Structural, optical and magnetic properties of Y$_{3-0.02-x}$Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$ ($0 < x < 0.20$) nanocrystals: effect of Yb content

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Abstract

The paramagnetic Y$_{3-0.02-x}$Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$ ($x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20$) nanocrystals (NCs) were synthesized by the microwave-induced solution combustion method. The XRD, TEM and SEM techniques were applied to determine the NCs’ structures and sizes. The XRD patterns confirmed that the NCs have for the most part a regular structure of the Y$_3$Al$_5$O$_{12}$ (YAG) phase. The changes of the distance between donor Yb$^{3+}$ (sensitizer) and acceptor Er$^{3+}$ (activator) were realized by changing the donor’s concentration with a constant amount of acceptor. Under 980 nm excitation, at room temperature, the NCs exhibited strong red emission near 660 and 675 nm, and green upconversion emission at 550 nm, corresponding to the intra 4f transitions of Er$^{3+}$ ($^4I_{9/2}$, $^4I_{15/2}$, $^4S_{3/2}$) → Er$^{3+}$ ($^4I_{15/2}$). The strongest emission was observed in a sample containing 18% Yb$^{3+}$ ions. The red and green emission intensities are respectively about 5 and 12 times higher as compared to NCs doped with 2% of Yb$^{3+}$. In order to prove that the main factor responsible for the increase of the upconversion luminescence efficiency is reduction of the distance between Yb$^{3+}$ and Er$^{3+}$, we examined, for the first time the influence of hydrostatic pressure on luminescence and luminescence decay time of the radiative transitions inside donor ion. The decrease of both luminescence intensity and luminescence decay times with increasing hydrostatic pressure was observed. After applying hydrostatic pressure to samples with e.g. 2% and 6% Yb$^{3+}$, the distance between the donor and acceptor decreases. However, for higher concentrations of the donor, this distance is smaller, and this leads to the effective energy transfer to Er$^{3+}$ ions. With increasing pressure, the maximum intensity of near infrared emission is observed at 1029, 1038 and 1047 nm, what corresponds to $^2F_{5/2} → ^2F_{7/2}$ transition of Yb$^{3+}$.

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1. Introduction

In modern biological and medical research, nanostructures (NS) based on oxide materials, are widely applicable as upconverting markers. Mainly in the use are the NS in which the upconversion process takes place using energy transfer between Yb\(^{3+}\) ion (donor, sensitizer) and Er\(^{3+}\) (acceptor, activator) ion. In this case, when the matrix is doped with two elements, Er\(^{3+}\) and Yb\(^{3+}\) the efficiency of upconversion process increases. The upconversion is a process of effective conversion of infrared radiation of 900–1000 nm to visible light. The Yb\(^{3+}\) ion exhibits a relatively large absorption cross-section (of 1.2 \times 10^{-20} \text{ cm}^2) at 980 nm. In comparison, the absorption cross-section of Er\(^{3+}\) ions is 1.7 \times 10^{-21} \text{ cm}^2 (at 980 nm) [1]. The ytterbium electron structure minimizes the disadvantageous damping concentration processes, which come from cross-relaxation (CR). The energy transfer between two ions (Er\(^{3+}\) and Yb\(^{3+}\)) leads to depopulation of the excited states. The Yb\(^{3+}\) ions in garnet structure have the ground \(^{2}F_{7/2}\) and excited \(^{2}F_{5/2}\) states splitted into four and three Kramer’s doublets, respectively [2]. It has a wide absorption band corresponding to \(^{2}F_{7/2} \rightarrow ^{2}F_{5/2}\) transition, in the range of about 900 to 1000 nm and generates radiation in a wide spectral range from about 1000 to 1100 nm. The luminescence lifetime of the excited state in different materials, for example oxyfluoride glasses [3] and Er,Yb:YAG ceramics [4, 5] ranges from 700 to 1400 \(\mu\)s [6].

For the practical applications, one strives to obtain the nanostructures with the highest luminescence efficiency. The upconversion luminescence efficiency depends, among others, on the type of the matrix, in which rare earth (RE\(^{3+}\)) ions are embedded.

The crystal structure of the matrix determines the symmetry of the surroundings of the embedded rare earth ions and thus the admissible kinds of radiation transitions. The type of atoms and their arrangement in space specifies the energy phonons of the crystal lattice and thus has influence on the radiation transitions in the RE\(^{3+}\) ion.

An important factor determining the quantum efficiency of luminescence in the upconversion process is the distance between the sensitizer and the activator [7]. The influence of Zn\(^{2+}\) ions doping on the crystal lattice constant of the Gd\(_2\)O\(_3\) matrix doped with Yb\(^{3+}\) and Er\(^{3+}\) ions is described in our previous work (Kamińska et al [8]). We have shown there that doping with Zn\(^{2+}\), whose ionic radius is smaller than that of Gd\(^{3+}\) ions, by contracting—reducing the crystal lattice constant, leads to an increase of the efficiency of the upconversion process, due to the decrease of the distance between sensitizer and activator.

Another important type of matrix in which the efficient luminescence of RE\(^{3+}\) ions is observed, is the yttrium aluminum garnet—YAG. The yttria-alumina system comprises of four crystalline phases: yttrium aluminum perovskite (YAP), Y\(_2\)Al\(_2\)O\(_5\); yttrium aluminum monoclinic (YAM), Y\(_2\)Al\(_2\)O\(_5\); yttrium aluminum garnet (YAG), Y\(_3\)Al\(_5\)O\(_{12}\) and yttrium aluminum hexagonal (YAH), Y\(_2\)Al\(_2\)O\(_3\) [9–12]. YAG is a promising host for upconverting materials, because of its high melting point (1940 °C) and good chemical stability and low phonon energy [13–16]. Low phonon energy increase the probability for upconversion (UC) process. This material also has high thermal conductivity and large mechanical strength. YAG is also a very valuable component in high temperature ceramic composites, because of its well known resistance to creep. The refractive index value of YAG matrix is \(n = 1.83\), the optical band gap is equal to \(E_g \approx 6.5 \text{ eV} [17]\) and phonon frequency is \(h\omega_{\text{max}} = 105 \text{ meV} [18, 19]\).

