Title of doctoral dissertation: **Double perovskites Ba_2MgWO_6 and La_2MgTiO_6 doped with Eu^{3+}, Nd^{3+} and Er^{3+} - synthesis, structure, and optical properties** (In the form of thematically coherent series of articles published in scientific journals)

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ABSTRACT

It is well known that, the rapid development of sciences and technology requires new materials. Double perovskites are among the most intensely studied compounds by virtue of their interesting chemical and physical properties and the possibility of modifying the composition of the sample significantly increases their application potential. To name a few, Ba_2MgWO_6 (BMW) and La_2MgTiO_6 (LMT) are novel double perovskites that were unexplored in spectroscopic properties. When I started my research for this dissertation, there were 19 publications of BMW and 9 publications of LMT in literature in early 2019. However, the authors of these papers focused mainly on structural properties, dielectric properties, theoretical calculations, and ceramic fabrication method for wireless and mobile communication applications. Only 2 articles reported spectroscopic properties of BMW and LMT hosts doped with lanthanides ions (Ln^{3+}) prepared by the traditional solid-state method.

The aim of this dissertation was to obtain BMW and LMT by a wet chemistry method, namely the co-precipitation method. The investigated hosts were singly doped with three chosen Ln^{3+} including neodymium (Nd^{3+}), europium (Eu^{3+}), and erbium (Er^{3+}) ions.

To characterize the structure and morphology of the samples, X-ray powder diffractogram (XRD) and scanning electron microscopy (SEM) were employed. It showed that the XRD results of all samples were in an agreement with the standard patterns. It also confirmed that BMW crystallized in a cubic structure (space group *Fm-3m (225)*), while LMT possessed an orthorhombic structure (space group *Pbnm (62)*).

The spectroscopic properties of all samples were investigated via the absorption, excitation, and emission spectra over a wide temperature range from 80 K to 600 K. The luminescent dynamics were verified using Inokuti-Hirayama's model. In addition, the Judd-

Ofelt parameters were calculated for Eu^{3+}. The optical analysis showed that the obtained materials were not only effectively excited by the UV radiation (266 nm) via the hosts but also through the typical *4f-4f* transitions of the activators.

Moreover, the optimal concentration of dopants exhibiting the most intense emission was determined. Besides, the thermal stability of representative samples was evaluated and quenching temperature of the luminescence was also verified. The cause of the thermal quenching phenomenon was clarified and the energy transfer efficiency from the host to the dopants was estimated. The prominent interaction between ions involved in concentration quenching was also investigated.

The chromaticity coordinates of the emitted light of BMW:Er^{3+} samples were presented on the chromaticity diagram CIE 1931. Based on thermally coupled levels, uncoupled levels and the relation between the host and the dopant’s emission, the suitability of all samples for temperature sensing was verified.

During the investigation, many intriguing findings have been found. The first observation was the unique emission spectrum of Eu^{3+} incorporated in BMW matrix. The spectrum was characterized by the dominance of the magnetic-dipole transition associated with the vibronic lines due to the substitution of Eu^{3+} in the highly symmetrical octahedral site of Mg^{2+}.

Another interesting observation was the asymmetric shape of the BMW emission band resulting from the presence of regular and irregular WO_6 groups. Interestingly, their emission intensity ratio was changed as a function of temperature and strongly affected by the synthesis method. In case of the sample prepared by the mechano-chemical method, only the emission of the irregular group appeared in the spectrum at room temperature. To explain the above-observed phenomenon, the energy scheme was constructed with the corrected energy position of the regular and the irregular WO_6 groups, as well as the Eu^{3+} energy levels. The influence of the distinct synthesis method on morphology, grain size, energy transfer process and thermal sensing performance of BMW doped with Eu^{3+} was explored.

Furthermore, since thermalization process of the higher ion levels of Nd^{3+} and Er^{3+} ions in the analyzed materials occurred, their uncoupled and thermally coupled energy levels were applied for designing optical thermometers. The obtained relative sensitivities of 0.83%K^{-1} for LMT:Nd^{3+}, 2.98%K^{-1} for LMT:Er^{3+}, and 2.78%K^{-1} for BMW:Er^{3+} demonstrated the application potential of the tested compounds in the field of optical thermometry.

My dissertation is a collection of 6 articles published in high-impact factor scientific journals. These journals possess high scores as well according to the evaluation of the Minister of Education and Science. The dissertation consists of 8 chapters:

- **The first chapter** is an introduction that clarifies the general state of the art of perovskite/double perovskite materials. The main goal of the dissertation was also defined there.
- **The second chapter** is a theoretical part which lays out the lanthanide ions and the spectroscopic properties of selected dopants are presented, as well as Judd-Ofelt's theory, energy transfer and Inokuti-Hirayama's model. The structure of the studied hosts, methods of obtaining luminescent materials and the basic assumptions of luminescence thermometry were also described.
- **The third chapter** is an experimental part including precursors, sample preparation, and measurements.
- **The fourth chapter** presents the most important results with regard to 6 scientific publications including the author's contribution declaration, copies of publications and supporting files.
- **The fifth chapter** is conclusions.
- **The sixth chapter** is about the scientific achievements of the author during the PhD program.
- **The seventh chapter** is bibliography.
- **The last chapter** is copies of the co-authors' contribution statements.