R E P O R T

on the PhD thesis entitled

Investigation of the influence of lanthanide ions on some physical properties of MW_2O_8 type tungstates (M=Zr, Hf)

**for awarding of educational and scientific degree "doctor"
in the field of 4. Natural sciences, mathematics and informatics;
professional field 4.2. Chemical Sciences (Inorganic Chemistry)**

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

Scientific Supervisors: Prof. Dr. Maria Milanova
Assoc. Prof. Dr. Martin Tsvetkov
Faculty of Chemistry and Pharmacy,
Sofia

Report from: Prof. Dr. Radostina Stoyanova, Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences

The PhD thesis of PhD student Martin Nedyalkov is dedicated to the synthesis and modification of zirconium and hafnium tungstates as materials with a negative coefficient of thermal expansion. The modification approach consists in doping of tungstates with lanthanide ions such as europium, terbium, thulium and lutetium. In this aspect, the hydrothermal synthetic method was adopted, which enables to achieve an uniform distribution of the modifying elements. The effectiveness of the modification process was evaluated in terms of the structural peculiarities of tungstates, the polymorphic phase transition, the coefficient of thermal expansion and the band gap energy. These investigations could be associated with one of the main areas of modern chemistry, namely understanding the fundamental relationships between the method of synthesis and the properties of substances in order to design materials with controlled thermal expansion.

PhD student Martin Nedyalkov is a graduate of FCP-SU, where he received his initial education on inorganic chemistry and engineering chemistry of advanced materials (bachelor and master). In 2018, he was enrolled as a PhD student in the Department "Inorganic Chemistry" at FCP-SU. The doctoral program has been successfully implemented thanks to the department's good research infrastructure.

The PhD thesis is structured in two main parts: a literature review and a part describing the results and discussions. In the literature part, an overview of the polymorphic modifications of zirconium and hafnium tungstates is presented, the main methods of their

preparation are described and the effects of metal substituents on some of properties are considered. The completed review allows the PhD student to precisely formulate the goals and objectives of the present study. In the next section, the research approach, which follows the logical links from synthesis to characterization of the tungstates with a complex of physico-chemical analytical methods, is presented sequentially. Based on the above studies, the following scientific contributions can be highlighted:

- The hydrothermal method, followed by thermal annealing, was adapted for the synthesis of zirconium and hafnium tungstates and their modified analogs. The synthetic method allows the formation of pure phases of the desired compounds at relatively low temperatures

- It has been found that modifying ions do not change the crystal structure of zirconium and hafnium tungstates, but they affect the lattice parameters, the temperature of the phase transition between the polymorphic tungstate modifications and the energy of the band gap.

- The coefficients of thermal expansion of the tungstates were calculated. For the zirconium tungstate, it is established a tendency for limited temperature contraction of two polymorphic modifications upon modification with europium and terbium. For hafnium tungstate, the lanthanide ions have a stronger effect on the coefficient of thermal expansion for the high-temperature polymorphic modification compared to the low-temperature one.

In general, the above studies contribute, on the one hand, to the enlargement of knowledge in the field of preparative chemistry of multicomponent tungstate compounds, and on the other, they would be of significance in developing of materials with negative temperature expansion.

The PhD thesis is based on two papers published in 2018 and 2022 in peer-reviewed scientific journals such as *Bulgarian Chemical Communications* (classified in quartile Q4) and *Crystals* (quartile Q2). So far, these publications received one independent citation. The thesis's results were presented at four scientific events. These facts reveal that thesis's work and the contributions therein are sufficiently personal work of the PhD student. The above analysis highlights that the PhD student fulfills the minimum national requirements for awarding the degree "doctor" in the professional field of chemical sciences, specified in the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations on Conditions and the procedure at SU-FCP.

I have no objections to the material in the dissertation. Taking into account the obtained results, I would like to put the following questions for discussion:

- In the PhD, four types of lanthanide ions were used as modifiers: europium, terbium, thulium and lutetium. In this regard, it is interesting to clarify the reasons for the selection of each of these ions.

- Given that the evaluation of the band gap energy of tungstates is the basis of the thesis work, it is necessary to describe in more detail the limitations in applying the Tauck method, especially in the presence of additional absorbing centers (such as defects and/or lanthanide ions).

These comments do not contradict my overall positive impression of Martin Nedyalkov's thesis work.

Conclusion

In the framework of his PhD studies, Martin Nedyalkov has carried out systematic research on the preparation, modification and analytical characterization of zirconium and hafnium tungstates. The PhD student demonstrates complex knowledge in several areas of chemical sciences, namely preparative inorganic chemistry and physicochemical analysis, which enables him to plan and execute research program. The scientific contributions and corresponding indicators of the PhD thesis fulfill the minimum national requirements of the Regulations of the FCP-SU for the awarding of the educational and scientific degree "doctor". All this gives me reason to propose to the Scientific Jury to vote for awarding doctoral student **Martin Nedyalkov** the educational and scientific degree "**doctor**".

Prof. Radostina Stoyanova

Sofia, 29.04.2023