Rare earth ions (Er\(^{3+}\), Yb\(^{3+}\)) doped Y\(_3\)Al\(_5\)O\(_{12}\) nanopowders are very important materials because of their applications: solid state laser, luminescence systems, fiber-optic telecommunication systems and as window glass materials [20, 21]. The RAlO\(_3\) perovskites (R = Lu, Gd, Pr, Tb and their combinations) are very good candidates for highly efficient single crystalline film scintillators [22–24].

Various types of nanomaterials of different dimensionality (0D clusters; 1D nanotubes, fibers and rods; 2D films and coats), based on YAG matrix doped with rare earth ions, were synthesized by several different methods. The zero dimensional nanostructured materials, the upconverting nanocrystals doped by Tm\(^{3+}\) and Yb\(^{3+}\) were prepared by a co-precipitation method [25]. Bi et al. [26] fabricated the quasi-one-dimensional YAG:Er\(^{3+}\), Yb\(^{3+}\) nanobelts by electrospinning technique. The Yb\(^{3+}\) ions, were used as activators in Y\(_3\)Al\(_5\)O\(_{12}\) host synthesized by solution combustion method, in the presence of a citric acid as fuel [27, 28]. Li [29] reported on the preparation of spherical Nd doped yttrium aluminum garnet nanocrystals by the solvothermal method. The Eu\(^{3+}\) doped YAG nanopowders have been synthesized by a combustion method using a mixture of citric acid and EDTA as fuels [30]. The single phase YAG nanopowders, were synthesized by solution combustion method using a fuel mixture (glycine and urea) by Laishram et al. [31]. The monodispersed nanospheres based on the YAG matrix was also doped by cerium (Ce\(^{3+}\)) ions applying the hydrolysis method [32]. Dong et al. [33] synthesized hydrophilic YAG nanoparticles doped Ce\(^{3+}\) ions by a solvothermal method and used them for cell-imaging. The YAG:Ce/YAG:Cr core–shell structure was designed and accomplished via the urea homogeneous precipitation method by the group of Qin et al. [34] Zammouri et al. [35] synthesized highly homogenous, with photocatalytic properties YAG:Ce/ZnO core/shell NPs using the high-energy ball milling technology.

The pure phase of cubic YAG doped with Yb\(^{3+}\) and Ho\(^{3+}\), 40 nm nanocrystals, has been synthesized by Liu et al. [36] using co-precipitation of nitrate and ammonium hydroxide carbonate. Marcinia et al. [37] prepared the YAG:Cr\(^{3+}\), Nd\(^{3+}\) nanocrystals by modified Pechini method, could be used as a triple luminescent thermometer. The transparent polycrystalline YAG ceramics have been successfully fabricated by vacuum sintering of co-precipitated raw powders [38]. The ceramics have been doped with different Er\(^{3+}\) concentration. The Yb\(^{3+}\) doping was used to enhance the photoelectrical properties of the laser action of the ceramics. The Tm\(^{3+}/\text{Yb}^{3+}\) and Er\(^{3+}/\text{Yb}^{3+}\) co-doped YAG single crystal
have been grown by laser heated pedestal growth. The crystal fibers have potential application in optical thermometry by the determination of the upconversion fluorescence intensity ratio [39, 40].

Bulk materials based on YAG doped with erbium and ytterbium ions has been synthesized by Mierczyk et al [41] with the use of the Czochralski method for eyesafe laser application.

The few reports are currently available concerning the YAG matrix doped Er³⁺ and Yb⁴⁺ ions. Desirena et al [42] prepared Yb⁵⁺/Er³⁺ co-doped YAG porous nanocrystals by glycolate method assisted with polyvinylalcohol (PVA) and urea. The NCs with 10% Yb⁵⁺ concentration, exhibited strong green emission, while above 20% of Yb³⁺ colour turned to orange-red. The energy transfer efficiency was 72% for 20% Yb⁵⁺ concentration. The enhancement of photocatalytic activity has been showed by Pickering et al [43] for the YAG: Yb³⁺, Er³⁺ composite in the presence of TiO₂. Spherical YAG:RE³⁺ (RE = Pr³⁺, Tm³⁺, Yb³⁺, Ce³⁺, Eu³⁺, Nd³⁺, and Er³⁺; Yb⁵⁺) nanoparticles obtained by Jain et al [44], are good candidates for applications in bioimaging, light display systems, and lasers.

The Yb and Er doped YAG monocrystals are active medium in lasers that emit ‘safe for the eyes’ wavelength of 1600 nm. As of late on one can find increasing interest in the lasers, which instead of monocrystals, use transparent ceramic nanopowders received by sintering at high temperatures and lasers, which instead of monocrystals, use transparent ceramic nanopowders.

### 2. Experimental details

#### 2.1. Synthesis of NCs

For preparation of \(Y_{3−x}Er_x0.02Yb_xAl_3O_12\) (\(0 < x < 0.20\)) NCs we applied a microwave-induced solution combustion synthesis. This process is an exothermic redox (oxidation and reduction reactions taking place simultaneously) reaction between an oxidizer and a fuel. The redox solution was made by mixing a stoichiometric amount of the metal nitrates (oxidizer) and urea (reducer, fuel) dissolved in water. After thorough mixing and obtaining clear solution, the substrates were placed in a microwave oven. A modified setup was previously shown in our previous work [8]. The microwave oven was used to achieve a homogeneous temperature distribution in the heated mixture. During the heating process water evaporated and the reagents’ temperature increased to about 700°C when an auto ignition of the mixture took place. Turbulent exothermic reaction occurred (at 1500°C) with a large amount of emitted heat and evaporated reagents. The released gaseous ingredients cooled and formed the metal oxides. Because of vapour-based formation the growth of the nanocrystals was restrained. The table S1 is available online at stacks.iop.org/NANO/31/225711/mmedia, the supporting information shows the chemical compositions of mixtures used in the synthesis of the nanocrystals.

The combustion formation process of the pure YAG by the redox mixture method is carried out as follows:

\[
3Y(NO_3)_3 + 5Al(NO_3)_3 + 20CO(NH_2)_2 = Y_3Al_5O_12 + 20CO_2 + 40H_2O + 32N_2.
\]

The NCs were investigated using a laboratory X’Pert Pro Alpha1 MPD (Panalytical) diffractometer (\(\lambda = 1.5406\) Å). The samples’ quantitative and crystal structure analyses were done with the help of Rietveld method.

