Ústav anorganickej chémie
Slovenská akadémia vied
Dúbravská cesta 9, 845 36 Bratislava

Reviewer's report on the habilitation thesis of

Dr. Jose Joaquín Velázquez García

„Nanostructured oxyfluoride glass-ceramics: relationship between synthesis, processing and structural and optical properties"

The habilitation thesis of Dr. J.J. Velázquez García is focused on the synthesis, processing, and characterization (mainly optical properties, phase composition, and crystallite size) of rare-earths elements doped transparent oxyfluoride glass-ceramics prepared by ether melt-quenching, or sol-gel method, followed by heat-treatment for nano-crystallization. The habilitation thesis was submitted in the form of 10 scientific papers published in a high ranking journals in the studied field, and are supplemented by a commentary on 55 pages.
The most important achievements in the presented thesis can be listed as follows:

a) $NaGdF_4$ and $NaLuF_4$ transparent glass-ceramics doped/co-doped with rare-earth elements (Er^{3+}-Yb^{3+},Pr^{3+}-Yb^{3+}, Tm^{3+}-Yb^{3+}) with different molar ratios have been prepared by ***melt quenching*** method. The upconversion emissions can be tuned by controlling the nanocrystals size.

b) LaF_3, GdF_3 and $NaGdF_4$ based transparent glass-ceramics doped with Er^{3+} and Eu^{3+} have been prepared using ***sol-gel*** method and appropriate annealing. The samples contained up to 20 mol% of nominal active phase, the highest content published until now. The sol-gel (SG) glass-ceramics were obtained at considerably lower temperatures (350-550 °C) compared to melt-quenching method. The strength of SG thin films (up to 1.4 μm) was remarkably improved by a partial replacement of TEOS with MTES as Si precursor, and the layers were crack free even after using relatively fast heating and cooling rate of 10 °C/min.

c) The crystallization mechanism of the glasses prepared by both, melt-quenching and sol-gel methods, are based on a diffusion-controlled process. An interesting finding of the authors is that in the case of ***melt-quenched*** glasses the diffusion-controlled

process starts from a constant number of nuclei followed by crystal growth, while in ***sol-gel*** samples the process proceeds through a chemical decomposition followed by crystal precipitation.

d) The size of nanocrystals prepared by melt-quenching method and annealing increases with treatment time at a fixed temperature until a nearly constant value is reached (range 8-50 nm). In the case of sol-gel method neither the crystal size, nor the fraction of glass-ceramics increases with increasing heat treatment temperature and time.

e) The crystal size increases with increasing rare-earth dopant content.

f) The crystalline phase fraction in $NaLuF_4$ glass-ceramics obtained by melt-quenching method was ~19 wt% and in $80SiO_2$-$20LaF_3$ samples ~18 wt%. These fractions are the highest so far reported for oxyfluoride glass-ceramics.

I have only one question: During melting of the starting powders at high temperatures up to 30-40% of fluorine can be lost (Introduction, page 4). How can you decrease the fluorine loss during the melting process?

I can conclude that the candidate is a recognized researcher in the field of optical glass-ceramics. He is an author or co-author of 1 book chapter, 1 instructional text (laboratory practices), 50 scientific papers in foreign and national peer-reviewed journals and conference proceedings with 516 citations (WoS and Scopus). His H-index is 17. He is recently a supervisor of 2 PhD. students, co-supervisor of 3 master and bachelor thesis. The candidate fulfils (in many cases exceeds remarkably) all the criteria in the Scientific and research activities required for obtaining the title "docent".

The candidate has proper teaching and pedagogical activities in bachelor and master study (topics: Physics II, Expanding optics, Applied physical foundations of engineering, Nanomaterials - structural and optical characterization - executed in Spain). Additionally, he had an extracurricular activities: 4 presentations on Renewable energies (Uni. de la Laguna, Spain) with the aim to hire a young students/scientists in to the field of functional opto-glass-ceramics.

Dr. Velázquez participated with his research activities also in several projects like CEGLASS (FunGlass), VEGA, and also in Spanish projects. He is a principal investigator of 1 project and is/was a co-investigator of 12 projects (in Spain and in Slovakia).

The plagiarism check protocol of the habilitation thesis gives only 0.66% agreement, what is considered as a negligible value.

Finally, it can be concluded that the habilitation thesis of Dr. Velázquez García has a good quality and fully complies with all the criteria required for the award of the title of 'docent' in the field of inorganic materials. Therefore, I suggest to the Scientific board of the Trenčianska univerzita Alexandra Dubčeka v Trenčíne to accept the submitted habilitation thesis of Dr. Jose Joaquín Velázquez García as a base for the habilitation procedure, and after successful defence, award him a title „**docent**" in the field of Inorganic technologies and materials (No. 2080).

V Bratislave, 7.3. 2022

doc. Ing. Zoltán Lenčéš, PhD.