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Wrocław 24.01.2022

REVIEW

of dissertation of Małgorzata Sójka, M.Sc.

"Wide-range, Highly-sensitive Luminescent Thermometers Activated with Pr^{3+} and Eu^{2+}".

carried out under the scientific supervision of Prof. Eugeniusz Zych,

auxiliary supervisor: Dagmara Kulesza, Ph.D.

The doctoral dissertation submitted for review was written at the Department of Chemistry, University of Wrocław, under the supervision of the prof. Eugeniusz Zych and auxiliary supervisor Dagmara Kulesza, Ph.D.. The dissertation, prepared in English, consists of a set of six thematically coherent co-authored articles, supplemented by a 60-page introduction. The 210-page dissertation was divided into 10 chapters containing a brief description of the spectroscopic properties of Pr^{3+} and Eu^{2+} ions and the current state of the art in the field of luminescence thermometry (Chapter 1), the aim of the work (Chapter 2), a description of

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measurement techniques used (Chapter 3), a description of the results obtained together with copies of the papers included in this dissertation (Chapters 4-9) and a summary (Chapter 10). In the final part of the dissertation, the PhD student included a list of Her scientific achievements. A wide range of works cited in the dissertation, including both fundamental works and the latest research results in the field, is appropriate and demonstrates Her adequate knowledge of the literature.

It should be noted that the publications constituting this dissertation were published in very prestigious journals with a high impact factor, such as, among others, Journal of Materials Chemistry C and Advanced Optical Materials. Sójka is the first author of all publications, and the description of each of them is accompanied by a statement of Her personal contribution. Undoubtedly, the Ph.D. student played a key role in the process of their creation. She was responsible for the synthesis of the materials, characterization of their structural and morphological properties, spectroscopic and thermoluminescence measurements, as well as analysis and interpretation of the obtained results and writing drafts of the manuscript.

At the outset I would like to draw attention to the significant scientific output of the Ph.D. student. She is a co-author of 9 scientific publications in excellent specialistic journals with high impact factors. In the vast majority of these works M.Sc. Sójka is the first author, which proves Her significant contribution to their development. A high number of independent citations of these works proves that they met with the great interest of the scientific community. Ph.D. student has extensive experience in the implementation of scientific projects. She acted as a contractor in three scientific projects. Moreover, it should be emphasized that M.Sc. Sójka

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managed independently the implementation of the Prelude project financed by the National Science Centre. During Her doctoral studies she completed numerous national and international scientific internships and was awarded many scientific scholarships. She presented the results of Her research at many international scientific conferences in the form of oral presentations and posters. A wide range of research and scientific activities undertaken by Her, significantly exceeding the scope of Her Ph.D. dissertation, undoubtedly demonstrates Her exceptional commitment and interest in inorganic chemistry and optical spectroscopy.

The thesis itself is written in a very accessible and clear manner and is carefully edited. The author has struck a very good balance between the partly theoretical introductory part and the description of the obtained results. The subject of this work concerns luminescence thermometry, which in recent years has been of exceptional interest to many scientific groups working all over the world. This interest involves a significant difficulty in proposing topics and carrying out work of a pioneering nature, and avoiding research bearing the hallmarks of increment. M.Sc. Sójka has undoubtedly achieved this goal.

The main research objective of this work was to verify the possibility of using the thermal variation of the intensity of emission bands associated with interconfiguration 5d→4f electronic transitions to develop a highly sensitive ratiometric luminescent thermometer. In the present work, the Ph.D. student proposed to use the mechanism of temperature-induced electron transfer from the 5d band of Pr^{3+} ions to the conduction band. The proposed mechanism allows to bypass the limitations of thermometric parameters in thermometers based on the thermal coupling of energy levels, which are commonly used and studied nowadays. Strong variation

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of *5d→4f* band emission intensity with temperature change allowed to develop ratiometric luminescent thermometers with very high relative sensitivities obtained in the cryogenic temperature range. In addition, the Ph.D. student proposed and experimentally proved the possibility of modifying the thermometric parameters of such thermometers by adjusting the width of the energy gap occurring between the valence and the conduction bands in $Sr_2(Ge,Si)O_4:Pr^{3+}$ and $Lu_2(Ge,Si)O_5:Pr^{3+}$ by changing the stoichiometry of the matrix. This was the final confirmation of the Ph.D. student's understanding of the processes occurring in the materials studied. The fact of comprehensive characterization of the materials studied, including, apart from the techniques commonly used in such studies, also thermoluminescence measurements, deserves a special mention. Such a multifaceted research testifies to the high reliability and meticulousness of M.Sc. Sójka in the verification of scientific hypotheses. In my opinion, the presented work has the hallmarks of a pioneering research of high substantive quality. In the further part of Her work, the Ph.D. student extends Her research interest to materials doped with Eu^{2+} ions. Here, the ratio of the emission intensity of the bands associated with the depopulation of the $5d^1$ and $^6P_{7/2}$ levels and the luminescence decay time recorded at λ_{em}=362 nm in $SrB_4O_7:Eu^{2+}$ were used as thermometric parameters. Due to the high thermal variability of both these parameters, very high relative sensitivities reaching 22.6%/K at 17 K and 10.47%/K at 21 K were obtained for the ratiometric and luminescence kinetics based approaches, respectively.

