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The gadolinium effect on crystallization behavior and luminescence of β-NaYF₄:Yb,Er phase

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Abstract: Single phase β-NaY₀.₈₆GdₓYb₀.₁₈Er₀.₀₂F₄ nanoparticles with different concentrations of gadolinium ions were prepared via PVP assisted solvothermal treating at 200°C (PVP-polyvinylpyrrolidone). With the increase of Gd³⁺ concentration, size of the nanoparticles decreased. The up-converting spectra recorded upon 980 nm irradiation showed the green
(510-560 nm) and red (640-690 nm) emissions, due to $^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions, respectively. The strongest up-conversion luminescence was detected in 15 mol% Gd$^{3+}$ doped nanoparticles obtained after 20 h of solvothermal treating. With the rise of Gd$^{3+}$ content up-conversion emission decreased due to increased defect concentration in the NaYF$_4$ matrix. Fourier transform infrared spectroscopy proved in situ generation of hydrophilic nanoparticles as a result of PVP ligands retention at the particle surface.

Keywords: Optical materials; Up-conversion; NaYF$_4$; Gd-doping

1 | INTRODUCTION

Up-conversion (UC) materials, which have the ability to covert low energy photons that belong to near infrared (NIR) part of spectrum into higher energy photons of visible light, are of a great interest in the last decade due to their wide application such as solid state lasers$^{1,2}$, optical data storage$^3$, solar cells$^4$, temperature sensors$^{5,6}$, drug delivery carriers$^{7-9}$, scintillators$^{10}$, biomarkers$^{11,12}$. Such materials include tungstates$^{13}$, molybdates$^{14}$, oxides$^{15,16}$, fluorides$^{17}$, oxyfluorides$^{18-20}$, etc. Fluorides of NaYF$_4$ type are considered to be representatives, due to their low phonon energy (about 350 cm$^{-1}$), low toxicity, high chemical stability and fact that are excellent hosts for rare earth elements doping. Rare earth (RE) dopants serve as sensitizers (Yb$^{3+}$, Nd$^{3+}$) or activators (Er$^{3+}$, Tm$^{3+}$, Ho$^{3+}$) in the up-conversion process. There are two polymorphs of NaYF$_4$ phase: high-temperature metastable cubic $\alpha$, and low-temperature stable hexagonal $\beta$-phase. The synthesis of a pure hexagonal phase in nanoparticles is of a great importance, because up-conversion efficiency of this phase is higher than that of $\alpha$-phase. This is due to existence of two independent cation sites for
dopant ions accommodation which quadruples the number of possible Yb$^{3+}$ to Er$^{3+}$ energy-transfer processes and increases the probability of efficient radiative decays$^{21,22}$. This fact is a challenge, because during the syntheses of nanoparticles through soft chemistry methods, cubic phase usually prevails$^{23}$. It was shown that the manner of NaYF$_4$:RE synthesis, as well as the used precursors, influence the morphology and the crystal structure of the final product. Thus, in the reverse microemulsion processing ratio of surfactant, oil and water, along with calcination temperature, affect the morphology and agglomeration state of the nanoparticles, as well as their crystal structure$^{24}$. In a synthesis method which employ high temperature boiling solvents (oleic acid or octadecene), it was revealed that high amount of sodium precursor promotes nucleation of NaYF$_4$:RE β-phase$^{25}$. During hydro/solvothermal synthesis temperature, time and structure directing agents determine which NaYF$_4$:RE polymorph will be obtained$^{7,26,27}$. The effect of polydentate ligands, such as EDTA (ethylenediaminetetraacetic acid) and citrates, on crystal structure and morphology of NaYF$_4$/Yb$^{3+}$, Er$^{3+}$nanoparticles was investigated by Sun et al. and it is founded that regardless of ligand used, the α→β phase transformation is sensitive to reaction time and reactant concentration$^{7}$. Li et al. fabricated hexagonal microprisms and octadecahedra of β-NaYF$_4$/Yb$^{3+}$,Er$^{3+}$ phase under different pH values and fluoride sources after 24 h of hydrothermal treatment$^{27}$. Wang et al. reported solvothermal synthesis of β-NaYF$_4$/Yb$^{3+}$,Er$^{3+}$ nanoparticles using stearate precursors and mix of solvents, i.e. ethanol, water and oleic acid$^{26}$. Apart of metallo-organic compounds exploitation, it was reported that doping of NaYF$_4$:RE cubic phase with Gd$^{3+}$, Fe$^{3+}$ or Ti$^{4+}$ ions also provokes α→β phase transformation. For instance, it was shown that gadolinium doping in content higher than 15 mol% enables full conversion of α- to β-NaYF$_4$ phase when oleic acid and RE-stearates are used during synthesis$^{26,28}$. Similar phase transition effect was achieved by introducing Fe$^{3+}$ into NaYF$_4$:Yb,Er in the range of 5-20 mol% during oleic acid assisted hydrothermal...
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solvolthermally treated at 200 °C for 2, 6, 12 or 20 h, with continual stirring (100 rpm). After cooling to the room temperature, the obtained powders were washed with water and ethanol several times, collected by centrifugation (7000 rpm) and dried at 80 °C for 3 h.

