Ion–ion interactions in \( \beta\)-NaGdF\(_4\):Yb\(^{3+},\) Er\(^{3+} \) nanocrystals – the effect of ion concentration and their clustering†

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In this work we report co-thermolysis as a suitable method for nanomaterial synthesis which allows the creation of hexagonal upconverting nanocrystals, NaGdF\(_4\):Yb\(^{3+},\)Er\(^{3+} \), in a wide range of sizes (20–120 nm). Only a very high Yb\(^{3+} \) concentration (above 70%) results in pure cubic-phase nanocrystals with irregular shape. Additionally, we showed that the impact of Yb\(^{3+} \), Er\(^{3+} \) and Gd\(^{3+} \) ions on the size and optical properties of nanocrystals is significant. We found that the main changes in optical properties do not depend on the nanocrystal size mostly, but are determined by the ion–ion interactions which include both Er\(^{3+}–\)Er\(^{3+} \) and Er\(^{3+}–\)Yb\(^{3+} \) cross relaxation.

Introduction

Colloidal nanocrystals (NCs) are of great fundamental and technical interest, due to their unique optical and magnetic properties and their potential applications in medicine. In particular, rare earth-doped fluoride nanocrystals (RENCs) are considered as promising tools for non-invasive in vivo and in vitro multimodal imaging of upconverted emission combined with X-ray computed tomography (CT),\(^1–3\) magnetic resonance imaging (MRI),\(^4–8\) single-photon emission computed tomography (SPECT) and positron emission tomography (PET) imaging.\(^9–11\)

Most of the lanthanide ions have to be excited in the ultraviolet and blue spectral region. However, high energy photons cause optical photodamage of biological tissue and give rise to undesirable autofluorescence signals from fluorophores placed in the human body.\(^12\) To overcome these obstacles an unique upconversion (UPC) process can be applied. In this process, visible emissions are generated after the near-infrared (NIR) excitation of the lanthanide-doped material. This NIR excitation with a large anti-Stokes shift, a sharp emission bandwidth, a long fluorescence lifetime, tunable emission, and low-power excitation (compared to two-photon absorption and SHG generation) constitute important advantages of these RENCs and allow for more straightforward signal detection.\(^13\)

Additionally, deep light penetration,\(^14\) suppressed autofluorescence, lack of photobleaching and photoblinking\(^15\) and a low phototoxicity\(^16\) make upconverting, fluoride RENCs suitable for in vitro and in vivo imaging.\(^4,6,13\)

Rare earth ions are generally characterized by a low absorption cross-section (~\(10^{-21} \) cm\(^2\)), however some of them possess a significantly higher absorption cross-section,\(^17\) for example the Yb\(^{3+} \) (1.16 \(\times\) \(10^{-20} \) cm\(^2\)) ion which, in addition, has a very simple energy level scheme.\(^17\) Its \(^2\)F\(_{7/2}–^2\)F\(_{5/2} \) transition is well resonant with f–f transitions of a few lanthanide ions (Er\(^{3+}, \) Tm\(^{3+} \) and Ho\(^{3+} \)), that is why these elements constitute the most efficient upconverting activators. In cubic sodium rare earth fluoride systems (NaREF\(_4\)) fluorite structures (CaF\(_2\)) are formed and they contain one type of high-symmetry cation site randomly occupied by Na\(^+ \) and RE\(^{3+} \) ions. In the hexagonal phase of NaREF\(_4\), an ordered array of F\(^–\) ions with two types of relatively low-symmetry cation sites selectively occupied by Na\(^+ \) and RE\(^{3+} \) ions is present.\(^18\)

Despite using the most efficient upconverting activators, efficient coupling between lanthanide ions becomes a key issue in order to obtain an intense emission. Additionally, when the crystal size is reduced to the nanoscale, the UPC efficiency is reduced because of the presence of different surface quenching sites (surface defects, additional ions, ligands, and solvent molecules).\(^19,20\) Thus, the best UPC quantum yield emission ranges between 2 and 5% and is reduced significantly for RENCs below 10 nm.\(^21,22\) This small quantum efficiency can be an effect of the nonhomogeneous distribution of lanthanide ions or their not optimal relative concentration and in consequence creation of Er\(^{3+} \) and Yb\(^{3+} \) clusters responsible for emission quenching, i.e. via the energy migration to the surface.\(^23\) Moreover, there is no discussion in
the literature from which sizes of nanocrystals, and the surface effects become significant and visible in optical measurements. For these nanoparticles shell protection indeed should significantly increase the emission intensity.

