OPINION

of **Prof. DSc Dimitar Stefanov Todorovsky**, pensioner, former professor in the Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia (appointed as a member of the Scientific jury by the Rector's order: РД-38-88/16.02.2023)

for the **dissertation submitted by Mr. Martin Krastev Nedyalkov**, MSc (Chemistry) "Investigation of the influence of the lanthanoid ions on some physical properties of the MW_2O_8 type tungstates (M = Zr, Hf)" for awarding of **the educational and scientific degree „Doctor"** in Higher education Pprofessional field 4.2. Chemical Sciences (Inorganic Chemistry)

1. Brief description of the applicant and the presented materials

Education. Mr. Martin Nedyalkov graduated from the Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia (2016 as bachelor of Chemistry and Teacher in Chemistry and Environmental Protection; 2018 with Master's degree in Chemical Engineering and Modern Materials, diploma work „Modification with hafnium ions of cobalt ferrite as an ethylacetat degradation catalyst"). In the period July 2018 - January 2022, he has been a PhD student in the Department of Inorganic Chemistry of the Sofia University under the scientific supervision of Prof. Dr. Maria Milanova and Assoc. Prof. Dr. Martin Tzvetkov.

Employment. Since 2018 Mr. Nedyalkov is working for an interactive scientific centre as demonstrator.

Publication activity. Mr. Nedyalkov is co-author of three papers (two of them are included in the dissertations) and 4 reports on scientific forums. Three citations are mentioned, one of them on paper included in the dissertation.

Projects. He has been member of the scientific teams working on two projects financing by the Bulgarian Scientific Investigation Fund and three Sofia University internal projects. Three of the projects are directly or indirectly connected with the thematic of his dissertation and two of them are in the photocatalysis field.

Documents presented. The documents presented by the applicant meet the requirements of article 67(5) of the Regulations for the Conditions and Order for Acquiring of Academic Degrees and Academic Positions in the Sofia University.

The dissertation contains 75 pages, 42 figures and 4 tables.

The synopsis contains 37 pages, 21 figures and 4 tables and sufficiently fully and accurately presents the main experimental result and scientific hypothesis presented in the dissertation. A small part of §III.5.2 is omitted in the English version.

2. **Assessment of the dissertation work**

The aim of the work is pointed out in its title - to establish the effect of the lanthanoid doping on the structure and some physical properties of the zirconium and hafnium tungstates.

MW_2O_8 and their solid solutions of the type $M_{1-x}Ln_xW_2O_{8-x/2}$ (where M = Zr, Hf; Ln = lanthanoid) are synthesized by a hydrothermal method and their high-temperature X-ray diffractograms, morphology, Raman, Infrared and UV/Vis spectra are studied and the resilts obtained are discussed.

2.1. Some important characteristics of the presented work should be mentioned:

- An interesting object of investigation is chosen – the ZrW_2O_8 and HfW_2O_8 with their negative thermal expansion coefficient can play the role of thermal-expansion compensators, so they could be considered important in the development of composites with adjustable thermal expansion. Further on, as the thesis shows, the introduction of Ln in the structure of

the studied tungstates permits control of their thermal expansion. So, one can suppose that, by means of the applied approach, a series of materials with controlled thermal expansion coefficients could be prepared.

- Appropriate selection of the modifying Ln is made based on their radii, compared with those of the matrix elements.

- Quite a few adequate physical methods of investigation and especially *in situ* high-temperature X-ray diffractometry (combined with an application of the Rietveld method for the unit cell parameters calculation) are applied.

- Very good knowledge of the relevant literature is seen from the literature review (78 sources, 51 of which published after 2000) and from the discussion parts of the articles and of the dissertation. To my opinion in the literature review (which is rather extensive) the results from the investigations of Ln-modified tungstates could be presented in little more details.

- The performed work and obtained results are clearly and competently presented.

- Careful and critical attitude to the explanation of the obtained experimental results is seen considering the mutually connected influence of number of factors.

2.2. Main results and scientific contributions

The obtained results reveal the significance and specific influence of:

(i) temperature (25-250 ^{o}C), (ii) nature of the main metal (M=Zr-Hf), (iii) nature of the Ln (Eu, Tb, Tm, Lu) introduced in the host cell, (iv) amount of these Ln (mole part 0.01-0.15 in different experiments depending of the nature of M and Ln)

on: (i) morphology, (ii) crystal structure (unit cell parameters, temperature of the phase transition, degree of WO_4-tetrahedra ordering), (iii) some spectral properties, (iv) thermal expansion coefficient, (v) band gap energy

of: pure MW_2O_8 and their solid solutions of the type $M_{1-x}Ln_xW_2O_{8-x/2}$,

received by: high-temperature X-ray diffractometry, IR, Raman and UV/Vis spectral analysis, SEM, TEM.

***The main achievements*/novelties** are in the areas of:

1. Synthesis. Some changes in the experimental conditions of the used known synthetic hydrothermal method are proposed aiming its elaboration. These changes could be defined as development of the now-how of the studied tungstates synthesis method. The proposed variant is applied (and cited in an international journal) by other Bulgarian authors.

2. Crystal structure.

(i) Based on literature data, the structure of the β-HfW_2O_8 is solved, thus solving the structure of the high-temperature modifications of the prepared Hf-Eu/Tm/Lu solid solutions get possible.

(ii) Based on the high-temperature X-ray diffraction patterns /the changes of the intensity of the reflexes (110) and (310)/, the phase transition temperature of the solid Hf – Eu/Lu solutions is determined.

