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Size and shape effects in $\beta$-NaGdF$_4$: Yb$^{3+}$, Er$^{3+}$ nanocrystals

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Abstract

Three sets of $\beta$-NaGdF$_4$-Yb$^{3+}$, Er$^{3+}$ nanocrystals (NCs) with different shapes (spherical and more complex flower shapes), different sizes (6–17 nm) and Yb$^{3+}$ concentrations (2%–15%) were synthesized by a co-precipitation method using oleic acid as a stabilizing agent. The uncommon, single-crystalline flower-shaped NCs were obtained by simply adjusting the fluorine-to-lanthanides molar ratio. Additionally, some of the NCs with different sizes have been covered by the undoped shell. The crystal phase, shapes and sizes of all NCs were examined using transmission electron microscopy and x-ray diffraction methods. Simultaneously, upconversion luminescence and lifetimes, under 980 nm excitation, were measured and the changes in green to red (G/R) emission ratios as well as emission decay times were correlated with the evolution of nanocrystal sizes and surface to volume ratios. Three different mechanisms responsible for the changes in G/R ratios were presented and discussed.

Supplementary material for this article is available online

Keywords: nanocrystals, lanthanides, aggregation, spectroscopy

(Some figures may appear in colour only in the online journal)

Introduction

In recent years, the study of nanomaterials in both fundamental and technological research has attracted considerable attention due to their potential applications in various fields, e.g. color displays, solid-state lasers, medicine and light-emitting diodes [1, 2]. Lanthanide-doped upconverting nanocrystals (UPC-NCs) are especially popular nowadays because of a good potential use as multimodal probes [3, 4]. This is due to the numerous advantages associated with near infrared (NIR) excitation such as the absence of autofluorescence background noise, deep penetration of NIR excitation light into biological tissues, reduced photodamage, lack of photobleaching and photoblinking [5, 6]. Among UPC-NCs, fluoride $\text{AREF}_x$ ($\text{A} = \text{alkali metal, RE} = \text{rare earth}$) has been investigated for several decades because of a relatively low phonon energy (about 400 cm$^{-1}$) [7, 8], which is reflected in a low efficiency of non-radiative transitions. Nowadays, the most popular crystal host is NaYF$_4$, especially a hexagonal phase ($\beta$-NaYF$_4$), where the local crystal field is less centrosymmetric than in a cubic phase ($\alpha$-NaYF$_4$), which results in more intense luminescence from lanthanides due to more efficient release of optical selection rules. Applying a $\beta$-NaGdF$_4$ matrix can reduce the phonon energy even to lower values [9]. This results in the decrease of the non-radiative relaxation probability and subsequently increases the upconversion luminescence efficiency [9]. Additionally, Gd$^{3+}$ ions possess paramagnetic properties, which enhances the potential of UPC-NCs being used as multifunctional markers, both optical and magnetic, in biology and medicine [10, 11].

One of the main challenges in this field is to obtain small NCs (<10 nm) with a high emission quantum yield (EQY > 1%) and a narrow size distribution. This is, however, still a challenging task because the size and EQY have so far been two anti-correlating parameters. However, a small size is crucial for efficient body clearance [12], efficient cell membrane transport [13, 14] and for designing high-contrast agents for magnetic resonance imaging (MRI) [15], which are all required for biomedical applications.
Controlling the shape of NCs is also a challenging task for UPC-NCs, especially if we also need to keep their size in a lower limit range and ensure a high EQY. Although RE ions are not significantly sensitive to the local environment, the influence of the surface is visible in their optical properties [16, 17]. This is mainly because of numerous non-radiative channels activated due to high frequency modes of ligands placed at the NC surface (e.g. –OH, –CH) and different local environments of the surface and core RE ions. This will be especially true for small NCs or for NCs with complex shapes, where the surface to volume (S/V) ratio is high. Thus, the NC size and shape are two parameters which have a strong influence on their optical properties because they affect the S/V ratio, which is equivalent to the contribution of surface ions in the total amount of ions participating in the observed emission.

The effect of the size on the optical properties of NCs was previously investigated by Wang et al [18], who found a strong quenching effect coming from the surface defects, impurities, ligands, and solvents. Schietinger et al [19] described a visible influence of NC size on their emission properties and correlated these observations with size dependent phonon confinement effects. A similar but more quantitative analysis was carried out by Yuan et al [20] who described the effect of the host lattice and phonon vibrations coupled with functional groups and defect sites on the optical properties of NCs.

