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Proposal for the distinction of a doctoral dissertation of M.Sc. Teng Zeng

Referring to my review of the doctoral dissertation of M.Sc. Teng Zeng "Lanthanide (III or II) activated Materials SrB_4O_7 and $BaTiO_3$ materials for luminescent manometers and non-linear optical thermometry", which is presented in the form of 6 thematically coherent series of articles published in scientific journals, I would like to propose its distinction.

The research undertaken in the dissertation under the supervision of the prof. dr. hab. Stefan Lis was inspired by the research area, carried out in the Department of Rare Earth, mainly related to the inorganic and coordination chemistry of 4f-electron elements, including the synthesis and physicochemical characteristics of new nanoluminophores containing lanthanide ions, luminescence studies and new analytical methods based on the luminescence method.

M.Sc. Teng Zeng doctoral dissertation fits perfectly into the most current issues of materials science, particularly in the field of optical pressure and temperature contactless sensing, making an important contribution to the physicochemistry of novel sensors.

The ambitious target of M.Sc. Teng Zeng research was to establish and characterize in detail new strategies for the construction of optical manometers and thermometers. I believe that a particular achievement of M.Sc. Teng Zeng were the syntheses, selection and characterization of appropriate borate and titanate matrices doped with Ln^{2+} or Ln^{3+} ions.

The successful research on the influence of the matrices on the structural, morphological and photoluminescence properties of lanthanide ions resulted in several strategies of optical pressure sensing.

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He is a co-author of the excellent, very sensitive bifunctional and multi-parameter optical sensor of pressure and temperature, based on Tm^{2+} luminescence, working in the visible spectral range as a visual sensor. Moreover, he participated very actively in the research that led, for the first time, to the simultaneous employment of the second harmonic generation (SHG) and upconversion luminescence (UCL) processes in $BaTiO_3$:Ho^{3+},Yb^{3+} material for optical temperature sensing. Finally, he was deeply engaged in the research, carried out for $BaTiO_3$: Er^{3+}, Yb^{3+} perovskite material. The authors discovered that two optical thermometric pathways could be realized simultaneously in a single material, *i.e.*, luminescence thermometry utilizing TCLs of Er^{3+} and NLO thermometry based on SHG/UCL band intensity ratios.

The successfully realized objectives of the doctoral dissertation are related to the impressive list of 6 publications from JCR list with a total IF of 46.08, co-authored by M.Sc. Teng Zheng as the first author.

The exceptional results presented in the doctoral dissertation on the construction and application of the borate and titanate perovskite materials doped with lanthanide ions, determining the relationship between the structure and their photoluminescence properties, which led to the obtaining of the novel, excellent luminescent manometer and non-linear optical thermometer, are the consequence of combining the intellectual abilities of M.Sc.Teng Zeng, his versatility, manual skills, commitment and passion of a real researcher of experimental work.

Due to the uniqueness of the results important for the current state of knowledge in materials science, particularly in the field of optical pressure and temperature contactless sensing, I strongly propose to distinguish the outstanding doctoral dissertation of M. Sc. Teng Zeng.

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Review of the Ph.D. dissertation of M.Sc. Teng Zheng
"Lanthanide (III or II) activated Materials SrB_4O_7 and $BaTiO_3$ materials for luminescent manometers and non-linear optical thermometry"
in the form of a thematically coherent series of articles published in scientific journals

M.Sc.Teng Zheng's doctoral dissertation was conducted at the Department of Rare Earths at the Faculty of Chemistry, the University of Adam Mickiewicz in Poznan under the supervision of the prof. dr. hab. Stefan Lis. This work is part of the research area of the Department, mainly related to the inorganic and coordination chemistry of 4f-electron elements, including the synthesis and physicochemical characteristics of new nanoluminophores containing lanthanide ions, luminescence studies and new analytical methods based on the luminescence method.