We obtained the crystal structure, morphology and size of the NCs by TEM measurements, in this case the \(Y_{3−x}Er_x0.02Yb_xAl_3O_12\) (\(0 < x < 0.20\)) NCs with 2% of Er³⁺ and different concentration of Yb³⁺ ions were dissolved in ethanol solution. Next, the samples were deposited on the copper mesh pre-coated with thin carbon film (300 Mesh Cu, Pacific Grid Tech.). After the complete evaporation of ethanol, the copper mesh was placed in the transmission electron microscope chamber. The selected nanocrystals were studied in three imaging modes: in a bright field, dark field and using high resolution TEM. The study was performed using Talos F200X (FEI) transmission electron microscope operating at 200 kV.

We applied a high resolution microscope SEM-Auriga (Carl Zeiss) to conduct the samples analysis. The electron beam acceleration voltage was regulated in the range from 1 to 5 kV for imaging mode and for the EDS mode from 10 to 15 kV. The samples in ethanol solution were dropped on silicon wafer glued by silver paste to the aluminum holders.

The photoluminescence spectra for \(Y_{3−x}Er_x0.02Yb_xAl_3O_12\) (\(0 < x < 0.20\)) NCs, were measured by Jobin Yvon spectrometer with SPEX 270 M monochromator equipped with a cooled liquid nitrogen CCD (Si) matrix. The samples
were excited by IR laser diode (Lumics model LU0980D300-DNA014) at 980 nm (continuous wave). The upconversion spectra were measured in the visible range from 500 nm to 700 nm, Shortpass Filter FES0700 (Thorlabs) was applied. In addition in DMSO solution absorptive neutral density filter (NE30B unmounted ø25 mm absorptive ND filter, optical density: 3.0, Thorlabs) was used.

In the time-resolved photoluminescence measurements of Yb$^{3+}$ ions in the presence of Er$^{3+}$ ions in the NCs with/without high hydrostatic pressure, we used the following instruments: the spectra in the NIR and VIS regions were determined by a double grating GDM1000 monochromator with photomultiplier tube (PMT) (H10330B-45 Hamamatsu). The SCHOTT long-pass filter (edge filter) RG1000 was used. The Yb$^{3+}$ ions in the selected samples were excited with 940 nm Shanghai Dream Lasers, in continuous mode (output power >100 mW). High pressure measurements were performed using a low-temperature diamond-anvil cell (Diaccell Products MCDAC-1). More details concerning this type of experiments is described previously in work: Kamińska et al [50]. We used two pressure-transmitting medium: argon (enclosed in a diamond chamber under liquid nitrogen conditions) and Poly(dimethylsiloxane) (PDMS) oil.

The magnetic properties of the examined compounds were characterized using a superconducting quantum interference device (SQUID magnetometer—Quantum Design MPMS XL-7, San Diego, CA, USA). The data was collected using the Reciprocating Sample Option (RSO) measurement. The sample (in powder form) was placed in a paraffilm capsule in a measuring holder. Measurements were carried out for multiple temperatures in the range 2.0–300.0 K (set with 0.01 K accuracy), using magnetic field up to 7.0 T (±0.05 G accuracy). Sample masses were measured using analytic scale (table S9, supporting information).

3. Results and discussion

3.1. Y$_{3-x}$Er$_x$Yb$_{0.02}$Al$_5$O$_{12}$ (0 < $x$ < 0.20) nanocrystals: structural and morphological properties

We synthesized, by a microwave-induced solution combustion method, six samples of Er$^{3+}$ and Yb$^{3+}$ doped nanocrystals, with the following compositions: Y$_{3-x}$Er$_x$Yb$_{0.02}$Al$_5$O$_{12}$ (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20). The list of the samples is presented in table S2 (supporting information). The Er$^{3+}$/Yb$^{3+}$ ratios in the samples are proportional and close to the reagents’ solutions compositions.

The crystal structure of the NCs was examined by XRD (figure S1(a)–(f), supporting information). Because the samples were not calcinated after synthesis, all of the obtained nanocrystalline samples were multiphase and consisted of three crystalline phases. In our samples, the dominant crystalline phase is cubic Y$_3$Al$_5$O$_{12}$ garnet (space group Ia-3d). This phase is the main source of Y$_{3-x}$Er$_x$Yb$_{0.02}$Al$_5$O$_{12}$ (0 < $x$ < 0.20) NCs luminescence. The second identified crystalline phase is orthorhombic YAlO$_3$ (space group Pnma) and the last phase was identified as hexagonal YAlO$_3$ (space group P6$_3$/mmc). Weight percentages of individual phases in samples are shown in table S3 (supporting information). Detection of the third phase (YAH) is a very interesting result. To our knowledge, the creation of this phase is possible only in the high-energy combustion method at a relatively high temperature by applying constant pressure. The presence of YAH phase in the Y$_{3-0.02-0.02}$Yb$_{0.02}$Al$_5$O$_{12}$ NCs which is also shown in table S3. The YAH phase in the non-equilibrium crystal structure has been previously observed in the Y$_3$Al$_2$O$_6$Ce$^{3+}$ crystals [12]. The presence of the minority phases, does not affect the luminescence properties of the NCs.

The literature data and experimental lattice parameters of the XRD Rietveld refinement of Er$^{3+}$ and Yb$^{3+}$ doped NCs at room temperature are shown in table S3. The effective radius of Yb$^{3+}$ (86 pm) is smaller than that of Y$^{3+}$ (89 pm), so doping Yb$^{3+}$ into YAG garnets reduces the crystal lattice parameters values. Generally, the size of the crystal unit is influenced by the size of the atom, but it can also depend on the presence of defects. Thus, in the case of Y$_3$Al$_5$O$_{12}$ cubic phase its lattice parameter value decrease from 12.0106(2) to 12.0078(1) with the increase of Yb$^{3+}$ concentration as shown in figure S2(a) (supporting information). It does present the linear dependence. On the other hand, in the orthorhombic YAI0$_3$ phase we observed the anisotropy of lattice constant changes. The a lattice parameter increase with function of Yb$^{3+}$ doping whereas the b and c lattice parameter decrease, as shown in figures S2(b)–(d) (supporting information). The lattice parameter a of the hexagonal YAI0$_3$ phase also decreases but c value slightly fluctuates (see figure S2(c) and (f), supporting information). These results confirm successful Yb$^{3+}$ samples doping.

