REVIEW

On a dissertation work for obtaining the educational and scientific degree "**doctor**" in Scientific field: 4. Natural sciences, mathematics and informatics, Professional direction 4.2 Chemical sciences (Inorganic chemistry)

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Scientific supervisors: Prof. Dr. Maria Milanova and Assoc. Prof. Dr. Martin Tsvetkov

Topic: "Investigation of the influence of lanthanoid ions on some physical properties of tungstates of the type MW_2O_8 (M=Zr, Hf)"

Reviewer: Associate Professor Maria Atanasova Petrova, Eng., PhD, DSc, UCTM−Sofia, member of the scientific jury, appointed by order No. RD-38-88/16.02.2023 of the Rector of SU "St. Kliment Ohridski"

Martin Krastev Nedyalkov completed his Bachelor's and Master's degrees in 2016 and 2018 years, respectively, in the specialty of Chemistry with a specialization in Inorganic Chemistry and a teacher of Chemistry and in the specialty of Engineering Chemistry and Modern Materials, at the Faculty of Chemistry and Pharmacy of SU "St. Kl. Ohridski". On 10.07. 2018, he was enrolled as a full-time doctoral student at the Department of Inorganic Chemistry of the same faculty, with the scientific supervisor Prof. Dr. Maria Milanova, and on 10.01.2022 he was dismissed with the right of defense his thesis. The presented work was examined and discussed at a meeting of the department council held on 30.01.2023 and it was sent for defense, and the decision was taken unanimously. He has submitted all the necessary documents for the procedure for awarding a degree doctor.

The dissertation presented to me for review reflects the work of the doctoral student in the Laboratory of Chemistry of Rare Earth Elements at the Faculty of Chemistry and Pharmacy at SU "St. Kliment Ohridski". Research on the modification of materials with lanthanoid ions in order to improve their properties is one of the scientific topics worked on in this laboratory. The scientific research carried out in recent years by the team on the modification of titanium dioxide, zinc-nickel spinels, as well as mixed-metal oxides with a perovskite structure, have shown beyond doubt the influence of lanthanoid ions on the properties of these materials. The work on the modification of zirconium and hafnium tungstate with some lanthanoid ions can be considered as a continuation of these thematic studies. Part of the research included in the dissertation was carried out within the framework of Contract No. DM19/5 of 20.12.2017, financed by the Bulgarian National Scientific Research Fund.

The dissertation contains 75 pages, 4 tables, 41 figures, 78 literary sources are cited. The exposition is precise and clear, with logical sequence and correct scientific style. The work is well structured and contains an introduction, literature review, aims and objectives, experimental part, results and discussion, conclusions are made, and the candidate's contributions are highlighted as well. Here I would like to point out the relatively small volume of the dissertation as a whole, especially the *Results and Discussion* section referred to the *Literature Review*, and I consider this to be unjustified. Purely technical, a lot of inadmissible mistakes were made for this type of monographic work. However, the goals and tasks are specifically set and fulfilled. The goals are of a marked fundamental-scientific nature and, as the obtained results show, completely realistically achievable. The experimental part is well explained and systematically follows the set tasks. The obtained experimental results are in full accordance with the set tasks, which demonstrates a good creative approach in

the selection of both the research methodology for the synthetic procedure and the analytical instrumental techniques used to achieve the goals of the dissertation work: scientific and educational. The conducted research is up-to-date in scientific and scientific-applied terms: innovative materials with very specific properties.

The *literary review* covers 63 literary sources, mostly articles, among them there are no Bulgarian authors. It is impressive to see an extremely large set of supporting figures included here, 19 in number. From this review presented to us, it is clear that the doctoral student knows how to work with the literature and make appropriate conclusions and generalizations related to his scientific work. The methods applied in the literature have highlighted the advantages of the hydrothermal method, among solid-phase and mechano-chemical synthesis, as well as sol-gel, for the synthesis and modification of the investigated zirconium and hafnium tungstates and the possibilities of controlling the dosage of the modifying ion, trivalent or tetravalent, characteristic of the wet methods, as well as the calcination of the samples at a significantly lower temperature compared to the solid-phase synthesis. All necessary concepts are introduced, the coefficient of thermal expansion, positive or negative coefficient of thermal expansion and the characteristic one for zirconium and hafnium tungstate are not omitted.