Most of the reported results are obtained for RENCs with a size between 20 and 50 nm (ref. 24–27) and only a few groups synthesized UPC RENCs with a size smaller than 15 nm.28–30 Small size in biomedical applications is required because of the possibility of using a higher dose of imaging agents and controlled body clearance.31 Thus, despite recent progress in the synthesis of sub-15 nm and monodisperse RENCs, efficient near-infrared to visible (NIR-to-Vis) energy transfer and intense emission still remain major challenges. This is because the size of the RENCs and the intensity of UPC emission are, in general, dependent parameters. Therefore, it is important to understand the mechanism of ion–ion interactions in RENCs of different sizes to maintain good optical properties regardless of their size. It is also important to investigate the ion–ion coupling efficiency, which can be done by detailed analysis of the NIR spectral range. Such kinds of results have not been widely reported so far.

Another important challenge in this research is to control the size of RENCs in a wide range, maintaining the narrow size distribution and β-phase, which is suitable for high quality optical markers. These features can be controlled using various synthesis parameters: temperature,32 ligand to solvent ratio,30 and alkaline earth metal doping.33 Moreover, different concentrations of lanthanide ions can result in various morphologies and sizes of the obtained RENCs.34

It has been shown that Gd3+ ions concentration can influence the fundamental nucleation and growth process of NaYF4 RENCs during hydrothermal synthesis, what results in tuning their size.35 Similar results were obtained by Li et al.27 who synthesized various kinds of fluoride RENCs using the co-thermolysis method and confirmed that the formation of monodisperse RENCs closely correlates with the inherent nature of lanthanide series from lanthanum (La3+) to lutetium (Lu3+). Smaller ionic radius of the dopant resulted in the formation of bigger RENCs. The effect of doping was theoretically explained by Wang et al.18 who used first-principles calculations to confirm that the influence of lanthanide doping on the crystal phase and size arises from the strong dependence on the size and dipole polarizability of the substitution dopant ion. Recently Damasco et al.26 have shown that introduction of Gd3+ ions to the NaYbF4 matrix can induce a significant decrease in the size of the nanoparticles. Low concentrations of Gd3+ ions in the crystal matrix caused the formation of big (above 100 nm) RENCs, while high concentrations allowed us to obtain small RENCs. Such phenomena were ascribed to the change of the surface charge density. A larger radius of Gd3+ ions (r = 93.5 pm) leads to a less electropositive surface in comparison with the smaller Yb3+ ions (r = 86.8 pm).26,36 This decreases the diffusion rate of the F− ions to the surface of RENCs and thus limits particle growth. Because of the correlation between the RENC size and the dopant concentration it is difficult to judge which of these factors has a dominant influence on the optical properties.

Herein, we present the results of NaGdF4:Yb3+,Er3+ RENC synthesis with various concentrations of dopant ions. Strong correlation between the concentration of dopants (Yb3+, Er3+, and Gd3+ ions) and the size of the obtained RENCs is observed. The UPC photoluminescence (PL) intensities and lifetimes of the resulting RENCs were studied and analysed in relation to their size and ion concentration. Based on optical spectroscopy and numerical simulation the ion–ion interactions have been discussed.

Experimental details

Synthesis of core nanocrystals

The applied synthetic method of β-NaGdF4:Yb3+,Er3+ RENCs was similar to the single step co-thermolysis method presented in our previous paper.37 Sodium trifluoroacetate Na(CF3COO) (98%), ytterbium(III) trifluoroacetate hydrate Yb(CF3COO)3·3H2O (99%), gadolinium oxide Gd2O3, erbium oxide Er2O3, trifluoroacetic acid CF3COOH, 1-octadecene ODE and oleic acid OA were purchased from Sigma Aldrich and used as received without further purification. Gd2O3 and Er2O3 were dissolved in trifluoroacetic acid. Appropriate amounts of precursors: 1.0 mmol of Na(CF3COO)3, 0.4 mmol of lanthanides [Gd(CF3COO)3, Yb(CF3COO)3, Er(NO3)3] were prepared in a three necked flask.

For RENC synthesis, a precursor mixture of an appropriate lanthanide composition was added to 5 ml of OA and 5 ml of ODE and was degassed at 120 °C while being stirred. After 60 min the reaction was purged with N2 and the temperature was increased to 300 °C. After 60 min the reaction was cooled to 70 °C and excess acetone was added to precipitate the nanoparticles. The resulting material was collected by centrifugation and excess OA and ODE were removed by washing with acetone several times and finally the material was redispersed in 4 ml of cyclohexane.