Nomenclature of NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ samples is given in accordance to gadolinium content and processing time as Gd-15-2, Gd-15-6, Gd-15-12 and Gd-15-20 (for Gd content of 15 mol% and synthesis times of 2, 6, 12 and 20 h, respectively) and Gd-30-2 and Gd-30-12 (for Gd content of 30 mol% and synthesis times of 2 and 12 h, respectively).

The phase composition of the as-prepared powders was determined by the X-ray powder diffraction (XRPD) using Rigaku SmartLab, equipped with a Cu-Kα source (λ= 1.5406 Å). The patterns were recorded with a step scan of 0.02° and accounting time of 2 s per step. Rietveld refinement of the samples structures was done in Topas 4.2 software using a Fundamental Parameter approach. The background was refined using a fourth-order Chebyshev polynomial. Refinement of the hexagonal phase was carried out in $P6_3/m$ (No. 176) space group. Isotropic size-strain analysis was performed using a predefined double-Voigt approach (volume weighted mean column height, FWHM based LVol). Due to the observed preferential orientation, the spherical harmonic formulation, also referred as “orientation distribution function”, is included in fitting of diffraction lines intensities.

The nanoparticles morphological characteristics and crystal structure were investigated by transmission and high resolution transmission electron microscopy (JEOL JEM 2100, operating at 200kV). Detection of polymer ligands on the particles surface was done by Fourier transform infrared spectroscopy (FTIR) using Thermo Scientific Nicolet 6700 spectrophotometer (Thermo Fisher Scientific) with a Smart iTR Diamond Attenuated Total Reflectance accessory. Spectra were recorded using typically 128 scans at the resolution of 4 cm$^{-1}$. Photoluminescence emission measurements were performed at room temperature using Spex Fluorolog with C31034 cooled photomultiplier under diode laser excitation at 980 nm.

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Figure 1a shows XRPD patterns of $\beta$-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles synthesized solvothermally for 2 to 20 h and with different concentration of Gd$^{3+}$ ions. As one could see, all of detected diffraction lines are in well agreement with ones related to $\beta$-NaYF$_4$:Yb,Er phase (JCPDS 28-1192), while narrow sharp peaks indicate the good crystallinity of samples regardless of the processing time. The most intense XRPD reflections of (110) and (101) planes are shifted to lower 2Theta with the rise of Gd$^{3+}$ content due to the unit cell expansion which resulted from partial substitution Y$^{3+}$ by larger Gd$^{3+}$ ions, Fig. 1b. It is obvious that gadolinium presence promotes direct nucleation of $\beta$-phase from precursor solution, while mixed $\alpha$ and $\beta$-NaYF$_4$:Yb,Er phased product crystallizes under the same processing conditions, as it was shown in our previous study$^{31}$. This could be a consequence of its different tendency towards electron cloud distortion and dipole polarizability when compared to yttrium$^{32}$. Namely, in cubic NaYF$_4$ lattice with CaF$_2$ structure, substitution of yttrium with gadolinium decreases the charge transfer with fluoride ions, resulting in the decrease of dipole polarizability and formation energy; contrary, in hexagonal lattice where two types of low symmetry cation sites exist along with ordered array of fluoride ions, introducing of gadolinium will facilitate the charge transfer to fluoride, provoking an increase of polarizability and formation energy of $\beta$-phase$^{32}$. Data obtained through Rietveld refinement of the XRPD patterns, Table 1, shows that introducing of gadolinium with a larger ionic radius led to the increase of crystal lattice proportionally to its content. Also, with a prolongation of synthesis time, better rearrangement of RE$^{3+}$ ions is indicative from the reduction of the microstrain values and the unit cell volume. Restricted augment of the crystallite size from 59 to 75 nm and from 64 to 67 nm, in samples with 15 and 30 mol%, respectively, with a prolongation of the solvothermal treating time (from 2 to 20 h and from 2
to 12 h, see Table 1) confirms gadolinium role in confinement of nanoparticle growth through increase of the charge density on the particles surface$^{32}$.