However, more general investigations of the surface influence on optical properties of NCs are challenging due to the fact that a precisely controlled synthesis is required to obtain different NC shapes, and NCs with sizes below 10 nm. To date, various wet chemical strategies were designed and developed for this purpose. Among all known methods, a hydrothermal synthesis in particular allows for simple manipulation of NC shapes [21–23]. This method of synthesis allows for control of various experimental variables such as temperature, reaction time, concentration of precursor compounds and surfactants [24]. Using this synthesis method Zhang et al [25] showed that NaMF_{4} (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y, Yb, and Lu) NCs with a variable size from 3 nm to several micrometers, and shape diversification from nanoparticles to tubes, rods, wires, disks, spheres, zigzagged rods, and flower-patterned disk arrays, can be effectively manipulated through careful control of the reaction temperature, time, reagent concentrations, and ethanol content. Although the range of the NC sizes was broad, a cubic phase was detected only for NCs smaller than 90 nm [25]. In addition, Liang et al [26] demonstrated the hydrothermal growth of NaYF_{4} NCs with a controllable phase and shape. In this case, a small NC size (9–25 nm) resulted in crystallization in the cubic phase, whereas the hexagonal phase was determined for NCs larger than 400 nm. The NaF to Y^{3+} ratio was responsible for the shape evolution while the temperature and reaction time were the key factors for the phase control of NaYF_{4} NCs. Thus, a higher ratio of NaF to Y^{3+} seems to be helpful for the anisotropic growth of hexagonal NaYF_{4} [26].

The above-mentioned examples prove that hydrothermal treatment is a convenient method in preparing fluoride nanostructures with diverse and controllable morphologies and architectures [21, 23]. Unfortunately, the main disadvantage of this synthesis method is that most small-sized NCs are obtained in a cubic phase which, from the point of view of efficient lanthanide emission, is much worse that the hexagonal β-phase. It is much more difficult to obtain small NCs in the hexagonal phase with different shapes using a co-precipitation method. Only a few authors reported the synthesis of NCs with complex shapes, resembling the shape of flowers, commonly called flower-shaped NCs: NaREF_{4} [23], Sm_{2}O_{3} [27], PbSe [28], and KY_{2}F_{10} [29]. To the best of our knowledge, no such single-crystalline NaGdF_{4}:Yb^{3+}, Er^{3+} NCs synthesized by the co-precipitation method have been reported so far.

In this study we present a synthesis of three sets of β-NaGdF_{4}:Yb^{3+}, Er^{3+} samples: NCs with different sizes (6–17 nm), different shapes and Yb^{3+} concentrations (2%–15%). All of the NCs were synthesized using a co-precipitation method and a variety of shapes were obtained by a simple adjustment of the fluorine–lanthanides molar ratio (F/La). Parts of the spherical NCs with different sizes were covered by an additional shell layer in order to investigate the effect of the surface on the optical properties of NCs. Based on transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements, surface to volume (S/V) ratios were calculated for two sets of NCs. In order to investigate the effect of the size and shape on optical properties of NCs, green to red emission ratios (G/R) were calculated and the obtained results were supported by the emission kinetics measurements.

Methods

General procedure for the synthesis of NCs with different sizes, shapes and Yb^{3+} concentrations

The applied synthetic method of β-NaGdF_{4}:Yb^{3+}, Er^{3+} NCs was similar to the procedure proposed by Wang et al [30]. Ytterbium(III) acetate hydrate Yb(CH_{3}COO)_{3}H_{2}O (99.9%), gadolinium(III) acetate hydrate Gd(CH_{3}COO)_{3}H_{2}O (99.9%), erbium(III) acetate hydrate Er(CH_{3}COO)_{3}H_{2}O (99.9%), sodium hydroxide, ammonium fluoride, 1-octadecene and oleic acid were purchased from Sigma Aldrich and used as received without further purification.

In a typical procedure allowing us to obtain NaGdF_{4}:Yb^{3+}, Er^{3+} NCs, 3 ml water solution of Ln(CH_{3}COO)_{3} (0.2 M, Ln = Gd, Yb, and Er) was added to a 50 ml flask containing 4 ml of oleic acid. In order to obtain NCs with different concentrations of Yb^{3+}, different proportions of the lanthanide solution was applied in each synthesis. The mixture was heated at 150 °C for 30 min to remove the water content from the solution. Then 6 ml of 1-octadecene solution was quickly added to the flask and the resultant mixture was kept in this temperature for another 30 min before cooling down to 50 °C. Shortly afterwards, 5 ml of methanol solution containing NH_{3}F and NaOH was added and the resultant solution was stirred for 2 h. In order to obtain NCs with
different shapes, the amount of NH₄F and NaOH was different in each synthesis. After the methanol was evaporated, the solution was heated up to 290 °C under argon for 1 h and then cooled down to room temperature. The resultant NCs with a yield of 80 mg were precipitated by adding ethanol, collected by centrifugation at 10 000 rpm for 4 min, washed with ethanol several times, and re-dispersed in 4 ml of cyclohexane.