Synthesis of core/shell nanocrystals

0.25 mmol of Na(CF3COO) (98%), 0.1 mmol of gadolinium trifluoroacetate Gd(CF3COO)3 (98%) and 1 ml of the previously synthesized core RENCs were added to 5 ml of OA and 5 ml of ODE and this was degassed at 120 °C while being stirred. After 60 min the reaction was cooled to 70 °C and excess acetone was added to precipitate the nanoparticles. The resulting core/shell RENCs were collected by centrifugation and excess OA and ODE were removed by washing with acetone several times and finally this was redispersed in 1 ml of cyclohexane.

Structural and optical characterisation

Samples for the TEM experiments were prepared by evaporating a dilute cyclohexane solution of the nanoparticles onto carbon coated copper grids and a FEI Tecnai G2 20 X-TWIN microscope equipped with an energy-dispersive X-ray micro-
analyzer was used to obtain the TEM images and EDXS spectra of the nanoparticles. X-ray powder diffraction patterns were obtained using a Philips diffractometer supported by a parallel beam optic and CuKα1 radiation source, λ = 0.15406 nm.

**Optical measurements**

For steady state PL as an excitation source, a 980 nm laser (Shanghai Dream Lasers Technology SDL-980-LM-1000T) was used. A HR4000 spectrometer (Ocean Optics, Dunedin, FL, USA) and an InGaAs linear CCD detector (Symphony® I line, Horiba Jobin-Yvon) were used as detection systems for measurements in the Vis and NIR spectral range, respectively. The PL decays were measured using a pulsed laser (Opolette™, Opotek Inc., Carlsbad, CA, USA) coupled to a gated detection system.

**Results and discussion**

**Structural results**

In order to check the effect of dopant concentration on the size and morphology of RENCs, we prepared two sets of samples: the first set with the Er3+ concentration equal to 5% and the Yb3+ concentration ranging from 10 to 70% and the second set with a constant Yb3+ concentration (20%) and Er3+ concentration ranging from 1 to 70%. Also two samples NaErF4 and NaYbF4 were prepared (as the references).

All the synthesized RENCs show well-defined peaks in diffraction patterns, confirming their good crystallinity. The positions of diffraction peaks of RENCs were consistent with reference patterns of hexagonal (ICDD no: 27-0699) or cubic (ICDD no: 27-0697) NaGdF4 crystals (Fig. 1(a) and 1S†). Hexagonal crystalline structures were determined for almost all the synthesized RENCs. The only exception was observed for the sample with an exceptionally high Yb3+ concentration (above 70%), where a mixture of cubic and hexagonal phases was determined. Similar results were obtained by Wang et al.18 and Damasco et al.26 The smaller radius of heavy lanthanides makes them less polarizable and less favourable for electron cloud distortion. Doping of heavier lanthanides into the host lattice can therefore result in preventing the α → β phase transition.26

The additional proof of hexagonal phase formation is the high resolution TEM (HRTEM) image presented in Fig. 1(b) showing a lattice distance of 0.532 nm, corresponding to the d spacing for the {100} lattice plane in the hexagonal NaGdF4 structure.

For low Yb3+ ion concentrations in the NaGdF4 matrix, small (~20 nm) RENCs were obtained and with increasing Yb3+ ion concentration the formation of bigger crystals is observed (Fig. 2(a, b) and 2S†). A significant increase of RENC diameter is observed for the Yb3+ ion concentration above 20% and above 50% stabilization of the RENC size takes place (Fig. 3(h)).

Additionally, for higher Yb3+ concentration (70%) two distributions of RENC sizes are observed (20 and 120 nm), which may indicate crystallization of RENCs in two different crystal phases (Fig. 2S†). A higher increment of Yb3+ ion concentration till 100% [NaYbF4] resulted in small (~20 nm) RENCs in the pure α-phase.

A similar effect of dopant on the size and phase of RENCs was observed for increasing concentration of Er3+ (Fig. 2(c, d) and 3S†). In this case the strong influence of Er3+ ions on the RENC size is visible above 50% of Er3+ concentration, while below this value the size of RENCs is almost unchanged (Fig. 3(d)).

Change of the dopant concentration affects the RENC surface charge, which may result in an increased or decreased diffusion rate of negatively charged F− ions to the surface. This thesis based on density functional theory calculations was proposed by Wang18 and it refers to different ionic sizes of dopants. The high concentration of Yb3+ and Er3+ ions in the crystal matrix caused the formation of big (above 100 nm)
RENCs (except for pure NaYbF₄ RENCs), while the low concentration allowed us to obtain small RENCs. Because the ionic radius of Er³⁺ (89.0 pm) is closer to the ionic radius of Gd³⁺ (93.5 pm) than Yb³⁺ (86.8 pm), changes in the size of RENCs start to be visible for higher concentrations of Er³⁺ ions (above 50%) (Fig. 3(d)) while for Yb³⁺ ions concentration they are already visible above 20% (Fig. 3(h)).

