Energy structure and spectroscopic properties of $3d^3$ ions (Cr^{3+}, Mn^{4+}) in crystalline matrices under extreme conditions

The proposed project is aimed at thorough and detailed investigations of the emission properties (both experimental and theoretical) of crystalline materials, in which a small fraction – about 1-2 % - of the host positively charged ions is replaced either by the Mn^{4+} or Cr^{3+} ions. Such materials, e.g. Cs_2GeF_6, $LaAlO_3$, $ZnGa_2O_4$ etc with the above-mentioned impurities are of paramount importance for various optical applications, such as solid-state lighting and optical thermometry. Nowadays the problem of development of white light-emitting diodes (LEDs) producing "warm" white light is very urgent. Most of the modern white LEDs are based on a combination of a blue LED and yellow phosphor. Such a combination produces "cold" white light because of absence of the red-emitting part of the LEDs. Therefore, an intensive search is being conducted now all over the world to find a proper red-emitting phosphor. The crystalline powders with the Mn^{4+} ions are very promising candidates for this role. In view of this, we plan to synthesize large groups of isostructural materials doped with the Mn^{4+} ions, such as perovskites, double perovskites, fluorides, oxyfluorides etc., with varying cation composition. Their spectroscopic properties under ambient and elevated hydrostatic pressure will be studied in detail in a wide range of temperatures relevant for the LEDs applications. The materials with the best performance – such as the brightness of the Mn^{4+} ions red emission, its wavelength, lifetimes etc. – will be identified. Spectroscopy at elevated pressure will help in understanding of the structural and electronic properties of these materials. Theoretical calculations of the electronic and optical properties of these compounds will be performed. They will aid in understanding of the experimental results and will help to find proper compounds by means of a scrutinized screening of large arrays of the experimental data with an aim of finding the so-called "structure-property" and "property-property" relations with predictive power.

Speaking about the optical thermometry – it is a rapidly developing area, which is very important for biological applications, since it is a non-invasive method that can be used to determine the temperature inside living bodies. The method is based on the variation of the ratio of characteristic emission peaks with temperature, or on the variation of the excited states lifetimes with temperature. The Cr^{3+} ions are excellent candidates for such thermometric probes, since their emission spectra in solids with the so called medium crystal field consist of a combination of the spin-allowed and spin-forbidden transitions, whose intensity depend on temperature. We plan to investigate from the fundamental point of view what are the main reasons that identify the intensity of these transitions and the limits of intensity variation, and this research will include the synthesis routes, spectroscopy at normal and elevated pressure and combined crystal field and density functional theory calculations of a wide range of physical properties of these compounds.

The project foresees unique combination of the experimental and theoretical activities and comprise efforts and expertise of three top-level research groups in Poland, which are also highly competitive and well-known worldwide. These groups are: theoretical group from Jan Dlugosz University (Prof. M.G. Brik, head of the project, responsible for the theoretical calculations of the electronic, structural and optical properties of all studied compounds) and two experimental groups: from Gdansk University (Prof. M.Grinberg, responsible for the high-pressure spectroscopy) and from Wroclaw University (Prof. E. Zych, responsible for the synthesis and ambient pressure spectroscopy). Experimental and theoretical skills and facilities of these groups, together with already existing long and productive cooperation between them, makes a firm basis for a synergetic development leading the overall success of the project.

It is hoped that project will bring a new fundamental knowledge about interactions between impurity ions and host ions, which will enhance our understanding of the performance of the phosphor and thermometric materials. It will have a profound positive impact on the development of fundamental and applied science (such as physics, chemistry, materials science, quantum chemical calculations etc.) in Poland by means of creation of new PhD and postdoctoral positions for young researchers, their active involvement into world-class research with pronounced international cooperation and promotion of Polish science through publications in the top-journals and participation in prestigious international conference.