OPINION

by Prof. Dr. George Tsvetkov

Faculty of Chemistry and Pharmacy, SU

for the dissertation work of Martin Krastev Nedyalkov, Sofia University "St. Cl. Ohridski", Department of "Inorganic Chemistry", presented for the award of the educational and scientific degree "Doctor" in professional direction 4.2 "Chemical Sciences" (Inorganic Chemistry)

Martin Krastev Nedyalkov is a graduate of the Faculty of Chemistry and Pharmacy of the SU. In 2018, he acquired the qualification Master of Chemistry in the specialty IHSM. In the same year, Martin Nedyalkov was enrolled as a full-time doctoral student in the "Inorganic Chemistry" department of the FHF of the SU with scientific supervisor Prof. Dr. Maria Milanova (subsequently his co-supervisor was Assoc. Dr. Martin Tsvetkov). He is eligible for protection in 2022.

The topic of the doctoral student's dissertation is "STUDY OF THE INFLUENCE OF LANTHANOIDE IONS ON SOME PHYSICAL PROPERTIES OF MW_2O_8 TYPE TUNGSTEN (M= Zr, Hf)". The following tasks were set before the doctoral student: synthesis of powder samples of ZrW2O8 and HfW2O8, pure and modified with lanthanoid ions (Ln = Eu, Tb, Tm, Lu), by hydrothermal method; characterization of the obtained samples using a set of instrumental methods, including high-temperature powder X-ray diffraction, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, infrared spectroscopy, UV/Vis absorption spectroscopy; determination of coefficients of thermal expansion and phase transition temperature by high-temperature powder X-ray diffraction. The above tasks are motivated by the importance of zirconium and hafnium tungstate and their properties for their practical application in obtaining composites with negligible thermal expansion or low negative CTP.

The dissertation contains 75 pages, 41 figures, 1 diagram, 4 tables are included. 78 literary sources are cited. The presented Abstract accurately reflects the main results and conclusions of the dissertation work. The presented results are original, with a significant scientific and applied contribution. They are included in 2 scientific publications with IF and 4 reports. The conclusions drawn are fully integrated into the conceptual framework of the previously set tasks. They are summarized as follows: By hydrothermal method, ZrW2O8 and HfW2O8 were modified and obtained solid solutions M1-xLnxW2O8 (M = Zr, Hf; Ln = Eu, Tb, Tm, Lu), for which the influence of the modifying lanthanoid ions on (i) the unit cell parameter, (ii) the phase transition temperature, (iii) the thermal expansion coefficient, (iv) the band gap energy, (v) the W-O-W

valence vibrations in the Raman spectra. The relatively low value of the limiting content of the modifying lanthanide ion, x = 0.07 for the solid solutions Hf1-xLnxW2O8 (Ln = Eu, Tm, Lu), could also be due to the synthesis method used.

The use of available data for isostructural compounds as well literature data for initial structural parameters, allowed by solving for the structure of the polymorphic modification β-HfW2O8 to be solved and the structure of the high-temperature modifications of the resulting solid solutions. The obtained KTP values for the low-temperature modifications α-ZrW2O8 and α-HfW2O8 are very close, while the values for the high-temperature modifications β-ZrW2O8 and β-HfW2O8 are significantly different, and the low absolute value for β-HfW2O8 is also significantly different from the literature data, which may also be due to the preparation method. The observed slight shrinkage in β-HfW2O8 compared to β-ZrW2O8 may result from a difference in (i) Zr/Hf atomic mass, (ii) Zr-O/Hf-O bond length, (iii) free volume of the crystal lattice, but the influence of other factors such as synthesis methods, their reproducibility, especially considering the established difference between our and literature data, but also between literature data from different sources, is also possible. The investigated properties of the obtained solid solutions based on zirconium and hafnium tungstate M1-xLnxW2O8(M = Zr, Hf; Ln = Eu, Tb, Tm, Lu) are largely determined by the arrangement of WO4 - tetrahedra, which is influenced by both secondary recrystallization and temperature and partial substitution of Zr4+/Hf4+ with Ln3+ in MO6 – the octahedron. The larger Ln3+ ions cause more significant WO4 distortion/disorder at low content of the modifying ion, x = 0.01, while the smaller ions close to the size of Zr4+/Hf4+ 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 dissertation work of Martin Nedyalkov corresponds to the requirements of ZRASRB and the Regulations for its application, as well as the requirements for acquiring the degree of "doctor" from the Regulations of SU "St. Kliment Ohridski". I give a positive assessment to the work presented to me for consideration and propose to the Scientific Jury to award the educational and scientific degree "doctor" to Martin Krastev Nedyalkov in scientific specialty 4.2. Chemical Sciences (Inorganic Chemistry).

30.04.2023

George Tzvetkov