**FIGURE 1** XRPD patterns of $\beta$-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles (a), (b) and Rietveld refinement of samples: Gd-30-2 (c) Gd-30-12 (d) Gd-15-2 (e) Gd-15-6 (f) Gd-15-12 (g) Gd-15-20 (h).

Table 1. Refined microstructural parameters of the $\beta$-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles

Morphological characteristics of synthesized powders are presented in Figure 2. All the samples are composed of irregularly shaped and slightly agglomerated particles which size is estimated to be 60-70 nm. These values match well with the size of crystallites determined through Rietveld refinement (Table 1). With the prolongation of the synthesis, nanoparticles grow to be more uniform in size and shape. Their HRTEM images show defect-free structure and presence of Moire fringes induced by the lattice mismatch of two adjacent crystallites. Clear lattice fringes with spacings of 2.92, 2.67 and 5.13 Å are consistent with (101), (200) and (100) planes of $\beta$-NaYF$_4$:Yb,Er phase (JCPDS 28-1192). The rings made up of discrete spots of indexed (hkl) planes, presented at SAED patterns in Figure 2 (last column), imply high crystallinity of all synthesized nanoparticles, while indexed (hkl) planes are consistent with XRPD data and JCPDS card (JCPDS 28-1192). It is noteworthy that SAED pattern of isolated nanoparticle presented in Figure 2l, which exhibits spots of the (001), (111) and (210) planes additionally confirms the monocrystalline nanoparticle formation.
FIGURE 2 TEM/HRTEM/SAED images of β-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles: Gd-30-2 (a-c) Gd-30-12 (d-f) Gd-15-2 (g-i) Gd-15-12 (j-l).

In order to explore retention of the PVP functional groups at the nanoparticle surface, FTIR spectra of the synthesized samples and of pure PVP were recorded. Following adsorption bands are detected at: 2950 cm$^{-1}$ (asymmetric CH$_2$ ring stretch), 2922 cm$^{-1}$ (symmetric CH$_2$ chain stretch), 1657 cm$^{-1}$ (C=O stretching), from 1465 to 1387 cm$^{-1}$ (pyrrolidone ring stretching) and at 647 cm$^{-1}$ (amide IV stretching). Decrease of their intensity and slight shifting of their positions (when compare with counterparts detected in PVP spectrum) implies successfully coordinated to the Na$^+$ and RE$^{3+}$ cations from the surface of the synthesized nanoparticles.$^{33,34}$

FIGURE 3 FTIR analysis of β-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles.

FIGURE 4 Up-converting spectra of β-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles excited at 980 nm (a) corresponding CIE and energy level diagram of Gd$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ dopants (b); inset in up-converting spectra shows enlarged spectrum of Gd-30-2 sample while numbers in CIE are assigned to samples in following manner: 1- Gd-30-2; 2- Gd-30-12; 3- Gd-15-2; 4- Gd-15-6; 5- Gd-15-12; and 6- Gd-15-20; green to red intensity ratio (c) and emission intensities vs synthesis time for samples doped with Gd 15 mol% (d).