Moreover, the shape of big RENCs (with high Yb³⁺ or Er³⁺ concentrations) is more like hexagonal flakes (Fig. 2S and 3S†).

These NaGdF₄ RENCs show a preferred growth direction along [0001] and are enclosed by the {10-10} and {0001} facets. Therefore, it can be concluded that the growth rate on the six lateral faces of the RENCs is faster than that along the [0001] direction with increasing RENC size.

In summary, in the case of our RENCs the dopant concentration affects weakly on phase of RENCs. Only for very high Yb³⁺ concentrations RENCs remained in the α-phase (α → β phase transition did not occur). On the other hand, the impact of Yb³⁺ ion concentration on the size of RENCs is strongly prominent in the entire range of Yb³⁺ concentrations, while for Er³⁺ ions it is visible at above 50% of Er³⁺ ion concentration.

**Optical results**

In fluoride RENCs, the lanthanide ions take at least two significantly different positions: as surface ions (REₛ) or volume ions (REᵥ). We have already shown that for β-NaYF₄:Eu³⁺ RENCs, the excitation, emission and even the relaxation mechanisms for the surface and volume sites are different. This is due to differences in the local environment (strength and symmetry of the local crystal field, local vibronic properties or surface chemistry).†

The phonon energies available for electrons in the excited states of Er³⁺ ions located inside the core (320 cm⁻¹) are smaller than in the case of ions placed at the RENC surface. This is mainly because of the lower coordination number of atoms at the RENC surface and the presence of ligands (i.e. OH ≈ 3700 cm⁻¹ or CH₃ ≈ 3000 cm⁻¹) in the close vicinity of the ions. In consequence, depopulation of higher energy levels of Er³⁺ ions (²H₁₁/₂, ⁴S₃/₂), responsible for the green emission, should be less probable in the case of REᵥ (the energy difference between ²S₃/₂ and ⁴F₉/₂ states is 3035 cm⁻¹, which corresponds to ~9 phonons) thus green light due to (²H₁₁/₂ + ⁴S₃/₂) → ⁴I₁₃/₂ transitions should dominate the spectrum. In contrast, excited REₛ ions can efficiently relax non-radiatively to the “red emitting” (⁴F₉/₂) state, because only 1–2 high energy phonons are required to depopulate ⁴H₁₁/₂ and ⁴S₃/₂ states. Thus, the dominating emission band should be the red one. Moreover, in this case the ions easily relax non-radiatively further from ⁴F₉/₂ down to the ⁴I₁₃/₂ level increasing the emission at 1550 nm. In consequence, the emission from REₛ is
spectrally more diffused, which makes emission intensities from individual states lower. Thus, the ratios of green-to-red (G/R) and green-to-NIR (G/NIR) emission intensities are lower for surface ions as compared to volume ions. Assuming homogeneous dopant distribution within the entire RENC and from the fact that carrier relaxation depends on the ion position (surface or volume) these ratios should depend on the RENC size as well. When the surface-to-volume ratio decreases the number of surface and volume ions is changed. Thus, in any case of macroscopic measurements we have always a superposition of signals coming from the ions placed at the two sites: RE$_S$ and RE$_V$. For the smallest RENCs, the dominating emission should be the red one ($^4$F$_{9/2} \rightarrow ^4$I$_{15/2}$), because the number of RE$_S$ is high in comparison with the number of RE$_V$. In contrast, the big RENC emission should be dominated by green emission ($^4$H$_{11/2} + ^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$) coming from the RE$_V$. Thus, we should observe an increase in G/R ratio when changing the RENC size from small to big.

To gain more insight on how the size of RENCs affects the optical properties, numerical Monte Carlo simulations have been performed. First of all, Fig. 4(a) shows how the ratio between the number of surface and volume ions ($N_S/N_V$) changes when the RENC size is varied for 2 different shapes. We can see that the significant changes of $N_S/N_V$ and thus changes of the relative emission intensities from RE$_S$ and RE$_V$ sites should be mainly visible for RENCs with sizes around 20–30 nm. For our samples, the size of RENCs varies between 20 and 120 nm, thus we should not observe a significant influence of the RENC size on their optical properties.

In order to check experimentally if there is an influence of the RENC surface on the G/R ratio in the case of our RENCs, we covered their surface with an undoped NaGdF$_4$ thin (2.8 nm) shell layer. TEM images have been presented in Fig. 4(a and b). After shell deposition the G/R ratio slightly increased in comparison with core RENCs (Fig. 4(b)). This means that for RENCs with sizes larger than 20 nm the surface effect is still visible, but not very significant and weakly visible in optical measurements.