The SEM images (figures 1(a)–(f)) show the morphology of the Y$_{3-0.02}$Er$_{0.02}$Yb$_{0.02}$Al$_5$O$_{12}$ (0 < $x$ < 0.20) NCs doped by Yb$^{3+}$ different concentrations. The size of the NCs (width and height) are summarized in table S4 (supporting information).

The high resolution TEM (HRTEM) was used to characterize crystallinity of the Y$_{3-0.02-0.02}$Er$_{0.02}$Yb$_{0.02}$Al$_5$O$_{12}$, x = 0.20 (IF10) NCs. The HRTEM images showed presence of Y$_3$Al$_5$O$_{12}$ garnet phase (figures S3(a)–(d), supporting information). The interplanar distances are about 4.95 Å and 3.21 Å, which can be ascribed to the (211) and (321) planes of cubic YAG NCs, respectively (figure S3(a)). The study revealed good crystallinity of the NCs. The diffraction peaks can be indexed to the cubic YAG phase (figure S3(b)). The selected area diffraction pattern of the YAG powder clearly indicates the polycrystalline nature of the particles [51] (figures S3(c)–(d)).

The presence of the main phase (Ia-3d) was studied by STEM. The contrast of the bright field STEM (BF STEM) image was mainly due to different orientations of the grains whereas the contrast of the high angle annular dark field STEM (HAADF STEM) image was due to local precipitation of other crystal structures (local chemical composition) [52].
Figure 1. The SEM images of Y_{3-0.02-x}Er_{0.02}Yb_{x}Al_{5}O_{12} (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) with different concentration of Yb^{3+} ions: (a) 2% (IF5) (b) 6% (IF6) (c) 10% (IF7) (d) 12% (IF8) (e) 18% (IF9) (f) 20% (IF10).

The BF STEM image presented in figure 2(a) shows an average grain size of 200 nm for the IF10 sample NCs. The HAADF STEM image (figure 2(b)) confirmed presence of cubic Y_{3}Al_{5}O_{12} phase. The energy dispersive spectroscopy (EDX) mapping was used to show the distribution of elements that form the nanocrystals.

The presence of the elements of the YAG matrix i.e. Y and Al (figures 2(c),(d), (g), (h)) and erbium (Er^{3+}) and ytterbium (Yb^{3+}) dopants (figures 2(e)–(f)) were corroborated. Figure 2(h) shows the EDX profile of the elements of the host material and doping ions with an additional signal from the copper mesh on which the NCs were deposited.

3.2. Optical properties of the Y_{3-0.02-x}Er_{0.02}Yb_{x}Al_{5}O_{12} (0 < x < 0.20) NCs

The higher Yb^{3+} is ion concentration, the smaller is the distance between Yb^{3+} and Er^{3+} ions. We observed the dependence of luminescence intensity of the upconversion [radiation transitions in the acceptor (Er^{3+}) ion] and the intensity of radiation transitions inside the Yb^{3+} ion (donor) as a function of the doping level.

In order to check the influence of different Yb^{3+} ions concentration in the starting solutions on the anti-Stokes emission in Y_{3-0.02-x}Er_{0.02}Yb_{x}Al_{5}O_{12} (0 < x < 0.20) garnets, photoluminescence measurements were carried out at room temperature.

We examined two forms of NCs samples: pure powder (figures S4(a)–(h), S5(a)–(d), supporting information) and powder suspended in a DMSO (dimethyl sulfoxide) solution (figures 3(b)–(c)). In the first case, the luminescence spectra of the NCs with 2% of Er^{3+} and different concentration of Yb^{3+} ions, in the visible area from 510 to 590 nm and from 640 to 700 nm are shown in figures S4(a)–(h) and S5(a)–(d) (supporting information). The spectra were obtained for excitation from a variable power density semiconductor laser at a wavelength of 980 nm (CW). The maximum of the green luminescence of the nanocrystals was received at 530 nm, what can be attributed to the characteristic transitions in Er^{3+} (4I_{15/2} \rightarrow 4I_{11/2}). The maximum of the red luminescence of the NCs was measured at 660 nm and it came from the 4I_{11/2} \rightarrow 4I_{15/2} and 4I_{11/2} \rightarrow 4F_{9/2} transitions, which contribute to the intra 4f–4f transitions of Er^{3+} ions. The area under the curve of green and red luminescence as a function of concentration of Yb^{3+} ions in the garnet matrix and the laser power densities were shown in figures S6(a)–(b) (supporting information).

The increase of luminescence intensities was observed with the change of Yb^{3+} doping ions concentration in the Y_{3-0.02-x}Er_{0.02}Yb_{x}Al_{5}O_{12} (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) NCs (figures S6(a)–(b), supporting information). The upconversion emission comes from the energy transfers (ET) between Yb^{3+} and Er^{3+} ion pairs. The emission depends on the ET processes in Er^{3+} ions: 4I_{15/2} \rightarrow 4I_{11/2}, 4I_{11/2} \rightarrow 4F_{9/2} [5]. The maximal intensity of green and red luminescence was observed for 18% Yb^{3+} (IF9) ions concentration, as shown in figures S6(a), (b) and figures 4(a)–(d). The optimum Yb^{3+} doping concentration is 18%, when Er^{3+} is 2% in the YAG NCs. This enhancement depends on the distance between the Yb^{3+} and Er^{3+} ions.

The average distance between the acceptor (activator) and donor (sensitizer) energy is a useful parameter for the estimation of the chosen dopant concentrations and the host lattice. Nadrot et al [7] calculated of the typical average distance between Yb^{3+} and Er^{3+} (20% Yb^{3+} and 2% Er^{3+}) in the NaYF_{4} (hexagonal structure). The Yb^{3+} and Er^{3+} can be used to substitute the host Y^{3+} ions without changing the crystal structure. The distance in this case was 6.5068 Å. In the cubic Y_{3}Al_{5}O_{12} garnet structure the coordinates (x, y, z) of the Y^{3+} ions are fixed: (0.125; 0.000; 0.25) and the distances between Er–Y, Yb–Er and Y–Yb are a function of the lattice parameter a. We calculated the average distance between
Yb\(^{3+}\) and Er\(^{3+}\) pair as a function of Yb\(^{3+}\) concentration for two phases in the Y\(_{3-0.02-x}\)Er\(_{0.02}\)Yb\(_x\)Al\(_5\)O\(_{12}\), \(x = 0.20\) (IF10) NCs. The element mappings of (c) Al and Y (d) O and Y (e) Er (f) Yb and (g) Al of the NCs. (h) Confirmed presence of Er\(^{3+}\) and Yb\(^{3+}\) ions in the EDX spectra of the NCs matrix.