**General procedure for the synthesis of core–shell NCs**

0.1 mmol of gadolinium acetate Gd(CH₃COO)₃·H₂O was added to a 50 ml flask containing 4 ml of oleic acid. The mixture was heated at 150 °C for 30 min to remove the water content from the solution. Then 6 ml of 1-octadecene solution was quickly added to the flask and the resultant mixture was kept in this temperature for another 30 min. After that the mixture was cooled down to 70 °C and 1 ml of core NCs (~10 mg) in cyclohexane was added and kept at this temperature for another 10 min. Then the mixture was cooled down to 50 °C. Shortly afterwards, 3 ml of methanol solution containing NH₄F (1.36 mmol) and NaOH (1 mmol) was added and the resultant solution was stirred for 2 h. After the methanol was evaporated, the solution was heated up to 290 °C under argon for 1 h and then cooled down to room temperature. The resulting NCs were precipitated by adding ethanol, collected by centrifugation at 10 000 rpm for 4 min, washed with ethanol several times, and re-dispersed in 4 ml of cyclohexane.

**General procedure for the synthesis of inverted core–shell NCs**

The synthesis protocol of the reversed core–shell NCs is the same as for core and core–shell NCs. The only difference is that the core is made of un-doped NaGdF₄ material, while dopants are placed in the shell layer. Concentrations of Yb³⁺ and Er³⁺ were 10 and 5%, respectively.

**Structural characterization**

The samples for TEM experiments were prepared by evaporating a dilute cyclohexane solution of NCs onto carbon coated copper grids. An FEI Tecnai G2 20 X-TWIN microscope (operating voltage: 200 kV, the current and voltage of x-ray beam: 200 kV and 9.49 μA, acquisition time: 0.25 s) equipped with an energy-dispersive x-ray microanalyser was used to obtain TEM images and EDXS spectra of the nanoparticles. X-ray powder diffraction patterns were obtained by using a Philips diffractometer supported by a parallel beam optic and CuKα1 radiation source, λ = 0.154 06 nm.

**Optical measurements**

For the steady state photoluminescence (PL), a 980 nm laser (Shanghai Dream Lasers technology SDL-980-LM-1000T) was used as an excitation source. An iHR550 spectrometer (Horiba Jobin Yvon) and two detectors (InGaAs NIR linear array detector and Symphony II CCD detector) were used as detection systems for measurements in NIR and UV–vis spectral ranges respectively. The emission spectra were not corrected spectrally. PL decays were measured by using a pulsed laser (978 nm, 7 ns, 20 Hz, PAV = 3 mW, Opotek™, Opotek Inc., Carlsbad, CA, USA) coupled to a gated detection system with a time resolution of 1 μs.

**Results and discussion**

It is already known that the reactant concentration may have a considerable influence on the size and the shape evolution of NCs [23, 31]. Recently, we reported on NC size control by doping NCs with different concentrations of Er³⁺ and Yb³⁺ ions [32]. This enabled us to tune the NC sizes from 15 to 120 nm. We showed [32] that in this range of NC sizes the dominant mechanisms responsible for changes in optical properties of NCs are not the surface related effects but mainly the ion–ion interactions. On the other hand, we predicted that the surface effects should be visible for NCs with sizes below 15 nm (S/V = 0.4 nm⁻¹) due to the high S/V ratio correlated with the efficient Er-surface coupling reflected in efficient multiphonon relaxation. Unfortunately, the thermolysis method prevents us from obtaining NCs smaller than 15 nm where the S/V ratio should start performing a dominant role. Therefore, to overcome this problem a co-precipitation method was selected and applied successfully to synthesize three sets of samples (NCs with different sizes, shapes and Yb³⁺ concentration) which were investigated in this study.

In the first set, the NC shapes were uniform (approximately spherical) and their sizes changed from 6.6 ± 0.8 to 17.4 ± 2.3 nm, which was equivalent to a 0.91 nm⁻¹ and 0.34 nm⁻¹ S/V ratio, respectively (figure 1). Two samples with sizes equal to 8.7 and 6.6 nm were in addition covered with the un-doped NaGdF₄ shell with a thicknesses equal to 1.65 and 1.8 nm, respectively.

In the second set of samples, the sizes of NCs were in the range from 17.4 ± 2.3 to 38.9 ± 7.3 nm (in the range where for spherical NCs the surface effects are expected to perform a negligible role). Nevertheless, their expanded shapes were changing from sample to sample (figure 2), which was expected to have an impact on presence of surface effects in these NCs. Thus, the S/V ratio has been chosen as a parameter, which enables comparison of the samples from both sets. The S/V ratio was calculated for all samples based on TEM (figure S1, available at stacks.iop.org/NANO/28/175706/mmedia) and AFM measurements. The obtained values are presented in figures 1(b) and 2(a)–(d). Moreover, since in the sample shown in figure 2(d) two different morphologies of NCs were obtained, the weighted average of the S/V ratio (S/Vav) was calculated according to the contribution of small-rounded and flower-shaped NCs. The S/V ratio calculation method is described in the online supplementary data.
In order to obtain various NC shapes, the amount of NH₄F water solution was changed in each synthesis. For 3.4–2.5 ml of NH₄F solution the nearly spherical shaped NCs were obtained as can be seen in figure 2(a). When the amount of NH₄F solution decreases to 2.3 ml, the shape of the NCs becomes more irregular and begins to resemble the shape of a limb (figure 2(b)). As the concentration of NH₄F solution was further reduced, the NCs grew larger and gradually adopted a flower-like morphology (figures 2(c), (d)). Moreover, in the case of the last sample (with the smallest amount of NH₄F solution), we observed the appearance of small and round NCs with a medium size of about 5 nm (figure 2(d)). For all of the samples mentioned above, the concentrations of Yb³⁺ and Er³⁺ ions were kept the same and they were equal to 10 and 5%, respectively.

