January 31, 2022, Częstochowa, Poland

Report on the PhD thesis "Wide-range, Highly-sensitive Luminescent Thermometers Activated with Pr^{3+} or Eu^{2+}" by Małgorzata Sójka (University of Wroclaw, Wroclaw, Poland)

The reviewed PhD thesis is devoted to the detailed experimental investigations of a series of strontium (lutetium, yttrium) germanates (silicates) and their solid solutions doped with the Pr^{3+} ions and strontium borate doped with the Eu^{2+} ions. These materials were shown to be good and reliable optical thermometers, pressure sensors and thermoluminescent phosphors. Complete cycle of experiments was conducted, starting from the samples' synthesis, structural investigations, scanning electron microscopy, FTIR spectroscopy, optical spectroscopic measurements at different temperatures and pressures, and deep analysis of the obtained results.

The thesis is very well-written. It starts with the introductory chapter, where the basic electronic and spectroscopic properties of the rare earth ions, foundations of the optical thermometry and dosimetry are all described at length.

This first chapter is followed by Chapter 2, in which the thesis main goals are formulated clearly. The third chapter introduced the experimental techniques used by the thesis author to perform the planned investigations. Chapter 4 is dealing with the $Sr_2(Ge,Si)O_4:Pr^{3+}$ phosphors, being focused on how varying the Ge/Si ratio can affect the material's luminescent thermometer properties. The $Lu_2(Ge,Si)O_5:Pr^{3+}$ luminescence thermometers are exploited in Chapter 5. The energy storage properties of the $Lu_2(Ge,Si)O_5:Pr^{3+}$ phosphors are considered in Chapter 6. The $Y_2(Ge,Si)O_5:Pr^{3+}$ phosphors as multimodal temperature and pressure sensors are highlighted in Chapter 7. Chapter 8 is devoted to the influence of the Ge/Si ratio on the carriers trapping in $Y_2(Ge,Si)O_5:Pr^{3+}$. Applications of the Eu^{2+} for optical thermometry are brought to light in Chapter 9. Finally, Chapter 10 lists the main conclusions of the thesis.

The author has clearly demonstrated a profound understanding of the main fundamental concepts that make optical thermometry and dosimetry possible; she has also shown high experimental skills and good analytical abilities needed for an analysis and proper interpretation of the acquired experimental information.

The thesis results are of dual importance. Firstly, they open a wide road towards real applications of the studied solid solutions as optical thermometers, thus making up an applied

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part of the performed research. Secondly, by means of thorough empirical analysis of the electronic band structure of the prepared cation-mixed materials and defects' localized energy levels within the host's band gap, the author has made an important contribution to the fundamental research, heling to understand (sometimes hidden, yet very important) "structure-property" and "property-property" relations, that can serve as useful guides to direct smart search for new materials with improved performance and enhanced capabilities.

The thesis novelty is a crucial factor to judge whether the thesis itself represents a valuable piece of scientific information. The novelty of the reviewed thesis cannot be questioned and it consists in using the interconfigurational 5d→4f transition of Pr^{3+} ions (for the first time) in the field of luminescence thermometry. Moreover, the concept of the band gap engineering through the chemical composition for optical thermometers is also new, as well as the simultaneous use of the 4f-5d and 4f-4f transitions of the Eu^{2+} ions for temperature measurements. These new ideas proposed and developed in the thesis and relevant publications are already well received by the scientific community and will open a new pathway leading to the creation of reliable optical thermometers with high precision working in wide temperature range.

The main results of the thesis were published in highly reputed international journals, such as Advanced Optical Materials, Journal of Materials Chemistry C, Journal of Alloys and Compounds. According to Google Scholar database (as of January 31, 2022), the author's papers were cited 162 times, with h-index=5, which is a very good result for the PhD student. It should be especially emphasized that one paper – "Widening the Temperature Range of Luminescent Thermometers through the Intra- and Interconfigurational Transitions of Pr^{3+}", by C.D.S. Brites, K. Fiaczyk, J.F.C.B. Ramalho, M. Sójka, L.D. Carlos, E. Zych, Advanced Optical Materials 6 (2018) 1701318 – has been already cited 92 times – this is a truly remarkable achievement.

I would like also to stress out that the thesis author has been involved into active international collaboration with leading research groups in the field from Portugal.

My overall impression about the thesis was very positive, and I really enjoyed reading it. Without any shadow of doubt, I conclude that the author fully deserves the PhD degree.

There are a few minor remarks, which I would like to list here (without any intention to lower down the thesis evaluation).

1. There is a typo on Page 15: instead of "L is the total spin quantum number" it should be written "L is the angular momentum quantum number".

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2. Page 16, the sentence "The degree of splitting is up to (2J+1) for integer J or (J+1/2) when J is a half-integer number. Yet, the exact number of Stark levels are strongly dependent on the symmetry of the Ln ion environment and are defined by the selection rules.[30–32]" is only partially true. The number of Stark levels is determined only by the environment; the selection rules determine the possible transitions between the pairs of energy levels, that are formed by the crystal field effects.
3. Page 19: "the ground and excited wavefunctions" - the word "states" should have been inserted before "wavefunctions".
4. Page 21: the capital T in Eq. (1.1) should be a small t (time, but not temperature). The negative sign is missed in the exponent's argument of Eq. (1.2).
5. Page 25, the figure captions to Fig. 1.6 (a,b) seem to be interchanged.
6. Page 28, the word "proceeded" in the sentence "Thermally stimulated luminescence (TSL) is an emission of light produced by heating a semiconductor or an insulator proceeded by the absorption…" should be replaced by "preceded".
7. Page 46 – a comparative table with absolute/relative sensitivity of different optical thermometers would be desirable in this part of the thesis.

All these remarks are just very minor things, which do not change my high evaluation of the performed research. The overall content of the thesis is well above the average PhD dissertation. I congratulate the author of the PhD thesis and the supervisor with successful and excellent completion of the job and I recommend the PhD degree with distinction (z wyróżnieniem) to be conferred upon Ms M. Sójka.

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