Damian Włodarczyk Warsaw, 17.06.2023

Dissertation: *Synthesis and physicochemical properties of novel, tungsten-oxide double perovskites and their derivatives doped with selected rare-earth ions.*

[PL]: *Synteza i właściwości fizykochemiczne nowych wolframianowych podwójnych perowskitów oraz ich pochodnych domieszkowanych wybranymi jonami ziem rzadkich.*

Abstract (Angielski)

This comprehensive work showcases four novel rock-salt type compounds as amphoteric rare-earth tungstates $A_xRE_yW_zO_{6z}$. Two of them belong to classic double perovskites, and the other two are more related to so-called ilmenites or garnets. All of them are acquired as microcrystalline powders via high-temperature solid-state reactions of pellets in inert atmospheres. This work aims to create and thoroughly describe novel materials that could possess superior optical or scintillating properties to their scheelite predecessors, like $BaWO_4$:Ce/Pr. Furthermore, due to precursors' unique PL behavior & polymorphism, a high chance of finding an efficient energy convertor or radiation temperature sensor was anticipated. Therefore, 3 of the investigated compounds were chosen to host cerates at their RE occupation sites (RE=Ce) and the remaining one in the form of praseodymate (RE=Pr). The former group was targeted to be double perovskites varying only by alkaline 2+ atoms (A= Ba, Sr, Ca^{2+}). However, due to significant ionic radii differences, the last two turned out to be rather large, tilted, and less ordered structures. Ilmenites and garnets are popular side products during the double perovskite production process but are also worth investigating. Regarding praseodymium, only the barium variant was attempted – mainly to comprehensively compare original properties and unique phenomena acquired later during the investigation process from the nearest isostructural member. Also, barium turned out to be the only large-enough ion to produce good quality, double perovskite matrix.

Presented studies will have fundamental meaning and focus on synthesis descriptions and experimental details regarding used methods and related equipment. The second chapter will present an essential physicochemical characterization of undoped structures at ambient conditions using: powder XRD patterns & SEM projections, FTIR with Raman spectra, and XPS joined with complementary XAS data. Thirdly, results from non-ambient (temperature versus pressure) conditions will be shown concerning possible polymorphism (Raman spectroscopy), structural diversity (XRD, XPS, XAS), stability (in inert gases), and decomposition (air-sensitivity) using DSC and TG. Lastly, EPR measurements concerning magnetically-active content properties will open a gateway into the fourth chapter concerning optical measurements and unexpectedly decaying emission spectra of barium double perovskites related to charge transfer and interstitial oxygen evolution. Other results regarding the time-resolved photoluminescence of doped and undoped samples, excitation, absorption, theoretical and experimental band-gap form estimations are also present. Chosen dopants concern mostly Yb^{3+} and Ce or Pr^{3+} depending on discussed material – cerate-tungstates hold Pr, praseodymates Ce. All were selected in favor of creating a friendly environment for long-range, far down-converting energy transfer towards infrared and Yb^{3+}: (sensitizer Ce/Pr) NUV→UV-VIS (mediator WO_x)→NIR (activator Yb).

The final verdict about this research, based on all justifiable evidence collected so far, is that all these materials are relatively weak phosphors – barium praseodymate being the most photosensitive in matters of intensity but short-lived just as his cerate cousin; Sr and Ca-related cerium-tungstates being, on the contrary, weak but stable and persistent sources of light. They do not possess good enough capabilities to function as efficient, long-term down-converters, especially if they overheat and decompose in the air due to the extensive power applied by the lasers. They carry, however, very interesting charge-transfer capabilities related to photobleaching and internal oxygen evolution that might be at value for some NUV or deeper radiation one-time sensors - they are unfortunately unrecoverable. Use-and-forget manner makes them a one-way sensor. Nevertheless, these new matrices open many new possibilities and routes for future scientific research, i.e., in terms of magnetism or other RE dopants if they possess such shallow charge-transfer states just below the 5d conduction band. This work may continue beyond the scope of a Ph.D. dissertation or serve as an inspiration for others later on.

Damian Włodarczyk