In the last set of samples the shapes were uniform and the sizes were in the range of 6.7 ± 0.8 to 8.3 ± 1.0 nm (online supplementary figure S2) but the Yb³⁺ concentration varied in a low range of concentrations (2%–15%).

The crystalline nature of the NCs was confirmed by XRD measurements (online supplementary figure S3(a)). Almost all NCs crystallized in the hexagonal phase. Only for the sample with S/V = 1.06 nm⁻¹, where bi-modal NC distribution was observed, a peak around 28° may suggest crystallization of part of the NCs in the cubic phase. It is probable that flower-shaped NCs were obtained in a hexagonal phase, with small-rounded NCs in a cubic phase. As proof, a TEM image of a single-crystalline flower-shaped NC with well resolved lattice fringes is shown in online supplementary figure S3(b). Determined lattice spacing of 0.54 nm corresponds to the (001) crystal plane of the hexagonal phase.

As it was reported recently, the upconversion emission from fluoride NCs strongly depends on their relative orientation [33], however because of the random orientation of NCs in the solvent this effect is negligible in our case. Additionally, Rodriguez-Sevilla et al [34] have shown that there are remarkable differences between single and multi-particle luminescence, caused by collision-assisted radiative self-absorption processes between NCs, due to the partial

![Figure 1. TEM images (a) and size distributions (b) of NCs with different sizes (core NCs—red histograms, core–shell NCs—grey histograms) (scale bar = 50 nm). The sample with a S/V ratio equal to 0.29 nm⁻¹ was synthesized using the co-thermolysis method and it was presented in our previous paper. Reproduced from [32] with permission of The Royal Society of Chemistry.](image_url)
overlap between absorption and emission bands. Thus, the emission spectra can be affected by the concentration of NCs. However, above a certain concentration of NCs, this phenomenon does not occur. In the case of our samples, the changes in the shape of the emission spectra are not observed, thus the effect of the radiative self-absorption can be ignored.

Another factor, which can influence the optical properties of NCs, is the kind of the solvent. Thus, in order to be sure that effect of the solvent is not observed in our NCs, the inverted core–shell NCs were synthesized (online supplementary figure S4). For that purpose, the un-doped NaGdF4 core NCs were synthesized. They were further covered by the shell layer which was doped with optically active ions (NaGdF4: Yb3+, Er3+). The shell thickness was determined using TEM and it was about 2.5 nm. Due to such a material combination we can assume that most of the optically active ions are in close proximity to the surface. Based on the PL spectra of inverted core–shell structures (figure S4(a)), the ratios of the appropriate emission bands were calculated (figure S4(c)). As can be seen, the G/R ratio is not sensitive to the kind of solvent in the given range of refractive index. Also other parameters which can influence the G/R ratio (power of the laser, integration time, silt width, etc) have been kept the same for all samples to ensure that the G/R ratio is not changing from sample to sample due to different experimental conditions.

In order to investigate the influence of NC sizes and shapes on their optical properties the photoluminescence spectra were measured (figures 3, online supplementary S5) and G/R emission ratios were calculated for all samples (figure 4).

Based on the values obtained for the ratio between the green (4H_{11/2} → 6S_{3/2} → 4I_{15/2}) and red (4F_{9/2} → 4I_{15/2}) emission band intensities, usually the efficiency of non-radiative relaxation processes between 4S_{3/2} → 4F_{9/2} and 4I_{11/2} → 4I_{13/2} levels is estimated. This non-radiative relaxation can occur due to either multiphonon relaxation (W_Mp), dipole–dipole type cross-relaxation (W_CR) between the Er^{3+} ions or at high

Figure 2. TEM images, calculated S/V ratios and size distributions of NCs with different shapes (scale bar = 50 nm).

Figure 3. PL spectrum of NCs with S/V equal to 0.94 nm⁻¹ (belonging to the set of NCs with different sizes), PL spectra of NCs with different sizes presented in the range from 640–680 nm and normalized at 540 nm (inset), resolution: 0.06 nm.
Yb$^{3+}$ concentration due to back energy transfer (W\textsubscript{BET}) from Er$^{3+}$ to Yb$^{3+}$ ions. However, it is worth mentioning that this ratio can also change due to the changes in the excitation mechanism to $^4\text{F}_{9/2}$ ($^4\text{S}_{3/2}$) levels and depopulation processes induced by energy transfer upconversion (ETU) or excited states absorption, which are rarely taken into account by other authors when analyzing G/R ratio behavior. The importance of these processes will be discussed in this paper because a deep understanding of the mechanisms responsible for changes in the G/R ratio can be crucial when designing UPC-NC-based nanothermometers \cite{35, 36} or when building the models for theoretical simulations of emission/ conversion processes in UPC nanostructures for PV applications.

