Study of energy transfer processes between the rare earth ions in tri-doped upconversion nanoparticles NaGdF$_4$:Yb-Er-Tm and NaGdF$_4$:Yb-Er-Ho

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The use of short-wave infrared region (SWIR), 1-2 μm spectral range, offers great opportunities for bioimaging due to higher penetration depth and reduced scattering of radiation in this range. One of the promising luminophores in this region are nanoparticles doped with rare-earth ions. They could be used for deep tissue layers visualization as well as thermal sensors operating in the SWIR region by the luminescence intensity ratio approach. However, the luminescence intensity strongly depends on the type and concentration ratio of the doping ions, as well as on the architecture of the core-shell nanoparticles.


• Luminescent thermometry with rare earth doped nanoparticles

• **Thermally coupled levels** of single rare earth ion could be used for temperature determination.
• According to Boltzmann distribution the ratio of luminescence intensity demonstrates exponential dependence on temperature.
• To obtain theoretical calibration curve the value of energy gap between thermally coupled levels should be known.

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\frac{I_2}{I_1} = \text{const} \cdot e^{-\frac{\Delta E}{k_B T}}
\]

\(\Delta E\) — energy gap between \(^3\text{F}_2\) and \(^3\text{F}_3\) states
\(k_B\) — Boltzmann constant
\(T\) — temperature

• **Temperature dependent energy transfer** between two rare earth ions (phonon assisted energy transfer, \(\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}\)) could be used for temperature determination.
• Resonance energy transfer (\(\text{Yb}^{3+} \rightarrow \text{Er}^{3+}\)) is used as reference signal.
• Main goal

- This work was devoted to the study of energy transfer processes between the rare earth ions in NaGdF$_4$ nanoparticles doped with rare-earth ions Yb$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, Er$^{3+}$
Materials and methods

- The study of the effect of the doping concentration, the shell thickness and the architecture of the core-shell nanoparticles on the luminescence characteristics and thermal sensitivity of the synthesized nanoparticles was performed.

- The luminescence spectra in 1000-1700 nm region were measured using an optical fiber spectrometer DWARF-Star (StellarNet, USA).

- Temperature control was performed using a thermometric infrared camera JADE MWIR SC7300M (CEDIP, France), synchronized with the spectrometer for the simultaneous measurement of the luminescence spectrum and the sample temperature.
Synthesis and characterization

Synthesis of Yb-Er-Tm and Yb-Er-Ho tridoped NaGdF$_4$ core-shell nanoparticles was performed by solvothermal technique in Laboratory of Technology of Nanomaterials for Photonics in GPI RAS (V.Yu. Proydakova, S.V. Kuznetsov, P.P. Fedorov).

According to XRD, the synthesized samples were a pure hexagonal phase. The sample consisted of particles with obvious core-shell architecture with semi-spherical morphology.

**XRD technique:**
D8 Bruker® Advance diffractometer with Cu-Kα radiation, Powder 2.0 software (Laboratory of Inorganic Crystallochemistry, MSU by Oleynikov Peter)

**TEM:**
Libra 200 FE microscope, Carl Zeiss AG, Oberkochen, Germany with ImageJ software (Uvarov O.V.)
Luminescence spectra in SWIR range:

Synthesized nanoparticles demonstrated 1050 nm (Yb$^{3+}$), 1150 nm (Ho$^{3+}$), 1550 nm (Er$^{3+}$), 1480 nm, and 1620 nm (Tm$^{3+}$) luminescence bands in SWIR range.

- NaGdF$_4$:Yb$^{3+}$, Ho$^{3+}$, Er$^{3+}$ NPs - Er$^{3+}$ → Ho$^{3+}$ energy transfer leads to Ho$^{3+}$ luminescence increase.
- NaGdF$_4$:Yb$^{3+}$, Tm$^{3+}$, Er$^{3+}$ NPs - Tm$^{3+}$ → Er$^{3+}$ energy transfer leads to Tm$^{3+}$ luminescence increase. Difficult to separate peaks.
- NaYF$_4$ passive shell leads to more uniform increase in the luminescence of both ions.

The NaGdF$_4$:Yb$^{3+}$, Ho$^{3+}$, Er$^{3+}$@NaYF$_4$ nanoparticles with 20:3:0.5 concentration ratio were chosen for experiments.
Luminescence spectra in SWIR in water

- All samples emit the characteristic Ho$^{3+}$ and Er$^{3+}$ luminescence at 1150 nm ($^5I_6 \rightarrow ^5I_8$) and 1550 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$) with no evident change in the band position.

- The emission intensity is strongly dependent on the interaction with the surrounding medium and decreases in water.

- Passive shell effectively prevents the quenching of their luminescence in media: the integral luminescence intensity in 1050-1600 nm region decreased 5-fold for core-shell NPs compared to 14-fold for core-only NPs.

- This phenomenon is well known and could be explained by the quenching of surface ions luminescence by high vibrational energy ligands in the surrounding medium or surface defects.

- The non-radiative losses mainly affect the sensitizer (Yb$^{3+}$) and, therefore, suppress the Ho$^{3+}$ and Er$^{3+}$ emission.
- Ho$^{3+}$ emission increases with the increase in temperature.

- Yb$^{3+} \rightarrow$ Ho$^{3+}$ the energy transfer is facilitated by the phonon-assisted processes, where the energy mismatch is compensated by simultaneous emission or absorption of one or more phonons by the host lattice. Phonon-assisted energy transfer is temperature-dependent, the Ho$^{3+}$ emission tends to increase with the increased temperature.

- The Yb$^{3+} \rightarrow$ Er$^{3+}$ energy transfer is resonant, so the temperature change does not affect the Er$^{3+}$ emission.

- The temperature-dependent changes in the luminescence spectrum of the core nanoparticles were negligible and difficult to detect due to the low intensity of the characteristic Ho$^{3+}$ peak at 1150 nm wavelength.
Thank you for your attention!

The research was carried out within the state assignment of fundamental scientific research for state academies of sciences for 2013-2021 (theme “Physical methods in medicine and biology” No. 0024-2019-0003).