In the *Results and Discussion* section, the PhD student presents the practical research both on the synthesis by hydrothermal method (the procedure is shown in scheme 1) and on the properties of the target compounds divided into two groups: Solid solutions based on ZrW_2O_8 modified with Eu^{3+} and Tb^{3+} and Solid solutions $Hf_{1-x}Ln_xW_2O_8$ (Ln = Eu, Tm, Lu). The set of experimental data and the interrelationships found between them were obtained by using to the maximum extent the possibilities of a combined instrumental protocol. The characterization of the obtained samples was carried out by a set of methods, including High Temperature Powder X-ray Diffraction (XRD), Raman Spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM)), Infrared Spectroscopy (FT-IR), UV/Vis absorption spectroscopy. This gives high value to the results and enables theoretical generalizations based on them. The Rietveld method was applied to calculate the coefficient of thermal expansion, with the data obtained and by applying the method to each diffractogram at different temperatures.

The most important new points and conclusions to the dissertation can be grouped into two main directions:

I. Solid solutions based on ZrW_2O_8 modified with Eu^{3+} and Tb^{3+}

1. Crystal samples of phase-uniform solid solutions $Zr_{1-x}Ln_xW_2O_{8-x/2}$, Ln = Eu^{3+} (x=0.01, 0.02, 0.05) and Tb^{3+} (x=0.01, 0.03) were obtained. 2. The α-ZrW_2O_8 → β-ZrW_2O_8 phase transition was confirmed by tracking the change of the (110) and (310) reflexes in the X-ray pattern with an increase in temperature from 25°C to 250°C, as they are the most intense and are characteristic of the low-temperature phase, α-ZrW_2O_8. 3. A different influence of the 4f-ions Eu^{3+} and Tb^{3+} on the temperature of the phase transition of the solid solutions was established, respectively an increase with the participation of Eu^{3+} and no change in the samples with Tb^{3+}. This is suggested to be due to partial conversion of Tb^{3+} to Tb^{4+} during synthesis, followed by partial replacement of Zr^{4+} by the closely related Tb^{4+}, the phase transition temperature does not change. 4. Values for the phase transition temperature for ZrW_2O_8 and for $Zr_{1-x}Eu_xW_2O_{8-x/2}$, Ln = Eu^{3+} (x=0.01, 0.02, 0.05) were obtained, which are higher compared to the literature data, because of secondary recrystallization leading to rearrangement of WO4 tetrahedra. 5. The presence of Eu^{3+}/Tb^{3+} in the crystal structure of ZrW_2O_8 leads to a decrease of the unit cell parameter, the absolute value of CTE for the low- and high-temperature modification. 6. An expansion of the band gap to 4.45 eV was found with increasing content of the modifying Eu^{3+} (1, 2, 5 mol %), and the values were obtained on the basis of UV/Vis spectra.

II. Solid solutions $Hf_{1-x}Ln_xW_2O_8$ (Ln = Eu, Tm, Lu)

1. The structure of the polymorphic modification β-HfW_2O_8 was proved, allowing to solve the structure of the high-temperature modifications of the obtained solid solutions $Hf_{1-x}Ln_xW_2O_8$ (Ln = Eu, Tm, Lu). 2. The α-HfW_2O_8 → β-HfW_2O_8 phase transition was confirmed by tracking the change of the most sensitive reflections

(110) and (310) in the X-ray images with increasing temperature. 3. The established differences in the absolute values of CTE for ZrW_2O_8 and HfW_2O_8, greater in the high-temperature modifications, may be due to differences in atomic masses, free volume, bond length. 4. Based on the high-temperature X-ray diffraction patterns of the solid solutions $Hf_{1-x}Ln_xW_2O_{8-x/2}$ (x = 0.01; Ln = Eu, Lu), the phase transition temperature was determined. 5. A difference was found in the influence of lanthanide ions on (i) band gap energy values for $Hf_{1-x}Ln_xW_2O_8$ (Ln = Eu, Tm, Lu); (ii) the coefficients of thermal expansion, where $Hf_{1-x}Lu_xW_2O_8$ (Lu^{3+} e with the smallest ionic radius of the studied lanthanides, with an atomic mass closest to hafnium) shows values closest to β-HfW_2O_8.