During his Ph.D. research, M.Sc. Teng Zheng has carried out a remarkable work on the synthesis, structural and photoluminescent properties of inorganic materials consisting of inorganic oxide matrices in the form of SrB_4O_7, $BaTiO_3$ and $Sr_3(BO_3)_2$ doped with Ln(II) or Ln(III) ions and their physicochemical characteristics. The research has been motivated by the relevance of their applications as luminescent manometers and optical thermometers. The research carried out by Teng Zheng is part of one of the most dynamically developing fields of science on the design and synthesis of new nanomaterials and is based on the vast experience of prof. dr. hab. Stefan Lis in this field. These studies are extremely timely and very valuable from the point of view of basic research and potential applications in optoelectronics, thanks to the control of luminescent properties by external stimuli.

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The research conducted by M.Sc. Teng Zheng was focused on developing and characterizing materials composed of Ln(II) and Ln(III) ions doped inorganic oxide matrices with high durability, for use in the design of a precise luminescent manometer and a nonlinear optical thermometer. He investigated the influence of oxide matrices on the structural, morphological and photoluminescent properties of the obtained materials. M.Sc. Teng Zheng has listed several research aspects, namely:

- The study of the influence of a borate matrix on the photoluminescent properties of the Eu^{2+}/ Eu^{3+} system.
- The investigation of the energy transfer process in a Sm^{2+}-Eu^{2+} -SrB_4O_7 material and the use of the ET for the augmentation of the Sm^{2+} pressure sensing signal.
- The study of the high-pressure enhancement 4f-4f transition of Eu^{2+} for application in high-pressure sensing.
- The examination of Tm^{2+}-SrB_4O_7 material as a bifunctional sensor of temperature and pressure.
- The study of the second harmonic generation signal and upconversion luminescence in the Er^{3+}-Yb^{3+} and Ho^{3+}-Yb^{3+} doped $BaTiO_3$ materials for the nonlinear optical thermometry.

The above objectives of the dissertation are followed by the impressive list of 6 publications, co-authored by M.Sc. Teng Zheng selected for doctoral dissertation. To have a slightly more complete picture of M.Sc. Teng Zheng scientific profile, it is worth emphasizing his remaining scientific achievements, which include 9 other publications in journals from JCR lists. He is first author of 12 of them (out of 15), with total IF of 108.473. One cannot ignore the fact that carried out research within the dissertation were funded as part of the two National Science Centre Poland projects and one High-Chem Project for Doctoral students (EU).

M.Sc. Teng Zheng's doctoral dissertation was written in English in the form of a thematically coherent series of 6 scientific articles from the JCR list with a total IF of 46.08 preceded by a concise presentation of essential concepts. The aim of the work was clearly and appropriately formulated.

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In the introduction, M.Sc. Teng Zheng has focused on the basic knowledge of luminescence of Ln ions, followed by the discussion of the emission 5d-4f process of selected Ln^{2+} ions (Eu^{2+}, Sm^{2+} and Tm^{2+}). Next, he has emphasized the important property, up-conversion luminescence of Ln^{3+} ions, with special attention to the combination of Er^{3+} -Yb^{3+} and Ho^{3+} -Yb^{3+} pairs of dopants. Finally, he has discussed the exceptional role of inorganic host matrices of strontium tetraborates (SrB_4O_7) and barium titanate perovskites ($BaTiO_3$) in the construction of designed materials. He has emphasized and explained the special role of strontium tetraborates SrB_4O_7 in the stabilization of Ln^{2+} ions and the uniqueness of barium titanate $BaTiO_3$ favoring superior up-conversion luminescence efficiency of appropriate Ln^{3+} dopant ions. Perhaps "hervidero hotbed" requires a small explanation.

Furthermore, he has introduced a description of luminescence sensing techniques, such as high pressure and optical manometry and luminescence thermometry concepts. The review of the state of knowledge related to research aspects is based on 197 publications and gives a useful guide of fundamental ideas. This part of the dissertation clearly indicates the thorough and extensive knowledge of the Ph.D. student in the subject of the dissertation.

Maybe this part of the dissertation would gain a bit if he paid the attention to the general aspects of the synthesis of the designed materials, the synthesis of which he had to face himself. However, in the Experimental part of the dissertation, M.Sc. Teng Zheng meticulously described the syntheses of the respective materials. This is followed by the pieces of information on the physicochemical methods of characterization of the investigated microparticles, such as X-ray powder diffraction, Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX), Raman spectroscopy, and Luminescence spectroscopy. Next, M.Sc. Teng Zheng described a high-pressure experiment setup, including HP Raman scattering and HP PL characterization. The extensive list of physicochemical methods is finished by the part of the thermal-dependent PL spectroscopy with high- and low-temperature PL characterization.