Kang et al \[53\] have found the optimal Yb\(^{3+}\) concentration for YAG: Er\(^{3+}\), Yb\(^{3+}\) powder synthesized by a flux (BaF\(_2\)) assisted solid-state reaction method. These authors do not discuss the enhancement of the upconversion luminescence. In their case, the optimum donor (Yb\(^{3+}\)) concentration for the highest red luminescence was 20\% and the acceptor (Er\(^{3+}\)) concentration was fixed at 25\%. Those results were received for the calcinated samples from 700 °C to 1500 °C. On the other hand, we present results for the not calcinated YAG: Er\(^{3+}\), Yb\(^{3+}\) nanostructures.

The higher Yb\(^{3+}\) ion concentration, the smaller the distance between Yb\(^{3+}\) and Er\(^{3+}\) ions, which enhances the...
The upconversion spectra of six $\text{Y}_3\text{Er}_{0.02}\text{Yb}_{0.02}\text{Al}_5\text{O}_{12}$ ($x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20$) samples (in powder form) under the 980 nm laser excitation for four selected laser power densities (CW): (a) 0.30 W cm$^{-2}$ (b) 0.80 W cm$^{-2}$ (c) 1.06 W cm$^{-2}$ and (d) 1.30 W cm$^{-2}$.

Figure 4. The upconversion spectra of six $\text{Y}_3\text{Er}_{0.02}\text{Yb}_{0.02}\text{Al}_5\text{O}_{12}$ ($x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20$) samples (in powder form) under the 980 nm laser excitation for four selected laser power densities (CW): (a) 0.30 W cm$^{-2}$ (b) 0.80 W cm$^{-2}$ (c) 1.06 W cm$^{-2}$ and (d) 1.30 W cm$^{-2}$.

Scheme 1. The effect of increasing the Yb$^{3+}$ concentration on the reduction of the average distance between Er$^{3+}$ and Yb$^{3+}$ ions.

Figure 3(a) shows the upconversion spectra of $\text{Y}_3\text{Er}_{0.02}\text{Yb}_{0.02}\text{Al}_5\text{O}_{12}$ NCs doped 2% Er$^{3+}$ and 20% Yb$^{3+}$ in DMSO solution (figures 3(b), (c)). The NCs exhibited highly efficient, visible to the naked eye luminescence in green region, with the maximum at the wavelength of 545 nm ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{15/2}$) and red luminescence, with the maximum at the wavelength of 661 nm ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$). The slope (n) value for the green emission was 2.07 ± 0.13 and for the red emission was 2.24 ± 0.11. Those emissions arose from a two-photon upconversion process (figure S8, supporting information). Wonsik et al. [54] synthesized cubic $\text{Lu}_{3-x-y}\text{Yb}_{x}\text{Er}_{y}\text{Al}_5\text{O}_{12}$ ($x = 0.18, 0.54, 0.90, 2.16; y = 0.03, 0.09, 0.15, 0.21$) powders by a flux method. The slopes values for the phosphors, $n = 1.83$ and $n = 1.64$ corresponding to 557 nm and 679 nm for powders, respectively, were estimated. Table 1 show comparison of different optimal donor to acceptor ratios and their influence on the luminescence intensity enhancement values of the YAG matrixes prepared by various synthesis methods, with different shapes of nanoscale materials (for samples in the form of powder) and ceramics.

The number of photons ($n$) involved in the upconversion process, both in pure powder form and suspended in a DMSO solution, was determined. These results were obtained from the area under the curve of the red and green luminescence, shown in figures S9 and S10(a)–(f). In the case of pure powders the measurements were carried out for 12 selected 980 nm laser power densities: 0.35, 0.48, 0.56, 0.60, 0.80, 0.83, 0.94, 1.06, 1.14, 1.22 W cm$^{-2}$. The luminescence intensity of the NCs was
Table 1. Comparison of the luminescence intensity enhancement values of different YAG nanostructures and ceramics doped with Er$^{3+}$ and Yb$^{3+}$ ions found in literature.

| Laser excitation (nm) | Composition Y$_3$Al$_5$O$_{12}$: x% Er$^{3+}$, y% Yb$^{3+}$ | Type of materials and calcinations condition | Power density (W cm$^{-2}$) | Increase of luminescence in powder form | Synthesis method | References |
|-----------------------|--------------------------------------------------|---------------------------------------------|----------------------------|--------------------------------------|--------------------|------------|
| 980                   | 2% Er$^{3+}$ 18% Yb$^{3+}$                        | Nanocrystals (not calcinated)               | 0.35 0.80 1.06            | 7.5 10 9.0 9.5                      | Microwave-induced solution combustion | In this work |
| 980                   | 1% Er$^{3+}$ 30% Yb$^{3+}$                        | Nanospheres (at 1100 °C for 3 h)            | 1.30                     | Not discussed                       | Energy-saving microwave-assisted synthesis | Jain et al [44] |
| 970                   | 1% Er$^{3+}$ 20% Yb$^{3+}$                        | Nanocrystals (at 1000 °C for 4 h)           | Data not shown 2.0       | Integrated intensity               | Glycolate method assisted with poly-vinyl alcohol (PVA) Co-precipitation method | Desirena et al [42] |
| 980                   | 1% Er$^{3+}$ 25% Yb$^{3+}$                        | Nanopowders (at 800 °C, 1100 °C, 1200 °C for 2 h) | Not discussed            | 554 nm 648 nm 5.0 10               | Electrospinning Technique | Bi et al [26] |
| 980                   | 1% Er$^{3+}$ 15% Yb$^{3+}$                        | Nanobelts (at 900 °C for 8 h)               | Data not shown           | 678 nm 20 60                        | High temperature solid-state reaction method under vacuum conditions | Tang et al [56] |
| 917                   | 0.5% Er$^{3+}$ 5.5% Yb$^{3+}$                     | Ceramics (at 1720 °C for 10 h with the vacuum condition; at 1450 °C for 10 h in oxygen atmosphere) | Not discussed            |                                      | —                  | Tikhomirov et al [57] |
| 980                   | 1.5% Er$^{3+}$ 4.5% Yb$^{3+}$                     | Glass-ceramics                              | Not discussed            |                                      | —                  | —          |
| 940                   | 1% Er$^{3+}$ 25% Yb$^{3+}$                        | Ceramics (at 1550 °C for 10 h)              | Data not shown           | 560 nm 678 nm 20 60                | Solid-state reaction and the vacuum-sintering technique | Zhou et al [5] |
measured in the visible area, and the increase of luminescence between Er$^{3+}$ levels with increasing laser power density is clearly visible. The interaction mechanism between the Yb$^{3+}$ and Er$^{3+}$ ions was verified by determining the relationship between the UC emission intensity ($I_{em}$) and the input (excitation) power ($P$) [54]. The UC emission intensity $I_{up}$ was proportional to the incident pumping power $P$ as $I_{up} \propto P^{n}$, where $n$ is the number of infrared photons involved in a single visible photon generation [52]. The number of photons $n$ involved in the upconversion process for Y$_{1−x}0.02−x$ Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$ ($0 < x < 0.20$) NCs were summarized in table S5 (supporting information).

