663/2-23-4> - samarium oxotellurites $\text{SmMgTeO}_{4.5}$ and $\text{SmBaTeO}_{4.5}$ were synthesized for the first time by ceramic technology and characterized by X-ray diffraction phase analysis. The temperature dependences of the dielectric permittivity and electrical resistance of the tellurites were investigated in the temperature range 293–483 K, and the band gaps of the compounds were calculated.

6. «New gadolinium oxotellurites: synthesis and characterization» <https://doi.org/10.29235/1561-8331-2024-60-4-281-289> - novel gadolinium tellurites of composition $\text{GdMeTeO}_{4.5}$ (Me – Mg, Ca) were synthesized for the first time. X-ray diffraction phase analysis established their crystal systems, unit cell parameters, and densities, and demonstrated that the compounds crystallize in a distorted perovskite structural form. The temperature dependence of the electrical resistance of gadolinium-magnesium tellurite was investigated; the compound was found to exhibit semiconducting properties, with a band gap of $\Delta E = 2.64$ eV.

Approbation of the work. The main results of the dissertation were presented and discussed at the following international scientific and practical conferences, and published in the respective conference proceedings:

X-ray study of tellurites of some s-f elements // Education and Science without Borders (Przemyśl, Poland, 2020); Quantum chemical study of novel binary samarium tellurites // VII International Scientific and Practical Conference dedicated to the 50th anniversary of the Faculty of Chemistry and the 100th anniversary of the first Dean, Prof. R.G. Omarova (Karaganda, 2023); Quantum chemical calculation of the structure of novel binary gadolinium tellurites // VII International Scientific and Practical Conference dedicated to the 50th anniversary of the Faculty of Chemistry and the 100th anniversary of the first Dean, Prof. R.G. Omarova (Karaganda, 2023); Synthesis and quantum chemical properties of tellurites $\text{LuMe}^{\text{II}}\text{TeO}_{4.5}$ (Me^{II} – Ca, Sr, Ba) // Effective Tools of Modern Science (Prague, Czech Republic, 2024); Synthesis and X-ray diffraction characteristics of novel europium oxotellurites // International Scientific and Practical Conference “Ruhaniyattagi gulama galymnyng roli” (The Role of a Scholarly Luminary in Spirituality), dedicated to the 125th anniversary of Academician Kanysh Satpayev (Karaganda, 2024); Synthesis and properties of polyfunctional inorganic compounds (materials) // Chemistry of the Silk Road: Modern Chemical Technologies and Science. Proceedings of the 1st International Scientific and Practical Conference dedicated to the 100th anniversary of Academician Ye.A. Buketov (Karaganda, 2025); Synthesis, X-ray diffraction and thermochemical

characteristics of some tellurium oxo-compounds of s-f elements // International Scientific and Practical Conference dedicated to the 100th anniversary of Academician Ye.A. Buketov “E.A. Boketovtin gylymi kokzhiektari” (Ye.A. Buketov's Scientific Horizons) (Karaganda, 2025); X-ray phase and quantum chemical study of a dysprosium-magnesium binary tellurite // International Scientific and Practical Conference dedicated to the 100th anniversary of Academician Ye.A. Buketov “E.A. Boketovtin gylymi kokzhiektari” (Ye.A. Buketov's Scientific Horizons) (Karaganda, 2025); Synthesis and physicochemical properties of tellurites of some s-f elements // Proceedings of the XXIII International Scientific and Practical Conference «Future Research – 2026» (Sofia, Bulgaria, 2026).

Publications. The main results of the dissertation research are published in 14 works, including 6 articles indexed in the international databases Web of Science and Scopus, and 8 articles and conference abstracts published in the proceedings of international scientific and practical conferences.