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M.Sc.Teng Zheng's doctoral dissertation culminates in six multi-author articles in journals of high scientific rank with him as a first author.

The Ph.D. student precisely defines the scope of his contribution to the co-authored publications. The co-authors' declarations of their contribution to individual publications were also attached to the dissertation.

The review of this part of the doctoral dissertation must necessarily be a kind of overview because these works had to fulfill all rigorous requirements and have already been criticized by international experts of recognized reputation.

In the first publication (Teng Zheng, et.al., Influence of matrix on the luminescence properties of Eu^{2+}/Eu^{3+} doped strontium borates: SrB_4O_7, SrB_2O_4 and $Sr_3(BO_3)_2$, exhibiting multicolor tunable emission, Journal of Alloys and Compounds, 2020, 822, 153511), the author carried out the syntheses of three complex strontium borate matrices doped with $Eu^{2+/3+}$ employing a high-temperature solid-state reaction method in the air. He has confirmed that, according to the XRD and SEM analysis, each obtained sample has a pure crystal structure. He has found that **the products obtained exhibited tunable multicolor luminescence from violet-blue to orange-red, depending on the excitation wavelength applied and the host matrix used. Moreover,** the intensity ratio of $Eu^{2+/3+}$ emission varies significantly in different matrices.

The subject of the second publication concerns the strong enhancement of Sm^{2+} emission through Eu^{2+} energy transfer in a SrB_4O_7 pressure sensor (Teng Zheng, et.al., Huge enhancement of Sm^{2+} emission via Eu^{2+} energy transfer in a SrB_4O_7 pressure sensor, Journal of Materials Chemistry C, 2020, 8, 4810-4817). The author conducted innovative research on the incorporation of Eu^{2+} ions into the original crystalline structure of Sm^{2+}- SrB_4O_7 material. As the result, an enhancement of about 60 times in the ultra-narrow $^5D_0$ - $^7F_0$ Sm^{2+} emission line was observed. The developed sensor exhibits favorable pressure sensing features, excellent temperature independence, sharp and single emission lines, and an intense luminescence signal. Depending on the excitation wavelength used and dopant content in the matrix, the samples also exhibit multicolor tunable luminescence from orange-red to amaranth,

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and to warm-white light, allowing their potential application in white light-emitting diode devices.

The result of the author's research presented in the third publication (Teng Zheng, et.al., Pressure-driven Configurational Crossover between $4f^7$ and $4f^65d^1$ States – Giant Enhancement of Narrow Eu^{2+} UV-Emission Lines in SrB_4O_7 for Luminescence Manometry, Acta Materialia, 231(2022)117886) is a discovery of the strong pressure-induced intensity enhancement of the $4f^7$ $(^6P_{7/2}) \rightarrow 4f^7$ $(^8S_{7/2})$ emission line of Eu^{2+}, originating from the pressure-induced configurational crossover between the excited $4f^65d^1$ and $4f^7$ energy levels in Eu^{2+}/Sm^{2+} doped SrB_4O_7 matrix. The exciting properties of the constructed pressure sensor are a significant red-shift and negligible temperature dependence of the line position. This remarkable achievement suggests that such luminescent material may significantly increase the accuracy of the non-invasive pressure determination and can be applied as a multimode pressure-enhanced measurer.

The impressive achievements have been presented in the fourth publication (Teng Zheng, et.al., Tm^{2+} Activated SrB_4O_7 Bifunctional Sensor of Temperature and Pressure — Highly Sensitive, Multi-Parameter Luminescence Thermometry and Manometry, Advanced Optical Materials, 2021, 2101507), where Ph.D. Student has stabilized Tm^{2+} ions in the SrB_4O_7 matrix, using the high-temperature solid-state method in air. The investigations of the spectroscopic properties of SrB_4O_7:Tm^{2+} as a function of high pressure and temperature resulted in the excellent, very sensitive bifunctional and multi-parameter optical sensor of pressure and temperature, based on Tm^{2+} luminescence, working in the visible spectral range as a visual sensor.