Fig. 4(b–e) present simulated distributions of surface ions for 10 nm RENCs doped with different ion concentrations. From these results we can see how the variations in the concentration of lanthanides influence the ion cluster formation, which causes efficient ion–ion interactions. These interactions, dependent on the cluster character, can be responsible for an efficient depopulation of the green emitting states ($^4$H$_{11/2}, ^4$S$_{3/2}$) down to the red emitting states ($^4$F$_{2/2}$) of Er$^{3+}$ ions in the cross-relaxation (CR) process changing the observed G/R ratio. For example, for 10–15 nm hexagonal NaYF$_4$:Eu$^{3+}$ RENCs we have estimated recently$^{34}$ that a significant increase in the ion–ion interaction (i.e. CR and energy migration) appears when the Eu$^{3+}$ ion concentration equals 5% which corresponds to the distance between the Er$^{3+}$ ions being around 6.5 Å.

This value is close to the lattice constant of the hexagonal phase of NaYF$_4$ ($a = 5.96$ Å, $b = 3.53$ Å)$^{38}$ suggesting that these interactions appear when two ions are very close to each other, forming the so-called chemical clusters. From Fig. 4(c) we can see that the clustering in the case of Er$^{3+}$ and Yb$^{3+}$ co-doped NaGdF$_4$ RENCs should also appear at very low concentrations (around 5%).

Based on our numerical modelling, for whole 10 nm RENC volume, we calculated also the probability of finding RE$_1$$^{3+}$ – RE$_2$$^{3+}$, RE$_1$$^{3+}$ – RE$_3$$^{3+}$ – RE$_4$$^{3+}$, RE$_1$$^{3+}$ – RE$_2$$^{3+}$ – … – RE$_{13}$$^{3+}$ clusters as a function of lanthanide concentration. The obtained results are shown in Fig. 3(a–c). From Fig. 3(a) we can see that the highest probability of finding Er$^{3+}$–Yb$^{3+}$ pairs is when the Er$^{3+}$ concentration is below 10% and the Yb$^{3+}$ concentration is in the range of 10 to 25%. This simple lanthanide configuration enables Er$^{3+}$ ions to be isolated from the other Er$^{3+}$ ions and thus non-radiative relaxation like down-conversion (DC) or CR is suppressed. This range of Yb$^{3+}$ concentration also limits the Yb$^{3+}$–Yb$^{3+}$ energy migration (i.e. from volume to surface) and non-radiative recombination of the absorbed photons. Thus, at this range of concentrations the green emission should dominate the spectrum. On the other hand, the excitation of Er$^{3+}$ via Yb$^{3+}$ ions cannot be optimal under these conditions, because only one Yb$^{3+}$ takes part in the 2-step or 3-step excitation process of the Er$^{3+}$ ion (Fig. 5(a)).

From Fig. 3(b) we can see that for Er$^{3+}$ concentrations below 10% and the Yb$^{3+}$ concentration above 25% the probability of finding Yb$^{3+}$–Er$^{3+}$–Yb$^{3+}$ clusters increases. In this concentration range, the Er$^{3+}$ ions can be excited by two or more Yb$^{3+}$ ions via multiple 1-step processes, which makes this excitation path more probable. Thus, this range of concentration seems to be optimal for efficient and intense light emission from Er$^{3+}$ ions, however the balance between the efficiency of Yb$^{3+}$ → Er$^{3+}$ excitation, Yb$^{3+}$–Yb$^{3+}$ interaction and emission from isolated Yb$^{3+}$ ions should be found (Fig. 5(b and c)).

A higher Yb$^{3+}$ concentration (above 50%) increases the probability of Yb$^{3+}$ cluster formation (more than two Yb$^{3+}$ ions as the first neighbours of Er$^{3+}$ ions). This results in multiple unwanted events i.e. radiative emission of Yb$^{3+}$ ions at...
1020 nm, excitation energy migration to the surface, co-operative Yb\(^{3+}\) emission or back energy transfer (BET) from Er\(^{3+}\) to Yb\(^{3+}\) (Fig. 5(c and d)). Thus, in this concentration range the emission is mainly red and the other processes like energy migration should be included which in consequence reduce also the total emission intensity from RENCs. The picture given above is symmetric and also can be discussed as Er\(^{3+}\)–Yb\(^{3+}\)–Er\(^{3+}\) and Er\(^{3+}\)–Yb\(^{3+}\)–Er\(^{3+}\)–...–Er\(^{3+}\) cluster formation which can promote the CR between Er\(^{3+}\) ions and increase surface losses of the absorbed photons.