**Size dependent relaxation mechanisms**

In the case of multiphonon relaxation, this mechanism can be related either to the coupling of core Er$^{3+}$ ions to vibrational modes of the matrix (phonons) ($W_{\text{V,M}}$) or coupling of surface Er$^{3+}$ ions to vibrionic modes of surface ligands ($w_{\text{A,M}}$). Both processes could be NC size dependent. This results from the fact that in lanthanide-doped NCs we always deal with two distinguished classes of lanthanide sites: core sites (RE$^{3+}$\textsubscript{C}) and surface sites (RE$^{3+}$\textsubscript{S}) (figure 5(b)).

The red emission intensity should be enhanced for the ions placed at the surface of the NCs because they are coupled with high vibrational ligand modes (e.g. –CH, –OH) \cite{17, 20}. These processes enable more efficient relaxation from $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ to $^4\text{F}_{9/2}$ or from $^4\text{I}_{11/2}$ down to $^4\text{I}_{13/2}$ energy levels, promoting the red emission from surface ions.

In contrast, for the core ions (which are separated from the surface) the multiphonon relaxation between the 4f energy levels is less probable because only low frequency phonon modes available in \textit{β}-NaGdF\textsubscript{4} matrix may contribute to this process, and thus the green emission should be preferential for these ions. Due to this fact, the macroscopically observed G/R ratio should depend on a relative number of surface and core ions and should decrease when the S/V ratio increases (or the size of the NCs decreases).

The second size dependent mechanism which could be responsible for changes in the G/R ratio can be related to phonon confinement. The quantitative results on phonon energy for \textit{β}-NaYF\textsubscript{4}:Yb$^{3+}$, Er$^{3+}$ NCs with a different size were reported by Yuan \textit{et al} \cite{20}. They showed that the main frequency mode increased from 432 to 440 cm$^-1$ with the size reduction of the NCs from micrometers down to 11 nm, which gives 8.38 and 8.22 phonons involved in the relaxation of carriers from the $^4\text{I}_{13/2}$ level down to $^4\text{I}_{11/2}$ or 7.64 and 7.50 for relaxation between $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels respectively. In our opinion, taking into account a broad shape of the Raman spectrum in NaYF\textsubscript{4} \cite{9} there should be no difference in multiphonon relaxation efficiency between these levels induced by the changes in phonon energy with NC size reductions. However, not only the energy of phonon modes, but also the number of available phonon modes can affect multiphonon relaxation process in NCs. According to Schietinger \textit{et al} \cite{19} the density of phonon modes is strongly reduced for small fluoride NCs and thus the multiphonon relaxation i.e. from $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ to $^4\text{F}_{9/2}$ energy levels of
Er\(^{3+}\) ions can be significantly reduced (figure 4(c)) and consequently the green emission from \(^2\text{H}_{11/2}\) and \(^4\text{S}_{3/2}\) is enhanced. Thus, for small NCs, the green emission should dominate in the spectrum, whereas for larger NCs G/R ratio should be lower and the red emission should be dominant in the spectrum. This hypothesis, even if probable, should be first confirmed experimentally by Raman spectroscopy on single NCs because with reduction of NCs more factors which have the influence on phonons modes change (lattice constant, new surface modes etc) and make this hypothesis highly speculative.

Another mechanism, often used to explain G/R changes, are ion–ion interactions (figure 5(d)) [32], which are strongly related to ion concentrations. This process is efficient mainly when the Er\(^{3+}\) ion is effectively coupled to other Er\(^{3+}\) ions. This means that this process should be important at higher Er\(^{3+}\) content (>5%). Another type of carrier relaxation path within the energy levels of Er\(^{3+}\) ions is back energy transfer from Er\(^{3+}\) ions to Yb\(^{3+}\) ions. This process should be dominant however at high Yb\(^{3+}\) concentration (>25% including homogenous ion distribution).