The slopes values with the logarithmic dependences of emission intensity as a function of laser power density were obtained (figures S10(a)–(f)). For the NCs with 2% Yb$^{3+}$ and 6% Yb$^{3+}$ concentrations, the green emission (515–570 nm) slopes values were 1.20 ± 0.20 and 1.58 ± 0.10, respectively. The values of $n$ were approximately equal to 2, which implied the lower thermal effect and saturation effect in the garnets. The thermal effect could be attributed to exposure to the laser beam at a wavelength of 980 nm. For higher concentration of Yb$^{3+}$ ions in the garnet’s matrix and for higher excitation of NIR laser power, more NIR photons are absorbed which could have led to the increase of the samples’ temperature. For the wavelength of 660 nm the slopes values were 2.10 ± 0.13 and 1.55 ± 0.10, respectively. For other samples doped with 10%, 12%, 18% and 20% Yb$^{3+}$ ions, the slopes for both green and red emissions were much larger than 1, indicating that a two-photon process is responsible for the emissions (table S5). The quadratic dependence indicates that all red emission arise from the two-photon UC processes.

3.2.1. High-pressure luminescence. Stationary and time-resolved photoluminescence measurements of Yb$^{3+}$ ions in the presence of Er$^{3+}$ ions in the Y$_{3−0.02−x}$ Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$ ($0 < x < 0.20$) nanocrystals.

In order to demonstrate that the main factor responsible for enhancement of the efficiency of the upconversion luminescence is reducing the distance between the Yb$^{3+}$ and Er$^{3+}$ ions, we studied the influence hydrostatic pressure on the luminescence (scheme 2) and luminescence decay time of the radiation transitions inside the Yb$^{3+}$ donor ion. To reduce the distance between the Yb$^{3+}$ and Er$^{3+}$ ions in the YAG NCs, the diamond anvil cell was used, which allows one to obtain hydrostatic pressure up to 20 GPa.

The stationary spectra of the luminescence of the NCs were measured in two areas, in the visible (VIS) region from 538 to 562 nm and in the near infrared (NIR) region, from 943 to 1064 nm, for two selected samples of garnets with variable Yb$^{3+}$ ion concentration, i.e. (2%) (IF5 sample) and 20% (IF10 sample). The NCs were excited by 940 nm laser, continuous mode, $P_{ext} > 100$ mW. In the first stage, in the VIS region, the measurements were carried out in ambient conditions. In the VIS region the luminescence of the NCs with 20% Yb$^{3+}$ was about 16 times greater than that of the sample with less Yb$^{3+}$ ion concentration (2%) in the garnet matrix, as shown in figure S11(a) (supporting information). It confirms that the energy transfers at 20% Yb$^{3+}$ is much better. Whereas in the second NIR region, the luminescence of the NCs with 20% Yb$^{3+}$ decreased, while from 2% Yb$^{3+}$ increased (figure S11(b)).

The next stage of the research was confined to the measurement of the effect of hydrostatic pressure on the luminescence spectrum of Y$_{3−0.02−x}$ Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$ NCs, $x = 0.02$ (figures S11(a), (b), (supporting information) and $x = 0.2$ (figures 5(a) and S12(a)–(c)). In both cases, the argon was used as a pressure-transmitting medium. Argon was enclosed in a diamond-anvil cell. We observed the change in the shape of emission peaks and a decrease of luminescence intensity of NCs with 2% Yb$^{3+}$ at a maximum wavelength of approximately 1047 nm ($^2F_{5/2} \rightarrow ^2F_{7/2}, 5 \rightarrow 4$) with an increase in applied hydrostatic pressure from 0.9 GPa to 6.5 GPa, as shown in figures S14(a), (b). The maximum emission peak shifts towards shorter wavelengths as shown in figures S14(b). The decrease in the intensity of the emission peak with the increase of the applied hydrostatic pressure was reported by Runowski et al. [58] for pressure measurements of LaPO$_4$ and YPO$_4$ phosphates co-doped with rare earths Yb$^{3+}$–Tm$^{3+}$ ions. This phenomenon was related to the increased probability of nonradiative energy transfer cross-relaxation (shorter interionic distances) and multiphonon (higher phonon energy and larger electron–phonon coupling) relaxation processes in the compressed materials [58].

The pressure dependence of the Yb$^{3+}$ in Y$_{3−0.02−x}$ Er$_{0.02}$Yb$_x$Al$_5$O$_{12}$, $x = 0.2$ nanocrystals luminescence is shown in figure 5(a) in the pressure range up to about 14.3 GPa. We measured the Yb$^{3+}$ luminescence in the NCs in the NIR region from 1000 to 1053 nm. Three emission peaks were recorded from the transitions between levels ($^2F_{5/2} \rightarrow ^2F_{7/2}$) in the Yb$^{3+}$ ions, at the maximum wavelengths: 1029 nm, 1038 nm (5 $\rightarrow$ 3) and 1047 nm (5 $\rightarrow$ 4).

With the increase of the hydrostatic pressure we observed a decrease in the intensity of the emission peak located at the wavelength of 1029 nm (5 $\rightarrow$ 3), which was visible during the measurements without pressure (figures 5(a) and S12(a)).