To validate our numerical predictions, regarding the influence of Er\(^{3+}\) and Yb\(^{3+}\) concentrations on their interactions and optical properties of RENCs, we analysed a set of \(\beta\)-NaGdF\(_4\): Yb\(^{3+}\),Er\(^{3+}\) samples with different Yb\(^{3+}\) and Er\(^{3+}\) concentrations and the obtained results are shown in Fig. 3(d–k).

First of all, from Fig. 3(d) we can see that an increase in Er\(^{3+}\) concentration, even up to 50%, does not change the RENC size. However, above this value, the RENC size increases from 20–30 nm up to 100 nm without a change in the crystal phase. On the other hand, from Fig. 3(e) we can see that with an increase in Er\(^{3+}\) content above 10% the green-to-red emission intensity ratio decreases. This is the opposite tendency to that expected for the size effect discussed above, indicating that the observed changes in the spectral response of RENCs are rather a consequence of Er\(^{3+}\)–Er\(^{3+}\) interactions (i.e., CR) which enables depopulation of green states to red states as an alternative to a less probable multiphonon relaxation process.

The significance of Er\(^{3+}\)–Er\(^{3+}\) interactions in our samples has also been confirmed by analysing the samples containing the Er\(^{3+}\) ions only. In this case, an increase in the number of Er\(^{3+}\) ions (from 5 to 100%) decreases the G/R ratio in the same way as for Yb\(^{3+}\), Er\(^{3+}\) co-doped samples. Based on the obtained results we can conclude that for RENCs bigger than 20 nm the ion–ion interaction, not the nanocrystal size, is the main factor influencing the optical properties of RENCs. Thus, our experimental results are in good agreement with numerical simulations.

From Fig. 3(f) we can see that the ratio between the intensities of emission bands at 1550 and 1020 nm slightly increases with Er\(^{3+}\) concentration. Because the concentration of Yb\(^{3+}\) ions is not increasing in this case, the changes in this ratio are due to Er\(^{3+}\) emission at 1550 nm or more effective energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) ions (more Er\(^{3+}\) ions in the close proximity of Yb\(^{3+}\) ions). At higher Er\(^{3+}\) concentration the relaxation from higher erbium levels is easier (Er\(^{3+}\)–Er\(^{3+}\) CR) down to the \(^{4}I_{13/2}\) level and in addition more Er\(^{3+}\) ions are excited directly to \(^{4}I_{13/2}\) which results in increasing down shifting emission at 1550 nm. In the meantime, emission from \(^{4}S_{3/2}\) is suppressed. Fig. 3(g) shows that also blue emission was still detectable for RENCs with the Er\(^{3+}\) concentration below 20%. Above this value strong CR mechanisms reduce also the emission by relaxing carriers to the lower Er\(^{3+}\) states.

In Fig. 3(h) a very similar tendency of RENC size like in Fig. 3(d) has been observed when the Yb\(^{3+}\) concentration increases. In this case however, an increase in Yb\(^{3+}\) concentration influences the morphology of RENCs even at low concentrations of Yb\(^{3+}\) and increases their size from 20 to 120 nm. Nevertheless, despite these morphological differences, the tendency in the G/R ratio is the same as for variations in the Er\(^{3+}\) concentration.

A low concentration of Yb\(^{3+}\) causes Er\(^{3+}\) ions to be excited via a 2-step process, which is less efficient. When we increase the concentration of Yb\(^{3+}\) ions the 2-step process can be replaced by multiple 1-step processes and the excitation to higher energy levels is more probable. However, for higher Yb\(^{3+}\) concentration the energy migration among Yb\(^{3+}\) ions starts. Significant coupling between the Er\(^{3+}\) and Yb\(^{3+}\) ions and the back energy transfer process enable depopulation of \(^{2}H_{11/2} + ^{4}S_{3/2}\) states down to \(^{2}F_{5/2}\) states, increasing the contribution of red emission for highly Yb\(^{3+}\) doped RENCs. As a result emission from green states is decreased significantly while the emission from blue states is not. Nevertheless, the strongest emission is from the red states. In addition, from Fig. 3(j) we can see that with an increase in Yb\(^{3+}\) concentration (except for low Yb\(^{3+}\) concentration – 10%), which causes Yb\(^{3+}\) and Er\(^{3+}\) to be separated from each other and the
energy transfer to be not efficient) we can observe a significant decrease in down-shifting Er\(^{3+}\) emission (1550 nm) and an increase in Yb\(^{3+}\) emission (1020 nm). The reduction in this ratio is due to an increase in Yb\(^{3+}\) emission. There is an optimal coupling between the Yb\(^{3+}\) and Er\(^{3+}\) ions and additional Yb\(^{3+}\) ions introduced into the matrix do not improve the UPC emission but only serve as 1020 nm emitters and reduce the green emission due to back energy transfer from Er\(^{3+}\) to Yb\(^{3+}\) ions. Also a higher Yb\(^{3+}\) content enables the existence of Yb\(^{3+}\)-Yb\(^{3+}\) networks where the excitation energy migration appears together with a non-radiative energy dissipation i.e. at the RENC surface.\(^{39}\) This process quenches emission from our RENCs for the Yb\(^{3+}\) concentration above 70%. All these conclusions are also consistent with our simulation results (Fig. 3(a-c)). Moreover, analyzing the results shown in Fig. 3(k) we can see a significant reduction in the blue to red ratio when the Yb\(^{3+}\) concentration increases. This is also a consequence of depopulation of blue states via Er\(^{3+}\) → Yb\(^{3+}\) BET.