### Size dependent excitation mechanism

In this paper, we propose a new NC size dependent mechanism which can explain untypical changes in G/R ratio behavior, which was obtained by us (increase in G/R ratio with size reduction of NCs). This mechanism assumes that with changes in a number of Yb\(^{3+}\) ions coupled to Er\(^{3+}\) ions, the excitation mechanism of Er\(^{3+}\) ions is changing. Since in all samples discussed in figure 4(a) Yb\(^{3+}\) and Er\(^{3+}\) concentration is constant, the only mechanism which can change the number of Yb\(^{3+}\) ions coupled to Er\(^{3+}\) ions with size reduction of NCs is the aggregation of Yb\(^{3+}\) ions. Due to the same properties of Er\(^{3+}\) and Yb\(^{3+}\) ions, the Er\(^{3+}\) ions can also aggregate in NCs. However, due to significantly different concentration of both ions the probability of Yb\(^{3+}\) aggregation should be much more visible in experimental data. Thus, for small NCs, clustering can occur and the probability of finding two or more Yb\(^{3+}\) ions coupled to one Er\(^{3+}\) ion increases. In such a configuration of ions, the excitation of Er\(^{3+}\) ions can change (be more efficient) due to simultaneous excitation of Er\(^{3+}\) ions by several Yb\(^{3+}\) ions (figure 5(d)), exciting the carriers quickly and directly from the \(^{4}\text{I}_{11/2}\) level to the green \(^2\text{F}_{7/2}\) level without previous relaxation from \(^4\text{I}_{11/2}\) down to the \(^4\text{I}_{13/2}\) level (path A in figure 5). At the limiting case for high Yb\(^{3+}\) concentration, this aggregation will also promote the energy migration between Yb\(^{3+}\) ions and back energy transfer (BET), processes which should reduce NC emission efficiencies [32]. For bigger NCs, the ionic distribution should be more homogenous and the number of Yb\(^{3+}\) ions coupled to Er\(^{3+}\) ions should be also reduced due to the absence of aggregates. In this case, the Er\(^{3+}\) ions should be excited in sequential (ground-state absorption (GSA) and/or ETU) processes assisted with non-radiative relaxation between the energy levels (path B in figure 5).

On the basis of this hypothesis the non-homogenous ionic distribution inside small NCs favors excitation to \(^2\text{H}_{11/2}\) and \(^4\text{S}_{3/2}\) states, whereas homogenous distribution of the ions (at a given Yb\(^{3+}\) concentration) in big NCs favors excitation to the \(^2\text{F}_{7/2}\) state.

Figure 4 shows values of the G/R ratio calculated for all samples, which were obtained by us. From this figure we can see that for NCs with different sizes, the G/R ratio rapidly increases with S/V ratio increase (or size reduction) until 0.7 nm\(^{-1}\) (figure 4(a)). Only two mechanisms described

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**Figure 5.** Schematic representations of the physical mechanisms responsible for changes in the G/R ratios in $\beta$-NaGdF$_4$:Yb$^{3+}$, Er$^{3+}$ NCs. (a) Cross-relaxation due to dipole type ion–ion coupling, (b) coupling between excited electrons in surface ions and vibrating modes of surface ligands, (c) phonon confinement due to localization of the phonon wave function $\Phi_{\text{ph}}(R)$, and (d) changes in Er$^{3+}$ excitation mechanisms due to Yb$^{3+}$ aggregation.
above can explain this untypical behavior: changes in phonon mode density or changes in Er\(^{3+}\) ionic excitation mechanism due to Yb\(^{3+}\) aggregation correlated with NC size reductions. As discussed, we believe that our results can be effectively explained by the second mechanism. In order to confirm our hypothesis a new set of NCs with a constant size of around 7 nm but with different Yb\(^{3+}\) contents (2, 5, 7, 12, 15%) was prepared. The obtained G/R ratios for these samples are shown in figure 4(b). We can see that the tendency of the G/R ratio is exactly the same as for the samples with a constant Yb\(^{3+}\)/Er\(^{3+}\) ratio but varied NC sizes (S/V ratios). It is worth mentioning that a further increase in Yb\(^{3+}\) concentration will reduce the G/R ratio due to strong enhancement of BET processes and reduce the UPC emission intensity due to energy migration (EM) or radiative emission of Yb\(^{3+}\). These processes are expected to appear when Yb\(^{3+}\) concentration will exceed 25\%–30\% (at 5\% of Er\(^{3+}\)), which corresponds to Yb\(^{3+}\) cluster formation around Er\(^{3+}\) ions [17]. A similar tendency is observed after further reduction of the size for the smallest NCs (6 nm).

In the case of NCs with different shapes (red pentagons) a G/R ratio tendency in the function of the S/V ratio is opposite. In such structures, due to their well-developed surface and flat shape, the participation of surface ions in the total amount of the ions embedded inside NCs is extremely large. This promotes a strong coupling between, dominant in this case, surface Er\(^{3+}\) ions and vibronic states of surface ligands when the S/V ratio increases (figure 5(b)).

