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Summary of the doctoral thesis

Synthesis and investigation of the up-conversion phenomenon in nanoparticles sensitized by Er^{3+} and Ho^{3+} ions

This doctoral thesis aimed to synthesize and investigate the up-conversion phenomenon in nanoparticles sensitized by Er^{3+} and Ho^{3+} ions. The appropriate parametrization and optimization of the synthesis method enabled obtaining nanoparticles with desired physio-chemical properties, such as a single-phase structure and small sizes. These characteristics render them promising for various applications, including biomedicine. The study of the up-conversion phenomenon in the prepared nanomaterials was based on observation of their luminescence under excitation with near-infrared (NIR) radiation. The nanoparticles were designed so that the mechanism of this phenomenon was based on the sensitization process by Er^{3+} and Ho^{3+} ions, providing an interesting alternative to commonly used up-converting systems based on sensitization by Yb^{3+} ions.

The first part of the dissertation focused on the theoretical aspects of the up-conversion phenomenon, which is a conversion of low-energy photons, usually from the NIR range to high-energy ones, from the ultraviolet (UV) to the visible (vis) range [1]. The up-conversion mechanisms were discussed, with a particular focus on the energy transfer up-conversion (ETU), in which one ion, called a sensitizer, absorbs energy, and transfers it to another ion, called an emitter, which emits absorbed energy [1,2]. The properties of lanthanide ions (Ln^{3+}), which play a crucial role in up-conversion processes, in connection with the specific electronic structure resulting from the 4f→4f electronic transitions, have been detail described [3-5]. The characteristics of up-converting nanoparticles were demonstrated, which properties, in particular optical ones, depend on their nanometric sizes [6]. The most important applications of up-converting materials were presented, especially in biology and medicine (tumor markers, bioimaging, and theranostics) [7-9].

The second part of the thesis discusses the synthesis and characterization methods of the obtained luminescent materials. Nanoparticles were synthesized by hydrothermal method and by coprecipitation in a high-boiling organic solvents method. Alkaline and rare earth fluorides (SrF_2, β-$NaYF_4$) were selected as matrices because of their relatively low phonon energies (~ 350 cm^{-1}), which reduce the multiphonon quenching processes [10]. Er^{3+} and Ho^{3+} ions, with

particularly suitable energy levels enabling efficient up-conversion phenomenon, were selected as dopant Ln^{3+} ions. In some samples containing only Ho^{3+} ions or both Ho^{3+} and Er^{3+} ions, nanoparticles with a core@shell structure were successfully synthesized, promoting the enhancement of the up-conversion processes [11]. The physicochemical properties of the prepared up-converting nanoparticles were analyzed using techniques such as X-ray diffraction (determination of the crystallographic structure), transmission electron microscopy (analysis of shape, size, and morphology), dynamic light scattering and zeta potential measurements (studies of the stability of the formed colloids) [12-14]. The up-conversion mechanisms responsible for the observed luminescence of the obtained nanoparticles were investigated using spectroscopic methods [15]. The emission spectra were registered in the vis and NIR range under the excitation at 975 and 1532 nm (Er^{3+} ions) as well as ~1155 nm (Ho^{3+} or Ho^{3+} and Er^{3+} ions). Moreover, for some nanoparticles, the dependencies of luminescence intensity on temperature were measured, and the quality of the obtained optical thermometers was determined using a ratiometric approach [16]. The numbers of photons involved in the up-conversion processes were concluded using the dependence of the sample emission intensity on the power/energy of the excitation radiation. Moreover, the luminescence lifetimes of selected excited states of Ho^{3+} and Er^{3+} ions were measured. Upon the obtained results, up-conversion mechanisms occurring in the prepared nanoparticles were proposed.

The third part of this work summarizes three published scientific articles on the up-conversion phenomenon in nanoparticles sensitized by Er^{3+} and Ho^{3+} ions. In the performed experiments, SrF_2 nanoparticles containing Er^{3+} (P1) or Ho^{3+} (P2) ions in various concentrations as well as core@shell β-$NaYF_4$ nanoparticles, with cores doped only with Ho^{3+} ions or both Ho^{3+} and Er^{3+} ions (P3), were obtained. The prepared nanoparticles were characterized by the desired single-phase structures, various (mainly oval) shapes, and small sizes, which were confirmed by the structural and morphological analyses. The spectroscopic analysis of the obtained samples allowed for the determination of up-conversion mechanisms.

SrF_2:Er^{3+} nanoparticles, excited by 975 and 1532 nm radiation, showed particularly intense luminescence in the NIR range. Therefore, a novel approach was proposed to determine thermometric parameters based on temperature-dependent changes in the emission intensities of 800 and 972 nm bands. The up-conversion mechanism of synthesized nanoparticles resulted mainly from excited state absorption (ESA) processes. However, it also underlined the contribution of the ETU, where Er^{3+} ions played the role of both a sensitizer and an emitter, indicating the self-sensitization phenomenon of Er^{3+} ions.

For the $SrF_2:Ho^{3+}$ nanoparticles irradiated at 1156 nm, the self-sensitization effect of Ho^{3+} ions was responsible for the intense red emission and NIR emission at 900 nm.

The luminescence of $NaYF_4:Ho^{3+}@NaYF_4$ nanoparticles caused by 1151 nm radiation was similar to that of $SrF_2:Ho^{3+}$ systems. However, in the case of the $NaYF_4:Ho^{3+},Er^{3+}@NaYF_4$ sample, the emission spectrum consisted of bands connected with the energy transitions of both Ho^{3+} and Er^{3+} ions, indicating that Ho^{3+} ions played the sensitizer role, transferring the energy to Er^{3+} ions, which were emitters of the absorbed energy. For both samples, opposite trends in temperature-dependent changes in the luminescence intensities were observed: as the temperature increased, the emission intensity of nanoparticles doped only with Ho^{3+} ions decreased, while the emission intensity of nanoparticles containing both Ho^{3+} and Er^{3+} ions increased, wherein this effect was more significant for the bands related to energy transitions of the Er^{3+} than Ho^{3+} ions. This system was characterized by a high value of the temperature relative sensitivity of 1.80%/K (378 K), calculated based on the temperature-dependent changes in the luminescence intensities of Ho^{3+} and Er^{3+} ions bands in the NIR range.

In the conducted research, the nanoparticles with the desired morphological and structural properties were successfully synthesized. The samples containing Er^{3+} and Ho^{3+} ions showed luminescence under the NIR radiation. The proposed up-conversion mechanisms, responsible for the observed emissions, were based mainly on the ETU processes between Er^{3+} or Ho^{3+} ions. The obtained samples are an interesting alternative to standard systems containing sensitizing Yb^{3+} ions due to the possibility of exciting and emitting in the range of biological windows. Moreover, thermometric properties based on the emission bands in the NIR range were determined for part of the prepared samples, which can contribute to the development of optical nanothermometry.