The maximum emission peak shifted towards longer wavelengths up to 1034 nm with increasing hydrostatic
pressure up to 14.3 GPa. An increase in the intensity of the emission peak was also observed for the second maximum peak at 1037 nm (from 0 GPa to 9.3 GPa) and its slight shift towards longer wavelengths to 1038 nm (from 9.3 GPa to 14.3 GPa) (figure S12(b)). After application of hydrostatic pressure (from 2.9 GPa to 9.3 GPa), the shift of the emission peak located at the maximum at a wavelength of 1047 nm towards shorter wavelengths was observed. The increase in hydrostatic pressure from 11.5 GPa to 14.3 GPa caused a slight shift of the emission peak towards higher wavelengths up to 1048 nm, as shown in figure S12(c).

We measured cooperative luminescence as a Yb\(^{3+}\) ion concentration function in the Y\(_2\)Al\(_2\)O\(_3\) matrix with the same concentration of Er\(^{3+}\) (2%) for two samples (IF5) 2% and 20% (IF10). The fluorescence lifetime plot of the \(^5\text{F}_{3/2} \rightarrow ^5\text{F}_{7/2}\) transition in Yb\(^{3+}\) was shown in figures S13 (a), (b) (supporting information). The luminescence decay curves measured at 969 and 1029 nm were fitted by a double-exponential functions, whose indexes t1 and t2 represent the luminescence decay times as shown in figures S13(a), (b). For the wavelength of 969 nm the luminescence decay times were 575 \(\mu\)s and 169 \(\mu\)s (2\% Yb\(^{3+}\)); 140 \(\mu\)s and 349 \(\mu\)s (20\% Yb\(^{3+}\)), respectively. We observed shortening of the luminescence decay time in the range of 1029 nm for 2\% Yb\(^{3+}\) and 20\% Yb\(^{3+}\), 167 \(\mu\)s and 511 \(\mu\)s; 123 \(\mu\)s and 249 \(\mu\)s, respectively, as shown in table S6 (supporting information).

The shortening of the luminescence decay time measured at a wavelength of 1030 nm, with increased concentrations of Yb\(^{3+}\) ions was also observed by Wu et al [59] in the Gd\(_2\)Ce\(_2\)O\(_7\): Yb\(^{3+}\), Er\(^{3+}\) phosphors for 980 nm excitation. As the cross relaxation CR1 process depends on the Yb\(^{3+}\) ion concentration and becomes more efficient with increasing Yb\(^{3+}\) ion concentration, the decreased CR1 probability in higher Yb\(^{3+}\) ion concentration doped samples may be due to the reverse CR1 process, i.e. \(^5\text{F}_{7/2} (\text{Yb}^{3+}) + ^{4}\text{I}_{9/2} (\text{Er}^{3+}) \rightarrow ^{5}\text{F}_{5/2} (\text{Yb}^{3+}) + ^{4}\text{I}_{13/2} (\text{Er}^{3+})\), which also relies on the Yb\(^{3+}\) ion concentration. In higher Yb\(^{3+}\) ion concentration doped samples, larger population in the \(^5\text{F}_{5/2}\) state results in an efficient reverse CR1 process, which counteracts the increased efficiency of the CR1 process, decreasing the calculated CR1 probability [58].

In order to check the influence of hydrostatic pressure on luminescence of garnets’ nanostructures, the time-resolved studies of NCs with the highest concentration of Yb\(^{3+}\) ions \(x = 0.2\) (Y\(_{1−0.02−}\)Er\(_{0.02}\)Yb\(_{0.02}\)Al\(_2\)O\(_3\)) were performed, as shown in figures S15(a)–(c) and 5(b).

The measurements were carried out at three wavelengths: 999 nm (5 \(→\) 1), 1030 nm (5 \(→\) 3) and 1047 nm (5 \(→\) 4) without pressure and at pressures from 2.9 to 14.3 GPa, when excited by laser with a wavelength of 940 nm (figures S15(a), (c)). The abridgment of luminescence decay time was observed with increasing hydrostatic pressure for all observed wavelengths (figure 5(b)). The luminescence decay curves measured in this case were fitted by a single-exponential functions, whose index t1 represent the luminescence decay time and the values are listed in table S7 (supporting information).

The luminescence decay time of Yb\(^{3+}\) ions for two samples with 2\% Yb\(^{3+}\) (IF5) and 6\% Yb\(^{3+}\) (IF6) concentration (figures S16(a), (b), supporting information) was measured, respectively. It turned out that after closing the samples in a pressure chamber filled with argon, the luminescence was strongly extinguished with only a slight increase of pressure. As a result of this strong extinguishment of luminescence, no decay times could be determined as shown figure S16(a). The disadvantageous effects of luminescence quenching in hydrostatic pressure after placing the samples in the chamber with diamond anvils may be related to the different surface structure of the crystals used in the experiment. The altered surface to volume proportions may affect the ion placement, and thus energy transfer processes and the different effects of excited individuals on the NCs surface. However, the physical cause of the drastic drop in the luminescence and luminescence decay at a low hydrostatic pressure requires further analysis and extended research.

The pressure dependence of the Yb\(^{3+}\) in \(x = 0.06\) (Y\(_{1−0.02−}\)Er\(_{0.02}\)Yb\(_{0.02}\)Al\(_2\)O\(_3\)) NCs luminescence was shown in figures S17(a), (b) (supporting information) in the pressure...
range up to about 20 GPa. In the second experiment the poly(dimethylsiloxane) (PDMS) oil was used as a pressure-transmitting medium. We measured luminescence of Yb$^{3+}$ ions in the matrix, in the NIR region from 1000 to 1053 nm. Three emission peaks were recorded from the transitions between levels in Yb$^{3+}$ ions $2F_{7/2} \rightarrow 2F_{5/2}$, with the maximum at wavelengths: 1029 nm, 1038 nm ($5 \rightarrow 3$) and 1042 nm ($5 \rightarrow 4$). In this case we observed a strong extinguishment of luminescence with increasing pressure and it was not possible to determine the luminescence decay times. The intensity of the emission peak at a wavelength of 1042 nm decreased with increasing hydrostatic pressure. The maximum of the emission peak moves towards shorter wavelengths (figure S17(a)). The intensity of the emission peak at 1047 nm fluctuated and initially increased from 0 to 0.7 GPa. Next, we observed a decrease in emission intensity and a shift of this peak towards higher wavelengths up to 1049 nm, at a hydrostatic pressure of 12.5 GPa. The increase in hydrostatic pressure to 20 GPa caused a decrease in the intensity of luminescence and a shift towards shorter wavelengths (figures S17(a), (b)).

