Project: **INFRARED-INFRARED AND INFRARED-ULTRAVIOLET UPCONVERSION PROCESSES IN RARE EARTH DOPED PHOSPHORS**
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Phosphors are defined as the materials (usually crystalline powders) which emit visible light under an external (pump) excitation: electromagnetic radiation (X, UV, VIS, IR), electron beams etc. In most situations, the energy of incident particles (photons, electrons) is higher than the energy of the emitted photons. For *upconversion phosphors* (pumped in IR, emitting in IR but at a shorter wavelength, visible or UV) the energy of the emitted photons is higher than the energy of the pump photons. The phosphors are composed from the host material (usually, crystalline) and the activators (transition elements or lanthanides). The excitation of luminescence can be performed directly in the activator absorption bands or, indirectly, when the host or a sensitizer absorbs the pump radiation and transfers excitation to the activator. The phosphors are inorganic (most of them) or organic materials.

The aim of this project is the synthesis and characterization of rare-earth doped upconversion phosphors pumped in IR at 940-980 nm (where cheap and high-powered InGaAs laser diodes exists) emitting in near IR (NIR) at 730-850 nm, visible an UV. Due to the superior penetration depth of IR (0.8-1 μm) radiation in biological tissues, the IR-NIR phosphors can be used as biomarkers observable deep in the tissue. In the NIR domain, cheap and sensitive detectors and cameras exist. Given the small penetration depth of the UV radiation in biological tissues or in turbid media, the IR-UV phosphors produce UV radiation deep inside the material, with applications in biology, medicine and treatment of wastewater. Even if the efficiency of such a multistep (at least, third order) process is low; the otherwise small penetration depth of UV radiation in biologic tissues or turbid media makes the IR-UV upconversion process competitive. Besides, irradiation of the biologic tissues with UV light would be very harmful.

The energy level schemes of Er^{3+}, Tm^{3+} and Ho^{3+} ions present multiple resonances between the energy levels, being very convenient for upconversion processes (excited-state absorption - ESA or energy transfer), but present narrow absorption lines. In order to improve the efficiency of the “compteur quantique”, Auzel introduced in 1966 Yb^{3+} as sensitizer for Er^{3+}. Since then, Yb^{3+} was used as sensitizer for Er^{3+}, Tm^{3+} and Ho^{3+}. Yb^{3+} has a very simple energy level scheme (only two levels, $^2F_{7/2}$ (ground) and $^2F_{5/2}$) and intense and broad absorption band in IR (~ 940 – 980 nm) and transfers very efficiently the excitation to Er^{3+} (resonant transfer) or Tm^{3+}, Ho^{3+} (phonon-assisted transfer). Er^{3+}, Tm^{3+} and Ho^{3+} emit in NIR, visible and UV. Depending on the host, the efficiency in the various spectral domains can be different. Since the energy gaps between the emitting levels and the next lower energy ones are usually rather small, hosts characterized by low energy phonons are preferred.

The main objective of this project is the finding of the optimal compositions of phosphors (host + dopants) excited in IR (940-980 nm) and emitting in NIR or UV (and, also, in visible) for specific applications in biology, medicine and purification of the wastewaters.

The methods of synthesis used are sol-gel (including Pechini) and solid-state synthesis. For structural characterization: XRD, FTIR, and, when necessary, electron microscopy are used; various spectroscopic techniques (absorption, fluorescence and excitation spectra, kinetics of the metastable levels) are used to find the spectroscopic parameters of the investigated materials. Based on the results of our measurements (as well as on the available data in literature) the energy transfer processes which control the population and de-excitation paths of the emitting levels are investigated.

OBJECTIVES

The main objective of this project is the finding of the optimal compositions of phosphors (host + dopants) excited in IR (940 - 980 nm) and emitting in NIR or UV for specific applications in biology, medicine and purification of the wastewaters.

2012 / Objective 1: Synthesis and characterization of phosphors doped with erbium and ytterbium.
2013 / Objective 2: Synthesis and characterization of phosphors doped with thulium and ytterbium.
2014 / Objective 3a: Synthesis and structural investigations of phosphors doped with holmium and ytterbium.
2015 / Objective 3b. Investigation of the emission properties of phosphors doped with holmium and ytterbium.

MAIN RESULTS

- Synthesis, using a modified Pechini sol-gel route, of langasite ($La_3Ga_5SiO_{14}$) nano-powders doped with Er^{3+} and Yb^{3+} or with Eu^{3+}. Using the solid-state synthesis, ceramic samples of langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) and langanite ($La_3Ga_{5.5}Nb_{0.5}O_{14}$) doped with Er^{3+} and Yb^{3+}, or with Tm^{3+} and Yb^{3+} with low concentration of color centers, were obtained. The samples were characterized by XRD and optical spectroscopy.

- Synthesis, using the solid-state reaction, of a new and efficient oxide compound $CaSc_2O_4$ doped with Ho^{3+} and Yb^{3+}, Tm^{3+} and Yb^{3+} and Er^{3+} and Yb^{3+}. This compound is characterized by low energy phonons and strong crystal field at rare-earth ion position.

- For each material, the energy transfer processes leading to upconversion emission are put in evidence. Thus, for the green emssion of Er^{3+} (transition $^2H_{11/2},^4S_{3/2} \rightarrow {}^4I_{15/2}$) and of Ho^{3+} ($^5S_2,^5F_4 \rightarrow {}^5I_8$) two steps are necessary while, for the blue emission of Tm^{3+} ($^1G_4 \rightarrow {}^3H_6$), three steps are necessary.

- Study of the energy transfer between Tm^{3+} ions in langatate; the microparameters C_{da} and C_{dd} were determined.

- Extension of the Judd-Ofelt analysis to ceramic samples doped cu Er^{3+}, Tm^{3+} and Ho^{3+}. These samples scatter the transmitted light. The absorption spectra are calibrated using the intensity of a magnetic-dipole transition ($^3H_6 \rightarrow {}^3H_5$, Tm^{3+}) or the lifetime of an energy level decaying radiatively ($^4I_{13/2}$ for Er^{3+} or $^5I_7$ for Ho^{3+}). The quantum efficiency of various emitting levels can be now determined. The possible errors produced by the light scattering on the values of the Judd-Ofelt parameters were evidenced.

- Study of the energy transfer between Ho^{3+} and Yb^{3+} in $CaSc_2O_4$; we found that the total number of photons emitted by Ho^{3+} and Yb^{3+} in the wavelength domain 500–1600 nm is augmented by the presence of Yb^{3+} (~30%).

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