The up-converting spectra (Figure 4a), taken upon 980 nm irradiation, show the emission in green (510-560 nm) and red (640-690 nm) regions. Green bands in the ranges of 510-530 and 530-560 nm were ascribed to $^2$H$_{11/2}$→$^4$I$_{15/2}$ and $^4$S$_{3/2}$→$^4$I$_{15/2}$ transitions, respectively. As can be seen from the Figure 4a, splitting of the green emission peak at 540 nm on several narrow lines is due to the $^4$S$_{3/2}$ energy level ripping, and is indication of the Er$^{3+}$ ions homogeneous distribution in the β-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ phase.$^{35}$ Red emission originates from $^4$F$_{9/2}$ to $^4$I$_{15/2}$ transition and is in accordance to the energy diagram of Yb$^{3+}$ and Er$^{3+}$ dopants (Figure...
Following the 980 nm excitation, Yb$^{3+}$ crosses from $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state by excited state absorption. Simultaneously, energy transfer provokes shifting of Er$^{3+}$ ion from ground $^4I_{15/2}$ state to intermediate $^4I_{11/2}$ state, and further to $^4F_{7/2}$ excited state. Afterward, the non-radiative decays to $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ states enable $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$ → $^4I_{15/2}$ radiative transitions and appearance of the green and red emission lines in photoluminescence spectra. As it is depicted at the same diagram, Gd$^{3+}$ energy levels are too far to participate directly in these processes. The change in the relative intensity of green to red emissions, obtained by dividing the respective integrated areas of the corresponding spectral lines (Figure 4c) are ranged in descending order as follows: 0.46 (Gd-15-20), 0.43 (Gd-15-12), 0.41 (Gd-15-6), 0.40 (Gd-15-2), 0.31 (Gd-30-12) and 0.30 (Gd-30-2). In particular, several groups of authors have been observed change of the relative intensity of the multi-peaks up-conversion with varying particle/crystallite size which could not be explained by classic theories but is rather attributed to a surface quenching effect. It is obvious that samples with lower gadolinium content, particularly one obtained during synthesis of 20 h, have the strongest green emission with CIE (0.37, 0.62). The explanation can be found in the reduction of the surface defects due to the longer thermal treatment and diminishing of microstrain, see Table 1, weakening the non-radiative decays. It is clear that intensities of green and red emissions exponentially rise with a prolongation of synthesis time in samples doped with 15 mol%, Figure 4d. Strengthening the of the $^4F_{9/2}$ → $^4I_{15/2}$ transition is most intense with the time (rise of about 70 times is detected) due to a more homogeneous distributions of dopants in crystal matrix which directly build-up energy transfer from Yb$^{3+}$ to Er$^{3+}$ ions. With further increasing of the Gd$^{3+}$ content to 30 mol% UC emission decreased as a consequence of the higher microstrain induced by the substitution of yttrium with bigger ion (Table 1, as well as due to increased rate of the non-radiative recombination which suppress the UC emission.
CONCLUSIONS

In conclusion, we have prepared single phased $\beta$-NaY$_{0.8-x}$Gd$_x$Yb$_{0.18}$Er$_{0.02}$F$_4$ nanoparticles from non-toxic inexpensive RE-nitrates through one-step PVP assisted solvothermal synthesis. With increasing Gd$^{3+}$ content up to 30 mol%, crystal lattice expands, while the size of crystallites become smaller. It was shown that 15 mol% of Gd$^{3+}$ is optimal doping concentration which ensures generation of a pure hexagonal phase with a low defect concentration and intense up-converting green light emission (0.37, 0.62) which can be clearly observed by the naked eyes. Due to in situ functionalization with PVP ligands, nanoparticles which size is of about 60 nm possess biocompatible hydrophilic surface convenient for further conjunction with antigens suitable for specific cell labeling.

Acknowledgements

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References


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Figure captures

**FIGURE 1** XRPD patterns of β-NaY₀.₈₋ₓGdₓYb₀.₁₈Er₀.₀₂F₄ nanoparticles (a), (b) and Rietveld refinement of samples: Gd-30-2 (c) Gd-30-12 (d) Gd-15-2 (e) Gd-15-6 (f) Gd-15-12 (g) Gd-15-20 (h).

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