(iii) It is shown that unit cell parameters of both pure and Ln-doped tungstates decrease with the temperature increase thus demonstrating the compounds negative thermal expansion coefficients.

(iv) A high crystal lattice order and well-defined crystal planes and interplanar distances for the Hf/Ln-tungstates are found by TEM. The larger ionic radius of Eu^{3+} (compared with Lu^{3+}) causes an increase of the interplanar distances.

(v) The upper value (mole part 0.07) of Ln content in HfW_2O_8 ensuring obtaining of a phase-homogeneous solid solution is determined.

(vi) It is supposed that a recrystallization taking place during the measurements, leading to rearrangement of WO_4-tetrahedra, might be responsible for the established

higher (compared with the literature data) temperature of the phase transformation of the pure and Eu-doped ZrW_2O_8.

3. *Thermal expansion coefficients.* Differences in the behavior of Zr- and Hf-compounds are found: while the values of temperature expansion coefficients for the low-temperature modifications are very close, the ones for β-form differ significantly. Numbers of possible factors (Zr/Hf atomic mass ratio; M-O bond length; free volume of the crystal lattice) are involved in an attempt to explain the observation.

4. *The effect of the type and amount of the introduced* Ln (Eu, Tb, Tm, Lu) *on the structure and some properties of the host* Zr/Hf *tungstates.*

(i) Differences in the lanthanoid influence on the unit cell parameter depending on the nature of the main metal are observed - while the presence of Eu/Tb decreases the Zr-compound parameter, a slight increase is observed for the Hf-one.

(ii) For the first time modification of ZrW_2O_8 with Tb is performed and the solid solution is studied. While the presence of Eu^{3+} causes an increase of the phase transition temperature, no effect is observed from Tb. An interesting hypothesis is proposed (and need a further verification) to explain the lack of effect of Tb - partial oxidation of Tb^{3+} to Tb^{4+} during the synthesis and, consequently, easier substituting of Zr^{4+} for Tb^{4+} in the crystal cell due to the closer ionic radii.

(iii) Decrease of the absolute value of the negative thermal expansion for both low- and high- temperature Zr-containing phases is shown.

The behavior of Hf-Ln solutions is more complicated. The above mentioned dependence is valid for β-modification and for α-Hf-Eu compound but not for α-Hf-Tm/Lu modification. This fact, as well some other peculiarities of the effect of the Lu, is explained with different solubility in the crystal lattice of the different Ln due to the differences of their ionic radii.

(iv) Monotonous expansion of the forbidden zone with the Eu^{3+} content increase (0.01-0.05 mole parts) is found in Zr-Eu solid solutions probably due to decrease of the crystallites mean size. The same effect is observed for Hf-compound containing 0.01 mole parts Eu^{3+}/Tm^{3+}/Lu^{3+}. However, the increase of their amounts up to 0.05 leads to lower energy band gap (even - for Tm and Lu - bellow the value for the pure tungstate).

(v) It is shown that the presence of Ln in HfW_2O_8does not cause any significant changes in the compound IR-spectrum.

The shift of some bands in the Raman spectra of Hf/Ln tungstates (compared with the spectrum of the pure compound) and change in the intensity of other one is attributed to the partial substitution of Hf^{4+} by Ln^{3+} in the HfO_6 octahedra, so affecting the Hf-O-W bond length, the WO_4 tetrahedra and, consecutively - the valence vibrations of the W-O-W bonds. Effect of the Ln-ionic radii is observed.

(vi) It is found that the presence of Ln^{3+} does not influence the morphology of the HfW_2O_8.

To my opinion the main **scientific contributions** of the dissertation are:

1. The possibility is shown to control the negative thermal expansion of the Zr- and Hf- tungstates by their modification with Ln.

2. The reported results and hypothesis add to science knowledge on influence of lanthanoid modification on the crystal structure, the phase transformations temperatures, the thermal expansion coefficients and band gap energy of $(Zr/Hf)_{1-x}Ln_xW_2O_{8-x/2}$, elucidating the determining role of the interrelation of the ionic radii and the atomic mass of Zr/Hf and lanthanoids.

3. Publications. Personal impressions

The main results of the work are presented in two papers published in Bulgarian Chemical Communications (SJR for 2018 0,137; Q4 according to quartiles journals assessment system) and Crystals (IF for 2022 2,670; Q2) and presented in 4 scientific forums, incl. two posters in international and national (with international participation) conferences and two oral presentations on events for young scientists mainly.

I have not personal impressions of the work of the candidate. Mr. Nedyalkov is first author in all of the reports in scientific conferences and second author in the articles. Along with his supervisors, in one of the papers a student and in the other one - a specialist in Raman spectroscopy are his co-authors.

Conclusion

Mr. Nedyalkov meets the requirements established by the national law and by the Faculty of Chemistry and Pharmacy recommendations for the educational and scientific degree ”Doctor”. Judging from the presented text of the dissertation, in the course of his PhD studentship he get into the chemistry of tungstates, solid state chemistry (especially in the crystallochemistry) and some physical methods of investigation, i.e. the educational aim of the doctorate work is fulfilled. The study performed has a fundamental character adding knowledge to the chemistry of tungstates, their solid solutions with lanthanoids and shows the possibility of controlling zirconium and hafnium tungstates negative thermal expansion by their modification with lanthanoids.

Taking in mind the above saying I recommend to the Scientific Jury **to award to Mr. Martin Krastev Nedyalkov, MSc the educational and scientific degree ”Doctor”** in the Professional field 4.2. Chemical Sciences, scientific field Inorganic Chemistry.

27.4.2023 Signature:

D. Todorovsky