Review

on Dissertation on the topic: "Study of the influence of lanthanoid ions on some physical properties of tungstens of the type MW_2O_8 (M=Zr, Hf)" for the award of the educational and scientific degree "Doctor", professional field 4.2 Chemical Sciences (Inorganic Chemistry).

PhD student: Martin Krastev Nedyalkov, Faculty of Chemistry and Pharmacy, Sofia University

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

Reviewer: Assoc. Dr. Joana Zaharieva, Faculty of Chemistry and Pharmacy, Sofia University

The presented Dissertation is made within the framework of a full-time PhD in the period 2018-2021 at the Department of InorganicChemistry at the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski". The PhD student Martin Nedyalkov has a bachelor's degree in specialty "Chemistry" with the field of "Inorganic Chemistry" and "Teacher of Chemistry and Environmental Protection" in 2016 and a Master's degree in “Chemical Engineering and Advanced Materials” in 2018. After passing an exam in the specialty, he conducted exercises in General and Inorganic Chemistry with students from the Faculty of Chemistry and Pharmacy. The heads of the PhD student are long-time researchers and specialists in the field of inorganic synthesis and chemistry of rare earths.

The dissertation work is written on 75 pages, illustrated with 41 figures and 4 tables. The literature reference contains 78 sources covering the years 1959-2019, which shows thoroughness in the theoretical preparation of the doctoral student. The results of the performed research are presented in **two publications** in journals with impact factor and have been reported as poster communications or oral papers at **four conferences**, two of them international. One publication citation related to

a modification of the method used to obtain single-phase tungstates was noted. These scientific indicators fully meet the criteria for acquiring the educational and scientific degree "Doctor" at Sofia University, field 4.2 Chemical Sciences.

The introduction of the dissertation briefly presents the significance of materials whose coefficient of temperature expansion can be controlled and their application in practice.

The literature review covers 28 pages. It discusses in detail the issues concerning the structure of tungsten, the polymorphic modifications of zirconium and hafnium tungsten, the conditions under which phase transitions are carried out in different forms, the methods of synthesis and the advantages of the one chosen in the study – the hydrothermal method. The values of the temperature expansion coefficient for the respective temperature strengths are quoted and the pressure at the phase transitions between the polymorphic forms of the selected tungstens. The ways by which composites with a controlled temperature expansion coefficient can be obtained are indicated, as well as the method used in the study – namely modifying pre-existing materials with lanthanoid ions.

The influence of the substituents used so far on the crystal structure of zirconium and hafnium tungsten is discussed and justification for the choice of the lanthanoid ions used in the study is given.

The literature review is thorough and the conclusions drawn are logical. It can be concluded that the PhD student has completed the educational part of his PhD.

The conclusions of the literature reference lead to the clearly formulated in the second section objective of the Dissertation, namely "To establish changes in the structure and certain physical properties of zirconium and hafnium tungsten as a result of their modification with lanthanoid ions".

The tasks to be solved to achieve this goal are set specifically and precisely:

1. Synthesis of powder specimens of ZrW_2O_8 and HfW_2O_8, pure and modified with lanthanoid ions (Ln = Eu, Tb, Tm, Lu) by hydrothermal method.

2. Characterization of the samples obtained by a set of physicochemical methods, including high-temperature powder X-ray diffraction, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, infrared spectroscopy, UV/VIS absorption spectroscopy.

3. Determination of thermal expansion coefficients and phase transition temperature by high-temperature powder X-ray diffraction.

The conclusions made on the basis of the literature review show the significance and relevance of this study.

In the **Experimental part,** the reagents and synthetic procedure used and the methods used to characterize the samples are described.

The synthesis method is described in detail and the changed conditions in obtaining the specimens are noted, associated with an increase in temperature resulting in a shortening of the procedure time by 40% and the preparation of a single phase product.

The methods for characterizing the samples are described briefly, focusing on the application of the Rietveld method to calculate the coefficient of temperature expansion for each of the samples. The complexity of the method and its use by the doctoral student shows a thoroughness of knowledge in the field of X-ray diffractometry.

In the chapter "**Results and discussion**" by logical interpretation of the data from the investigations the obtaining of phase uniform specimens has been demonstrated. The influence of Eu^{3+} on the temperature at which the phase

transition between the two polymorphic forms of zirconium tungsten takes place is shown and a hypothesis is proposed, why no such influence is observed when modified with Tb^{3+}.

The selected concentrations of the lanthanoid ion used are in accordance with data from the literature review, showing the preparation of solid solutions when varying the lanthanoid ion concentration to a mole fraction of 5%. By calculating the forbidden zone energy for the zirconium tungsten based samples it was found that the change of the Eu^{3+} concentration in a small interval does not affect its value, but an increase in its quantity leads to its expansion.

The preparation of lanthanoid modified iodine hafnium tungsten with the same lanthanoid ion contents is difficult due to the limited solubility of the lanthanoid ion and therefore the inability to obtain solid solutions of similar composition to the modified zirconium tungstate. By X-ray powder diffraction the phase uniformity of the samples was demonstrated. Careful analysis of Raman spectra logically proves the presence of the lanthanoid ion in the crystal structure of hafnium tungsten.

By calculating the forbidden zone of the samples it was shown that modifying hafnium tungsten with Ln^{3+} (Ln=Eu, Tm, Lu) hardly affects its value.

By itself, this study of modified hafnium tungsten specimens is extremely useful from the point of obtaining knowledge on their crystal structure, missing so far in the literature.

The analysis of this chapter shows that the doctoral student has to a considerable extent mastered the ability to draw logical conclusions from the data obtained using different methods of analysis.

In the chapter "**Deductions and conclusions**" the studies conducted are briefly listed and the way in which the coefficient of temperature expansion changes in the different polymorphic forms of zirconium and hafnium tungsten when modified with Ln^{3+} (Ln=Eu, Tb, Tm, Lu) is noted.

The presented **autoabstract** fully meets the requirements and presents clearly and accurately the content of the dissertation.

The dissertation was carefully designed. The scientific language used is sufficiently precise and clear. I highly appreciate the results achieved. The questions and remarks asked do not affect the essence of the study.

I have the following **questions and remarks** for the PhD student:

1. The exhibition would be enriched if the main characteristics of the samples obtained by the method cited in the literature and the method of synthesis modified by the doctoral student were compared.

2. It seems to me that it would be good to have a separate chapter "Contributions" in which more specifically to present the novelties in the work and to outline the significance of the results obtained both in terms of the crystal structures of the synthesized specimens and in terms of subsequent studies to obtain composites with a controlled coefficient of thermal expansion.

3. Have attempts been made to confirm the presence of the lanthanoid ion by fluorescence spectroscopy - indeed the contents of thulium and lutetation are low, but for terbia and europia they are sufficient and if they are not registered - what is the possible cause?

4. Could you give an example of a system (composite) where the use of modified tungsten would improve its performance compared to the use of unmodified tungstens.

Conclusion

It is worked precisely in a modern and promising scientific field. New and interested trial results have been obtained. In general, it can be concluded that the doctoral student has formed himself as a built specialist in the field of inorganic chemistry. Based on what has been said so far, I believe that Martin Krastev Nedyalkov has successfully risen to the occasion with the task assigned to him. The presented work fully meets all legal requirements regarding the educational and research part.

I recommend to the distinguished members of the scientific jury of Martin Krastev Nedyalkov to award the educational and scientific degree "Doctor" in field 4.2. Chemical Sciences.

Sofia
02 May 2023 Prepared the review:

/ Assoc. Dr. Joana Zaharieva /