The last part of the research is related to the fundamental second-order nonlinear optical processes, i.e., second harmonic generation (SHG) and upconversion luminescence (UCL) phenomena of Ln^{3+} ions in $BaTiO_3$ perovskite matrix.

In the fifth work, the authors for the first time simultaneously employed the second harmonic generation (SHG) and upconversion luminescence (UCL)

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processes in $BaTiO_3$:Ho^{3+},Yb^{3+} material for optical temperature sensing (Teng Zheng, et.al., Nonlinear Optical Thermometry — A Novel Temperature Sensing Strategy via Second Harmonic Generation (SHG) and Upconversion Luminescence in $BaTiO_3$: Ho^{3+}, Yb^{3+} Perovskite, Advanced Optical Materials, 2021, 9, 2100386). The application of both the SHG and UCL bands in $BaTiO_3$:Ho^{3+}, Yb^{3+} material for temperature sensing purposes was motivated by different spectroscopic behaviors of SHG and UCL processes under controlled temperature conditions i.e., while SHG is sensitive to the inversion symmetry breaking, UCL is monotonously thermally quenched. The temperature dependences of the SHG and UCL phenomena in the optically active $BaTiO_3$:Ho^{3+}, Yb^{3+} perovskite material were investigated in the temperature range of 25–305 °C. The band intensity ratio of SHG to UCL undergoes a significant inflection point during the gradual tetragonal-to-cubic phase transition, which confirms that the authors discovered a new method for detecting the symmetry change of the crystals. The authors emphasize that the intensity ratio of these NLO processes can also be used as a new thermometric parameter, with a remarkable relative sensitivity of 2.78% $°C^{-1}$, showing the possibility of applying various NLO effects for sensing purposes.

Finally, to explore the NLO spectroscopy further, the Ph.D. Student participated in the research, carried out for $BaTiO_3$: Er^{3+}, Yb^{3+} perovskite material (Teng Zheng, et.al., Boltzmann vs. non-Boltzmann (non-linear) Thermometry - Yb^{3+} -Er^{3+} Activated Dual-mode Thermometer and Phase Transition Sensor via Second Harmonic Generation, Journal of Alloys and Compounds, 2022, 906, 164329). The authors discovered that two optical thermometric pathways could be realized simultaneously in a single material, *i.e.*, luminescence thermometry utilizing TCLs of Er^{3+} and NLO thermometry based on SHG/UCL band intensity ratios. The authors demonstrated the advantage of the NLO thermometry, *i.e.*, higher relative thermal sensitivity (S_r) of ≈ 4%/K *vs.* ≈ 1.2%/K for the luminescence thermometry. Furthermore, the SHG/UCL band intensity ratio was introduced as a parameter for phase transition detection, from tetragonal to cubic phase in the synthesized materials. These results show the effectiveness of NLO

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spectroscopy for the construction of an accurate and highly sensitive, remote temperature sensor.

I have no serious substantive comments on the dissertation under assessment. In turn, I have a few questions, that I would like to discuss in the defense.

1. I have not found the information on the reproducibility of the syntheses of the investigated luminescent materials and therefore their physicochemical properties.
2. What is the influence of the size of microcrystallites on the photoluminescence properties?
3. What is the stability of the investigated materials?
4. What are the drawbacks of the presented materials?

In summarizing, the doctoral dissertation of M.Sc. Teng Zeng contains extremely valuable experimental material characterized by scientific novelty. Undoubtedly, it is the result of the competent presentation of research problems, their implementation and analysis of the obtained results. All ambitious research objectives set out in the assessed dissertation were achieved, which will contribute to the construction of new luminescent manometers and nonlinear optical thermometers.

For that reason, I conclude that the doctoral dissertation of M. Sc. Teng Zeng meets all the substantive requirements for the doctoral thesis of Article 187 of the Act of July 20, 2018 - Law on Higher Education and Science. Consequently, I request admission to M.Sc. Teng Zeng to the next stages of the doctoral dissertation procedure. Moreover, due to the uniqueness of the results obtained important for the current state of knowledge in materials science, particularly in the field of optical pressure and temperature contactless sensing, I propose to distinguish the dissertation of M. Sc. Teng Zeng.

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