I rate the substantive level of the work very high, and the presented results prompted me to ask the following few questions:

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- When describing the results obtained in Paper 1 (Adv. Opt. Mater. 7 (2019) 1901102), the Author mentions the influence of the optical excitation wavelength, and more precisely the corresponding energy, on the thermometric properties of thermometers exploiting the luminescence of Pr^{3+} ions in $Sr_2(Ge,Si)O_4$. The Author verified experimentally the described hypothesis by using two excitation wavelengths of 253 nm and 244 nm. The proposed explanation of the described effect is convincing, and the presented strategy enables the control of the thermometric properties of the phosphor by selecting the excitation wavelength. This is very important from the perspective of potential applications. However, as can be seen in the luminescence spectra of the investigated materials presented in this work, when 244 nm optical excitation is used, the emission intensity of the *5d→4f* band drastically decreases in respect to the intensity of the emission band associated with the *4f-4f* electronic transitions, which certainly affects the reliability of temperature readout taken under these conditions (low signal-to-noise ratio). Therefore, I wonder if the Ph.D. student verified the effectiveness of the proposed explanation and the possibility of smooth adjustment of thermometric parameters of $Sr_2(Ge,Si)O_4:Pr^{3+}$ at other excitation wavelengths in the 240-265 nm range?
- Has the applicability of the abovementioned approach been verified for $Lu_2(Ge,Si)O_5:Pr^{3+}$? Taking into account the higher temperature variation of the luminescence intensity ratio (LIR) parameter described by the Ph.D. student for this material, reflected in the higher values of relative sensitivity for the 250 nm optical

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excitation, it can be expected that by increasing the optical excitation energy it will be possible to obtain relative sensitivities exceeding the 9%/K recorded for $Sr_2(Ge,Si)O_4:Pr^{3+}$.

- In the work described above, the PhD student has consistently used low concentrations of Pr^{3+} dopant ions, which is understandable in the context of a desire to reduce the probability of inter-ion interactions that can lead to concentration quenching of Pr^{3+} luminescence. However, I would like to know what temperature dependence of Pr^{3+} ion luminescence, and thus the LIR parameter, the PhD student expects for higher molar concentrations of the dopant?
- In the work described in Chapter 7 of this dissertation, the Ph.D. student describes the spectroscopic properties of $Y_2(Ge,Si)O_5:Pr^{3+}$ verifying the possibility of using this material for remote pressure and temperature measurement. I would like to ask how the applied pressure affects the integral emission intensity of the band associated with the *5d→4f* electronic transition? Can changing the pressure applied to a luminescent thermometer affect the reliability of the temperature readout?

The above questions arise from the reviewer's curiosity aroused by the inspiring research and do not relate to undermining the substantive level of the dissertation, which I assess as very high. This work proves that Małgorzata Sójka is a talented young scientist with extensive research experience and broad knowledge in the field of optical spectroscopy of materials doped with lanthanide ions. She has knowledge of a wide range of measurement techniques and the ability to apply them rationally to verify research hypotheses. What is important, and as I have

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already emphasized in this review, the Ph.D. student carried out the described research in a reliable manner, while maintaining a critical perspective.

The dissertation presented for review is a work of a very high scientific level, making a significant contribution to the development of the field. The works included in it are of pioneering character and have already met with considerable interest from the scientific community, which is reflected in the number of citations.

I have no doubts that Małgorzata Sójka's doctoral dissertation meets the statutory requirements for doctoral dissertations set out in Article 13 of the Act of 14 March 2003 on Academic Degrees and Academic Title and Degrees and Title in Art (Journal of Laws No. 65/03, item 595, as amended), in the Regulation of the Minister of National Education and Sport of 15 January 2004 (Dz.U. nr 15/04, poz. 128) and in the Regulation of the Minister of Science and Higher Education of 30.01.2018 on the detailed procedure of conducting activities in doctoral dissertation, in habilitation proceedings and in proceedings for granting the title of professor (Dz.U. 2018, poz. 261). Therefore, in the light of above, I submit a recommendation to admit the Candidate to further stages of the doctoral defense.

Additionally, taking into account the pioneering, on a global scale, the character of the works conducted and high reliability of the analysis of the results obtained, as well as the scientific achievements of the Candidate, I apply for a distinction of the Ph.D. thesis of M.Sc. Małgorzata Sójka,

Łukasz Marciniak