Optical gain in capillary light guides filled with NaYF₄: Yb³⁺, Er³⁺ nanocolloids

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Abstract: A capillary light guide optical amplifier using nanocolloids of Yb^{3+} -Er³⁺ co-doped NaYF₄ as a filler was successfully demonstrated. A 7-cm-long and 150-micron-innerdiameter capillary light guide was capable to amplify a pulsed optical signal at 1550 nm with a gain coefficient of 0.15 cm⁻¹ at a pump power of 4 mW (980-nm wavelength). The nanocolloid gain medium was prepared by pulverizing the phosphor powder with a highspeed planetary ball mill. Ball milling of the powder in water produced nanoparticles with a size of approximately 130 nm that after drying were transferred to a liquid with high refractive index (1.551 at 1550 nm) required to maintain light confinement within the fused silica capillary light guide. The results show that RE-doped colloids of nanocrystals can be potentially used as liquid gain media fillers in capillary light guide lasers and amplifiers with high photostability and low toxicity.

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1. Introduction

Nanocolloids of highly efficient downshifting and upconversion phosphors made of rare earth (RE) doped fluorides have attracted a lot of attention due to their potential application as biomarkers, optical gain media, solar spectrum converters for photovoltaic power, infra-red taggants, and anti-counterfeit inks [1-5]. Substantial amount of work has been done on preparing the nanocolloids of rare earth fluorides directly by various chemical methods [2, 6– 14]. The rationale was mainly to achieve high concentration of the particles in the colloid and their monodispersity. The tradeoff was the limited selection of the solvents and limited control of the size of the particles, their crystalline structure, and light emitting properties. In this regard, physical methods of reducing particle size of the compounds in order to turn them into nanocolloids suspended in a variety of liquids, such as by ball milling [15], present a reasonable alternative. After the powders are synthesized, they can be pre-treated (for instance, baked) in order to optimize their properties of interest (such as the brightness of downshifting or upconversion emission) before turning into nanocolloids, etc. This paper investigates the feasibility of using the exemplary nanocolloids of RE doped fluoride compound NaYF₄: Yb³⁺, Er³⁺ prepared by industrially accepted ball milling as a gain filling medium in capillary light guide optical amplifiers at 1550-nm wavelength. The approach can be extended to a wide variety of other RE compounds and spectral regions.

2. Preparation of the powders and characterization of their structural and optical properties

Compound NaYF₄: Yb³⁺, Er^{3+} (the well-known efficient downshifting and upconversion phosphor) has been was used in the past as a nanocolloid gain medium in the free-space optical amplifier configuration at 1550 nm [2]. The efficiency of conversion of the energy of pump radiation (from a 980-nm laser diode) in the phosphor is determined by the host:

hexagonal-phase crystalline fluoride NaYF₄ (β -NaYF₄). The low phonon energy of the crystal lattice of the host minimizes non-radiative multi-phonon relaxation processes of the excited RE dopants. The mechanisms of downshifting and upconversion of the phosphor have been studied since the early 1970-s [2, 8–16]. The energy level diagram of the RE ions of Yb^{3+} and Er^{3+} presented in Fig. 1 explains the mechanisms. The trivalent ion of Yb acts as a "sensitizer" efficiently absorbing the photon of a 980-nm pump radiation. The Yb is excited from its ground state ${}^{2}F_{7/2}$ to the ${}^{2}F_{5/2}$ state. Then, in the case of downshifting presented in Fig. 1(a), the energy transfer from Yb³⁺ to Er³⁺ occurs, resulting in the population of energy level ${}^{4}I_{11/2}$ of Er³⁺. The emission at 1550 nm then occurs after the Er³⁺ relaxes nonradiatively to its ${}^{4}I_{13/2}$ level and, then radiatively back to the ${}^{4}I_{15/2}$ ground state. In the case of upconversion illustrated in Fig. 1(b) there are three major emission bands at 515 nm (green light), 540 nm (green light), and 660 nm (red light), which are assigned to the ${}^{2}H_{11/2}$ to ${}^{4}I_{15/2}$, ${}^{4}S_{3/2}$ to ${}^{4}I_{15/2}$, and ${}^{4}F_{9/2}$ to ${}^{4}I_{15/2}$ transitions of the Er³⁺ ion, respectively. The energy transfer from the excited Yb³⁺ ion can promote Er^{3+} ion from the ${}^{4}I_{15/2}$ level to the ${}^{4}I_{11/2}$ level and from the ${}^{4}I_{11/2}$ level to the ${}^{4}F_{7/2}$ level by another energy transfer upconversion process (or a second 980 nm photon), if the ${}^{4}I_{15/2}$ level is already populated. Then, the Er^{3+} ion can relax nonradiatively to the ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ levels, and the green emissions occur (during transitions from level ${}^{2}H_{11/2}$ to ${}^{4}I_{15/2}$ and from ${}^{4}S_{3/2}$ to ${}^{4}I_{15/2}$). Alternatively, the ion can further relax and populate the ${}^{4}F_{q/2}$ level leading to the red emission (during transition from ${}^{4}F_{9/2}$ to ${}^{4}I_{15/2}$) [11, 14, 15]. The exact wavelength of the downshifting and upconversion photons can deviate by up to 10-15% from the abovementioned values (1550, 515, 540, and 660 nm) due to the doping rate, impurities, temperature, and other factors.