To prove our main hypothesis, the surface of selected NCs was covered with an additional layer of the un-doped (NaGdF\(_4\)) material and the core–shell structures were formed. According to Wang et al [18] and our results [32], this approach should improve the Er\(^{3+}\) ions’ emission intensity and should promote the emission from higher levels of Er\(^{3+}\) ions due to the reduction in coupling of Er\(^{3+}\) ions with the surface ligands and thus a reduction in multiphonon relaxation between \(4F_{9/2}\) and higher levels of Er\(^{3+}\) ions. Consequently, the G/R ratio should increase. However, as it can be seen in figure 4(a), the G/R ratio decreases after the shell formation for NCs smaller than 15 nm. This result is consistent with our aggregation hypothesis. We assume that this phenomenon is connected with an increase in the distance between Yb\(^{3+}\) and Er\(^{3+}\) ions after the shell growth and the reduction in number of Yb\(^{3+}\) ions coupled to Er\(^{3+}\) ions due to Yb\(^{3+}\) ions diffusing out from the core to the shell region. A similar effect was already reported by Voß et al [37] and also found in our group for \(\beta\)-NaGdF\(_4\):Eu\(^{3+}\) core–shell structures [38]. Hence we can conclude that for the core–shell structures the excitation mechanism is changing and seems to be the same as in the case of the ions distributed homogeneously in big NCs. Surprisingly, for bigger NCs the shell formation changes the G/R ratio in the opposite way but also with much less difference. This results from the fact that for big NCs, the distribution of ions is already homogenous and the shell formation reduces only the number of surface Er\(^{3+}\) ions and increases the green emission from the core Er\(^{3+}\) ions. For much bigger NCs we expect no difference between the G/R ratio for the core and core–shell structures due to the dominant contribution to the total emission from core ions.

The emission intensity depends on the efficiency of both excitation and recombination mechanisms. Thus, from this experiment it is difficult to conclude which mechanism (population via path A or B or depopulation via BET or ETU) dominates the observed behavior of the G/R ratio, whereas the emission decay time measurements are sensitive to the depopulation mechanism only. Therefore, in order to better understand the results we obtained, the emission decay spectra were collected for all of the investigated samples (see online supplementary figures S6 and S7). To analyze these results, the simplest approach was used, and for all the decay curves an effective decay time \(\tau_{\text{eff}}\) was calculated on the basis of the following equation:

\[
\tau_{\text{eff}} = \int_{t_0}^{t_f} \frac{1}{I(t)} \, dt
\]

where \(I(t)\) represents the phospholuminescence intensity at time \(t\) after cutoff of the excitation light, \(t_0 = 0\) s is the initial time when the signal starts to decay and \(t_f\) is the time value where the luminescence intensity reaches the background.

From figures 6(b), (d) we can see that for all of the investigated samples the effective emission decay time for green and red emissions are reduced with the increase in S/V ratio. This results from the fact that with NC size reductions (or S/V increases) the contribution of the non-radiative component (\(\tau_{\text{NR}}\)) in the measured emission decay time (\(\tau_{\text{PL}}\)) increases (\(\tau_{\text{PL}} = \tau_{\text{PL}}^{-1} = \tau_{\text{R}}^{-1} + \sum \tau_{\text{NR}}^{-1}\)). In this case, however, the non-radiative component includes contributions from coupling of Er\(^{3+}\) ions to surface ligands or matrix phonons (\(w_{\text{BET}}\)), from Er\(^{3+}\)–Yb\(^{3+}\) BET (\(w_{\text{BET}}\)) as well as from other processes like ETU depopulation (\(w_{\text{ETU}}\)), Er\(^{3+}\)– Er\(^{3+}\) cross-relaxation (\(w_{\text{CR}}\)) or Er\(^{3+}\)–Er\(^{3+}\) EM (\(w_{\text{EM}}\)). The last two mechanisms should be considered as significant only at high Er\(^{3+}\) concentrations (or Er\(^{3+}\) aggregation), whereas BET at very high Yb\(^{3+}\) concentration and can be excluded from our consideration in the first approximation.

We believe that the main mechanism, which can reduce the measured emission decay time with S/V ratio is the increase in efficiency of coupling of surface Er\(^{3+}\) ions to surface ligands (\(w_{\text{MP}}\)) and increase in Yb\(^{3+}\)–Er\(^{3+}\) interactions (\(w_{\text{ETU}}\)) inducing Er\(^{3+}\) levels ETU depopulation related to aggregation of Yb\(^{3+}\) ions. This is shown schematically in figure 7(a).

As we can see in figures 6(d), (b), this conclusion can be true for both red and green emissions. The significant dependence of red emission decay time on the S/V ratio also indicates that the \(4I_{9/2}\) level is coupled with some non-radiative processes dependent on the S/V ratio. These processes also could be related to wCR, \(w_{\text{MP}}\) (populating \(4I_{9/2}\) level) or ETU (\(w_{\text{ETU}}\)) (populating \(4I_{9/2}\) level).

Thus, when effective decay time decreases monotonically with Yb\(^{3+}\) content, the G/R ratio shown in figure 4 follows nonlinear behavior. This indicates that the main contribution to the increase in the G/R ratio with the reduction in the size of NCs is change in the excitation mechanism,
which was related to aggregation of Yb\(^{3+}\) ions, not to the mechanism related to depopulation of levels. However, when the NC sizes became small enough (or more generally when the S/V ratio is sufficiently high) most of the ions became surface ions coupled with surface ligands and the G/R ratio follows the expected tendency and decreases with S/V increasing.