To analyse our results in a more quantitative way, relative changes in emission bands in the VIS and NIR spectral range have been analysed and are shown in Fig. 5. The emission spectra were recorded in a wide spectral range from 200 to 1600 nm by using two different CCD detectors. The Er\(^{3+}\) emission band at around 800 nm (\(T_{15/2}\)–\(T_{13/2}\)) was measured using both detectors and then was used to normalize the emission spectra recorded in two spectral ranges. This procedure enables us to analyse in a quantitative way the changes in the ratio between the down shifting emission (1550 nm or 1020 nm) and up-converting emission between different samples. Firstly, from Fig. 5 we can see that there is no Yb\(^{3+}\) in the RENCs (NaGdF\(_4\):Er\(^{3+}\)) upconverting emission is still present in the samples due to the self-absorption process, however it is at least 10 times less intense than the down shifting emission at 1550 nm.

From the green-to-red emission intensity for two samples with different Er\(^{3+}\) concentrations (no Yb\(^{3+}\)) we can also see that an increase in Er\(^{3+}\) concentration reduces the green-to-red emission intensity ratio. This tendency is similar for the co-doped samples, as shown in Fig. 3(c). In addition, the green emission observed for the NaErF\(_4\) sample is significantly lower than the case of the low doping regime (5% of Er\(^{3+}\)) due to ion–ion quenching effects i.e. excitation energy migration to the surface and its non-radiative dissipation. Secondly, from Fig. 5 we can see that adding 10% of Yb\(^{3+}\) to NaGdF\(_4\):5%Er\(^{3+}\) RENCs does not change the (G/R) ratio significantly but the up-converting emission increases around 10 times in relation to the down-shifting emission at 1550 nm when compared to Yb\(^{3+}\) free samples. Thus, it is clear evidence that Yb\(^{3+}\) ions participate in efficient Er\(^{3+}\) excitation and improve the UPC emission intensity even if some of the photons have been still lost in radiative Yb\(^{3+}\) emission or due to down-shifting Er\(^{3+}\) emission at 1550 nm. Also in the case of all NaGdF\(_4\):Yb\(^{3+}\),Er\(^{3+}\) samples, we can see a weak emission at around 400 nm which was absent in the case of NaGdF\(_4\):Er\(^{3+}\) samples due to the weak efficiency of the self-absorption process as compared to multi-step energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) ions. Moreover, after detailed analysis of the emission spectra shown in Fig. 5 we did not find an indication of Yb\(^{3+}\) co-operative emission, usually observed at 500 nm, and thus evidence of isolated Yb\(^{3+}\) chemical clustering.

In the next step, to better understand the Er\(^{3+}\)-Yb\(^{3+}\) and Er\(^{3+}\)-Er\(^{3+}\) interactions in our RENCs, the photoluminescence kinetics have been investigated. Since the model of interacting Er\(^{3+}\)-Yb\(^{3+}\) ion pair relaxation is complex and should be further expanded in order to take into account the variation of Er\(^{3+}\) and Yb\(^{3+}\) concentrations and different positions in the lattice, we analysed our results qualitatively using an average decay time approach. Fig. 6(a) shows the emission decay curves of the \(\beta\)-NaGdF\(_4\):Yb\(^{3+}\) (20%),Er\(^{3+}\) (2%) sample detected at different emission bands, under 980 nm excitation. The decay time varies between 187 and 400 µs for visible emission bands and is significantly longer for the 1550 nm band (3550 µs). For all emission bands however, the emission rise time is similar (∼65 µs) and most probably relates to the time needed to transfer the excitation energy from Yb\(^{3+}\) to Er\(^{3+}\) ions. To confirm this hypothesis, the Er\(^{3+}\) emission decay time of a red band at 650 nm has been measured at two excitation wavelengths 980 nm and quasi-resonantly at 540 nm. Independent of the excitation wavelength the red emission band has the same decay time. However, the emission rise time is below the resolution of our setup (∼2 µs) for quasi-resonant excitation. This result suggests that the relaxation within the Er\(^{3+}\) ions is a fast process (<2 µs), while the energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) ions is slow (on the order of tens of µs). The long rise time suggests that the Yb\(^{3+}\)-Er\(^{3+}\) energy transfer is a dipole–dipole type interaction and energy migration UPC (EMU) can also take place.\(^{40}\)