For the sample with 6% Yb$^{3+}$ (IF6) concentration (in the oil medium) it was possible to determine the luminescence decay as a function of the hydrostatic pressure as shown in figures 6(a) and S18(a) (supporting information). The luminescence decay time for the sample as a function hydrostatic pressure at the excitation 940 nm was measured. The signal was monitored at the wavelength of 1047 nm ($5 \rightarrow 4$) (figures S18(a) and 6(b)). The luminescence decay time have an exponential profile for 6% Yb$^{3+}$ in the tested sample as shown in figure 6(b), and have shortened from 500 ± 4 μs (for 0.7 GPa) to 269 ± 5 μs (for 20 GPa). The luminescence decay time for the nanocrystals without hydrostatic pressure was 526 ± 2 μs (table S8, supporting information). The shortening luminescence decay time for the YAG nanostructures doped only with Yb$^{3+}$ ion was observed by Boulon et al [60]. This quenching phenomenon means there is an increase of the nonradiative links due to the increasing of the pressure, that is to say the increasing of perturbation on Yb$^{3+}$ sites with a stronger effect on the sites in the vicinity of the grain boundaries.

The above results show that the measure of the enhancement of the upconversion luminescence efficiency can be the transitions intensity in the NIR inside Yb$^{3+}$ ion and luminescence decay time.

3.3. Magnetic properties of the $Y_{3-x}AlO_3$ $Er_{x}Yb_{0.02}Al_5O_{12}$ ($0 < x < 0.20$) NCs

Magnetic properties of the up-converting $Y_{3-x}AlO_3$ $Er_{x}Yb_{0.02}Al_5O_{12}$ ($x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20$) NCs (see table S2, supporting information) were measured using superconducting quantum interference device magnetometer (Quantum Design SQUID MPMS XL-7). Measurements were performed in temperatures from 2.0 to 300.0 K and under magnetic fields up to 7.0 T (figures 7(a), S19 supporting information).

The results showed that the all up-converting NCs reveal paramagnetic properties at a low temperature. Magnetization (equation (1), supporting information) of the measured nanocrystals increases linearly with Yb$^{3+}$ concentration (figure 7(b)) and can be reasonably described by a combination of the Brillouin functions (equation (2), supporting information) appropriate for the spins $J = 15/2$ (Er$^{3+}$) and $J = 7/2$ (Yb$^{3+}$) (see table S9, supporting information), especially for the lowest Yb$^{3+}$ concentrations. The experimental details are described in the supporting information.

The observed paramagnetism of up-converting NCs opens a possibility to use external magnetic field to additionally control (for example magnetic targeting [33] or hyperthermia [61]) multifunctional nanocrystals with both optical and magnetic properties. Unfortunately for the studied samples, with up to $x = 0.2$ of Yb$^{3+}$, at the temperature of human body paramagnetic properties of $Y_{3-x}AlO_3$ $Er_{x}Yb_{0.02}Al_5O_{12}$ ($0 < x < 0.20$) were dominated by their diamagnetism.
between Yb$^{3+}$ and Er$^{3+}$ for the optimum Yb$^{3+}$ doping concentration (18%) in the NCs is 3.676 Å. The study confirms that the main factor responsible for the enhancement of the efficiency of the upconversion luminescence is reducing the Yb$^{3+}$–Er$^{3+}$ distance. The effects of the hydrostatic pressure on the decay time of emitting $^2F_{5/2}$ level for the x = 0.20 has been observed. It has shortened from 397 ± 4 μs to 221 ± 2 μs (999 nm) and from 450 ± 2 μs to 252 ± 1 μs (1030 nm) (at the pressure of about 14 GPa). At the same time, as the pressure increases, we observe a drop of the intensity of the luminescence of the Yb$^{3+}$ ions. Both these facts suggest the increase of the non-radiative processes with the increase of the hydrostatic pressure and thus decrease of the inter-ionic distances. Thru analogy with the experiments with increasing the Yb$^{3+}$ dopant concentration, where decrease of the average distances between ions leads to the increase of energy transfer between Yb$^{3+}$ (donor) and Er$^{3+}$ (acceptor) we can postulate, that the increase of the non-radiative processes caused by the pressure have the same mechanism.

Magnetization of examined up-converting NCs increases linearly with Yb$^{3+}$ dopant concentration, as expected for a paramagnetic system, where ion-ion interaction can be neglected.

### 4. Conclusions

The YAG NCs are a good candidate for nanoscintillators and lasers. The material is ideal host for the Er$^{3+}$ and Yb$^{3+}$ doping. The $Y_{3-x}Er_{x}Al_5O_{12}$ (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) can be successfully synthesized applying the solution combustion method. The NCs were multi-phasic, but it does not affect the luminescence of the tested material. About 70% of nanostructures’ volume have a cubic crystal structure $Y_3Al_5O_{12}$ ($Ia3d$), about 20% is the orthorhombic YAO$_3$ (Pnma) and the rest consists of hexagonal YAO$_3$ (P63/mmc) phase. The presence of the main YAG phase is confirmed by XRD and HRTEM studies. The NCs exhibited the visible luminescence at 530 nm ($^4I_{11/2}$/$^2S_{1/2}$ $\rightarrow$ $^4I_{15/2}$) and 660 nm ($^4I_{11/2}$ $\rightarrow$ $^4I_{15/2}$) in the organic environment. We observed a 12-fold (550 nm) and a 9.5-fold (660 nm) increase of luminescence intensity in the NCs, compared to the lowest concentration of Yb$^{3+}$ ions for the continuous wave laser excitation at 980 nm (1.30 W cm$^{-2}$ and 1.06 W cm$^{-2}$), respectively. This emission arose from a two-photon upconversion process. We have calculated the average distance between Yb$^{3+}$ and Er$^{3+}$ pairs as a function of Yb$^{3+}$ concentration, only for dominant crystalline phase of the NCs. The average distance

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