

AN ABSTRACT OF DOCTORAL DISSERTATION

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„The influence of composition and chemical architecture on luminescent properties of colloidal NaYF₄ codoped with lanthanide ions”

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Nano-sized inorganic crystals activated with lanthanide ions have attracted great interest in recent years. They show the upconversion (UC) phenomenon, in which after absorption of the photons of excitation radiation in the near infrared (NIR) range by Yb³⁺ ions and as a result of Energy Transfer upconversion (ETU) to the activator ions (e.g. Er³⁺, Tm³⁺, Ho³⁺) the emission of photons with higher energy than the energy of the excitation photons occurs. Due to their specific properties (i.e. narrow emission bands, long luminescence life times, high photochemical stability), upconverting materials can be applied in medicine, biology or technology. However, despite many advantages and significant potential, their practical use has so far been limited. Unfortunately, these materials are characterized by low quantum yield due to the forbidden nature of f-f lanthanide transitions, which results in low absorption and emission cross-sections. Quite low quantum efficiency is also related to the size of crystallites, as on the nano scale, the surface to volume ratio increases significantly, which means that a large portion of the activator ions (lanthanides) stay at the surface on nanoparticle, where nonradiative energy quenching by ligand and solvent phonons occurs. Due to these limitations, scientist are still trying to find luminescent materials based on lanthanide compounds, in which these 'parasitic' effects will be minimized. Several methods to increase the emission intensity and UC quantum yield can be found in the literature. For example, by optimizing the concentration of active ions, selecting a proper matrix, co-doping with passive ions, and also using an undoped shell, which significantly reduces the influence of the environment on the emission intensity have been proposed. So far, the focus has been solely on passivation of the surface and the creation of a 'protective layer', however, the core-shell structures offer many more possibilities. By appropriately designing the material, it is possible to control the spectroscopic properties depending on the potential target applications. To achieve this, it is necessary to thoroughly understand the energy transfer processes taking place in core@shell materials. The research hypothesis put forward in the doctoral dissertation is: **the 'chemical**

architecture' of the material, i.e. the intentional distribution of dopant ions in various material coatings, will have a strong impact on the spectroscopic properties of the material, such as: quantum yield, lifetime or the ratio of the intensity of emission bands.

The research results have been included in four papers, published in international journals from the Philadelphia list. The doctoral dissertation was divided into four stages: (i) optimization of the core @ shell structure synthesis process (ii) examination of the influence of doping ions concentration on the up-conversion phenomenon (iii) examination of the influence of the chemical 'architecture' on the spectroscopic properties of core @ shell nanomaterials (iv) the effect of co-doping with Ce^{3+} ions on the spectroscopic properties of up-conversion materials based on the $NaYF_4$ matrix doped with Yb^{3+} and Ho^{3+} ions.

In the first step, the synthesis protocol of core@shell lanthanide ions doped with sodium yttrium fluoride was optimized. The materials were synthesized by thermal decomposition method in high-boiling solvents such as oleic acid and octadecene. Optimization of parameters such as temperature and reaction time allowed for the reproducible synthesis of core@ shell materials, in which the spherical core is about 20 nm in size and the shell thickness can be controlled from 2.5 to 20 nm (+/- 1 nm). The obtained materials demonstrated high homogeneity and a narrow size distribution.

In the second stage, the influence of the Ho^{3+} ion concentration on the efficiency of upconversion in the $NaYF_4$ doped Yb^{3+} , Ho^{3+} was analyzed. A series of $NaYF_4$ materials was synthesized with a constant concentration of Yb^{3+} ions amounting to 20 mol % and a variable concentration of Ho^{3+} ions (from 0.1 to 5 mol%). Based on the analysis of emission spectra obtained after 976 nm photoexcitation, decay curves and quantum yields, it was shown that the material doped with 20% Yb^{3+} and 2% Ho^{3+} was characterized by the most intense upconversion emission.

Then, the influence of the distribution of Yb^{3+} and Ho^{3+} ions in the layers of the material with the core@ shell structure on its spectroscopic properties was examined. The research carried out as part of the third stage included a detailed structural-morphological and spectroscopic analysis of a series of six $NaYF_4$ materials with a core@shell structure with a constant concentration of Yb^{3+} and Ho^{3+} ions (20 mol% and 2 mol%, respectively). The formation of core@shell structures was directly demonstrated, and parameters such as emission intensity, quantum yield, rise and decay time values were compared. The obtained results proved that all these parameters are closely related to the chemical 'architecture' of the composition of a given material. The analysis of these materials revealed the advantages and disadvantages of each of the synthesized 'combinations', which in turn allows to design

materials for specific applications. The resulting knowledge was used in a practical way to create a material that combined three properties: effective light to heat conversion, efficient emission in the NIR range, and the possibility of remote temperature sensing. The material $\text{NaNdF}_4 @ \text{NaYF}_4 @ \text{NaYF}_4: 1\% \text{Nd}^{3+}$ was synthesized, in which the core (NaNdF_4) allowed for absorption and light to heat conversion of radiation under 808 nm photoexcitation, and the $\text{NaYF}_4: 1\% \text{Nd}^{3+}$ shell was acting as a nanothermometer. The relaxation processes between Nd^{3+} ions serving as thermometers and Nd^{3+} ions serving as heaters were eliminated by the use of an internal passive (NaYF_4) intermediate shell.

In the fourth stage, the influence of Ce^{3+} co-doping of yttrium-sodium fluoride doped with Yb^{3+} and Ho^{3+} ions on its spectroscopic properties was investigated. Optically active ions participate in transfer processes and can radically change the luminescent properties of nanomaterials. To achieve this goal, a series of materials with a variable concentration of Ce^{3+} ions (0, 2, 5, 10, 15 mol%) was synthesized while maintaining a constant concentration of Yb^{3+} and Ho^{3+} ions of 20% and 2 mol%, respectively. Detailed spectroscopic analysis including the analysis of emission spectra, rise and decay times as a function of temperature showed that the introduction of Ce^{3+} ions changes the emission color of the $\text{NaYF}_4: \text{Yb}^{3+}, \text{Ho}^{3+}$ material and also allows it to be controlled by changing parameters such as power and duration of the excitation pulse.

The research carried out as part of this doctoral dissertation is part of the main global trends in basic research and applications of functional nanomaterials. Understanding the relationship between composition and spectroscopic properties is key to design materials capable to fulfill requirements of specific applications.