More detailed analysis is summarized in Fig. 6(b and c) where the decay times of a green emission at 540 nm have been shown for samples with different Yb\(^{3+}\) and Er\(^{3+}\) contents. When the Er\(^{3+}\) ion concentration increases the emission decay time exponentially reduces. This is because the Er\(^{3+}\)-Er\(^{3+}\) coupling became more efficient and that the ion–ion interaction influences the emission decay time via the non-radiative component (\(\tau_{NRAD}\)) of the emission decay time

\[
\frac{1}{\tau_{PL}} = \frac{1}{\tau_{NRAD}} + \frac{1}{\tau_{Rad}}.
\]

Similar reduction in rise time can be due to more probable coupling between Er\(^{3+}\) ions at higher Er\(^{3+}\) ion concentrations.

The situation is very different however, when the Yb\(^{3+}\) content in \(\beta\)-NaGdF\(_4\):Yb\(^{3+}\),Er\(^{3+}\) (5%) RENCs changes. In this case, the green emission decay time is almost constant in the entire range of Yb\(^{3+}\) concentrations. This is because the green emission of Er\(^{3+}\) ions is not in resonance with Yb\(^{3+}\) levels thus resonant dipole–dipole interactions reducing \(\tau_{PL}\) can be excluded. However, for the increasing Yb\(^{3+}\) concentration we observed a decrease in the green emission rise time, which may be an effect of more efficient Yb\(^{3+}\) to Er\(^{3+}\) ET, because of the presence of a higher number of sensitizers (Yb\(^{3+}\) ions).
Conclusions

In summary, we have investigated the impact of the dopant concentration on the phase, size and optical properties of Er\textsuperscript{3+} and Yb\textsuperscript{3+}-doped NaGdF\textsubscript{4} RENCs. It has been shown that the hexagonal crystal phase of RENCs can be maintained for a wide range of dopant concentrations. Only high Yb\textsuperscript{3+} concentrations resulted in the formation of RENCs in the cubic phase, because of the raising of energy barrier for \( \alpha \rightarrow \beta \) phase transitions due to the doping of the smaller ions. Physical properties of lanthanides, like the ion size, strongly influence the morphology of the obtained RENCs, especially the size of RENCs. When the extent of Er\textsuperscript{3+} and Yb\textsuperscript{3+} substitution of Gd\textsuperscript{3+} ions increases, the size of RENCs grows. Because the ionic radius decreases in the order Gd\textsuperscript{3+} (93.5 pm), Er\textsuperscript{3+} (89 pm) and Yb\textsuperscript{3+} (86.8 pm) the change in the size of RENCs is detectable at 60\% of Er\textsuperscript{3+} concentration, while 20\% of Yb\textsuperscript{3+} ion doping is enough to influence the size of RENCs.

Because both the dopant concentration and RENC size influence the optical properties of upconverting RENCs, and in our synthesis these are dependent parameters, the analysis of the impact of the Er\textsuperscript{3+} and Yb\textsuperscript{3+} ion concentration on photoluminescence is challenging. However, according to our numerical simulations the impact of RENC size on their optical properties (e.g. G/R emission ratio) is negligible for RENCs bigger than 20 nm. This was further confirmed through the investigation of core–shell structures. We suggest that in the case of the investigated RENCs, the intensities of particular emission bands are primarily governed by formation of dopant clusters and their efficient ion–ion interactions. Because of this, with the increasing Yb\textsuperscript{3+} and Er\textsuperscript{3+} concentration the emission from green states is reduced, while the emission from red states is increased. Additionally, we showed that at high Yb\textsuperscript{3+} concentrations the less desirable cubic phase is obtained. Such RENCs do not show an improved UPC emission but rather serve as efficient down-converting emitters at 1020 nm.

Acknowledgements

This work was supported by the grants from the National Science Centre, Sonata Bis 3 Project No. UMO-2013/10/E/ST5/00651. M. B. would like to acknowledge the Foundation for Polish Science (FNP) “Start” for the financial support. A. N. would like to acknowledge the Ministry of Science and Higher Education in Poland for the financial support.

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