To prove that aggregation of Yb\(^{3+}\) ions can also have a significant influence on emission decay time via the \(w_{ETU}\) mechanism only, we measured the emission decay for a reference set of samples with varying Yb\(^{3+}\)% and NC sizes kept nearly the same. In figures 6(a), (c) we can see that by adding Yb\(^{3+}\) ions we can also influence both red and green emission kinetics of Er\(^{3+}\) ions. From these results we can see that effective decay time decreases monotonically with Yb\(^{3+}\) increase which is similar behavior observed when the S/V ratio was increased.

On the other hand, the manifestation of changes in excitation mechanisms of Er\(^{3+}\) ions due to Yb\(^{3+}\) aggregation could be seen in the behavior of the emission rise time. To get any quantitative data for this physical quantity we used three exponential models instead of the effective decay time approach. However, it is worth mentioning that the obtained values do not have any physical interpretation and are encumbered with a high error. These results can be discussed only as relative to each other and having a qualitative character only.

In figures 8(a) and (c) we can see that in the case of small NCs (6 nm) the rise time related to the \(^5S_{3/2}\) state is equal to 7 \(\mu s\), whereas for big NCs (18 nm) this value increases up to 22 \(\mu s\). This results from the fact that for small NCs, Er\(^{3+}\) ions are excited by several Yb\(^{3+}\) ions simultaneously (because of Yb\(^{3+}\) aggregation) but for big NCs this excitation is fulfilled more in a sequential way with the contribution of non-radiative relaxation between the energy levels of Er\(^{3+}\) ions. Thus, the emission rise time is longer for big NCs. Moreover, in figures 8(a) and (c) we can see that when the shell is grown on core NCs, the rise time increases significantly (from 7 to 20 \(\mu s\)) for small NCs and only a little for big NCs (from 22 to 27 \(\mu s\)). This means that the excitation/relaxation mechanism does not change significantly for big NCs when the shell is formed.

This is because the ions are distributed homogenously. In contrast, for small NCs with Yb\(^{3+}\)–Er\(^{3+}\)–Yb\(^{3+}\) aggregates, shell formation enables ions to diffuse and thus achieve homogenous ionic distribution. Figures 8(b) and (d) show the same results which were obtained for the \(^1F_{9/2}\) state. Analyzing the obtained results, we can see that the conclusions are similar to the green emission. These results show also that the excitation mechanism for both schematic explanations given in figure 5(d) should be considered as an idealistic limit because the clustering of Yb\(^{3+}\) ions has an impact on the excitation mechanism of both energy levels (green and red).
Moreover, efficient reduction of the rise time in the case of red emissions can occur also due to more effective coupling of the ions to surface ligands as well as Er$^{3+}$–Er$^{3+}$ cross-relaxation and thus faster relaxation of carriers from $^{4}S_{3/2}$ down to $^{4}F_{9/2}$ for smaller NCs.

Conclusions

In this study three sets of the samples (with different sizes, shapes and Yb$^{3+}$ concentrations) were investigated.

For the samples with different shapes, the emission and excitation properties of Er$^{3+}$ ions were mainly determined by the interaction of Er$^{3+}$ ions with the surface of the NCs (i.e. ligands) via multiphonon relaxations between the energy levels of Er$^{3+}$ ions. This results in G/R ratio decrease with an increase in S/V ratio and a small reduction in the effective emission decay time for both red and green emissions.

However, for the samples with different sizes, where the NC sizes were reduced, we found an untypical increase in the G/R ratio and the significant effective emission decay time reduction with the NC size reductions. We proposed that observed results can be understood if we assume NC ion aggregation is size dependent. We showed that this aggregation (Yb$^{3+}$ mainly) had an impact not only on the relaxation but also on the excitation mechanisms of Er$^{3+}$ ions. As a consequence, this aggregation was manifested in the properties of Er$^{3+}$ ions and also had an influence on the emission decay via the depopulation of emitting levels due to ETU processes. For small NCs, when Er$^{3+}$ ions are in a Yb$^{3+}$ cluster environment, the ETU mechanism depopulates emitting energy levels more effectively. Also in these conditions, the main excitation mechanism due to ETU (+GSA) is related to the red emitting level. In the case of big NCs we deal with more homogenous ion distributions and the main excitation channel is related to the green emitting level and also depopulating mechanisms are much less efficient.

Moreover, we showed that aggregation of ions can be reduced for small NCs when the un-doped shell is grown on the NC core due to out-diffusion of both ions from the core to the shell region.

Figure 7. Schematic diagrams defining processes which should be taken into account when analyzing emission and excitation processes in small and big $\beta$-NaGdF$_4$:Yb$^{3+}$, Er$^{3+}$ with relatively low concentrations of ions.
Acknowledgments

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Figure 8. Emission decay curves together with three exponential fits obtained for core-β-NaGdF4:Yb3+(10%), Er3+(5%) and core–shell-β-NaGdF4:Yb3+(10%), Er3+(5%)/NaGdF4 NCs for (a), (b) a small core diameter (7 nm) and (c), (d) a big core diameter (17 nm).
28 Nanotechnology (2017) 175706


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