The conclusions are clearly formulated and correctly reflect the main achievements of the PhD student in the field. In general, it can be said that the studied properties of the obtained solid solutions based on zirconium and hafnium tungstate $M_{1-x}Ln_xW_2O_8$ (M = Zr, Hf; Ln = Eu, Tb, Tm, Lu) are largely determined by the arrangement of WO_4 - the tetrahedra, which is influenced by both the secondary recrystallization and the temperature and the partial replacement of Zr^{4+}/Hf^{4+} with Ln^{3+} in the MO_6 - octahedra. The larger Ln^{3+} ions cause more significant WO_4 distortion/disorder at low modifier ion content, x = 0.01, while the smaller ions close to Zr^{4+}/Hf^{4+} size due to their better solubility in the crystal structure, have a stronger influence at the higher content of the modifying ion x = 0.05.

The obtained results enrich and complement the existing scientific knowledge in the field. Convincing results have been achieved through the research carried out within the framework of the dissertation work, which expand the knowledge of the properties of solid solutions synthesized on the basis of zirconium and hafnium tungstate. They shed new light on the processes that take place and the changes in the main characteristics and properties of these compounds, namely the unit cell parameter, the phase transition temperature, the coefficient of thermal expansion, as a result of modification with different ions. Regardless of the limited solubility of lanthanoid ions in solid solutions, the research confirms the possibility of controlling some specific properties precisely by modifying with their participation, and provides a basis for further research and challenges in the given area, as well as for the design of new composite materials with set properties, thereby facilitating their potential application.

The abstract is made according to the requirements and fully reflects the main points, scientific conclusions and conclusions, and is in full accordance with the dissertation work in a synthesized form.

The dissertation work is based on two scientific articles that were published in 2018 and 2022 years in specialized international journals (Bulg. Chem. Comm. (Q4) and Crystals (Q2). In both publications, Martin Nedyalkov is the second author and this gives me reason to believe that the contributions in the dissertation work are to a significant extent his personal work. With a minimum number of required 30 points for the sum of indicators 5-10 (group D) to fulfil the minimum national requirements, the dissertation student collects 32 points. On these articles, 3 citations indicated by the student were noticed, which are 6 additional points in the indicator from group D. The results were also presented at 4 international and Bulgarian scientific forums: 2 oral reports were presented personally by the doctoral student and 2 posters. The publications and participation in the mentioned forums have popularized the work to a sufficient extent among the scientific community.

Apart from the dissertation, the PhD student is also a co-author of another article published in 2020 in a specialized international journal with a high impact factor (Catalysis Today). His participation in five scientific projects, two of which were financed by the National Institute of Scientific Research, is impressive. The scientific data and the monographic nature of the prepared dissertation undoubtedly present Martin Nedyalkov as a promising young researcher. All research has been carried out at a high scientific level and is combined with modern analysis methods. The personal contribution of the doctoral student to the obtained results, which are discussed analytically and sufficiently critically in the published materials, is indisputable.

Based on all of the above, I consider that the proposed dissertation fully satisfies all the requirements of the law and the corresponding recommended criteria for acquiring scientific degrees and occupying academic positions at SU "St. Kl. Ohridski" for professional direction 4.2. "Chemical Sciences".

Convinced and with pleasure, I recommend to the Honorable Scientific Jury to award doctoral student Martin Krastev Nedyalkov the educational and scientific degree "**doctor**" in professional field 4.2 Chemical Sciences (Inorganic Chemistry).

Reviewer:

April 28, 2023, Sofia (Assoc. Prof. Eng. Maria Atanasova, DSc)