2.1 Synthesis and heat treatment

In this work NaYF₄ crystals co-doped with trivalent ions Yb³⁺ and Er³⁺ were synthesized using a solution based technique (wet process) [17] that was essentially a simplified version of the co-precipitation procedure in the presence of ethylenediaminetetraacetic acid (EDTA) [18]. First, 0.5 mol of NaF was dissolved in 60 ml of water. Second, the following aqueous RE chloride solutions were mixed together: 0.2 mol of YCl₃ in 16 mL of water; 0.2 mol of YbCl₃ in 3.4 mL of water; and 0.2 mol of ErCl₃ in 0.6 mL of water. The produced mixture of the aqueous solutions of the RE chlorides was added to the solution of 0.2 mol of EDTA in 20 mL of water to let the metal-EDTA complex to occur. All the RE chlorides, EDTA and NaF were obtained from Aldrich. The EDTA complex solution was quickly introduced into the NaF solution and the mixture was allowed to stir vigorously for several hours. After stirring, the mixture was allowed to stay overnight for the precipitate to settle. The precipitate was filtered, washed several times with distilled water and with ethanol. The precipitate was dried under vacuum to remove any traces of water. The resulting white powder had the doping rates according to formula NaY_{88%} Yb_{10%} Er_{2%} F₄.

Figure 2 presents the X-ray diffraction spectra of the synthesized NaYF₄:Yb³⁺, Er³⁺ powder baked after preparation for one hour at different temperatures in open air in comparison with the reference cubic α -phase NaYF₄ and hexagonal β -phase NaYF₄. The XRD spectra were taken with Bruker D2 Phaser X-ray diffractometer. With the increase of the baking temperature from "no-baking" to 300°C the powder remained in the α - NaYF₄

(cubic) phase. Starting from 400°C, the β - NaYF₄ (hexagonal) phase started to dominate. After 700°C, the β - NaYF₄ (hexagonal) phase was converted to the α -NaYF₄ (cubic) phase. Despite the fact that the powder was made using a solution-based process at near ambient conditions (no high temperature), the as-synthesized powder was the cubic, high temperature phase. The transition of low temp (hex) to high temp (cubic) phases is well-established to be at about 700°C, so that conversion is not surprising. Based on the "no baking" XRD, it can be assumed that the cubic phase appeared as a metastable phase synthesized at low temperature. The data suggest that heating to 400°C overcame a metastable barrier. There was a slight shift of the observed diffraction peaks from the synthesized powder baked at higher temperatures to the right from the peaks of the reference spectra. The higher the temperature, the larger was the shift (0.25, 0.5, 0.7, and 0.82 degree in average for 500°C, 600°C, 700°C, and 800°C respectively). This could be explained as follows. Since a solution-based synthesis approach was used, it might be OH substituting for F (which is quite common). Those OH groups were going to decompose upon heating somewhere in the 300-600°C range. That decomposition $(2OH = H_2O + O)$ would probably cause the unit cell to contract, as an OH group was missing from the structure, and the remaining deprotonated oxygen atom (the structure was still charge balanced in this way) would be a bit smaller than the original OH. This would result in a shift of the observed peaks to higher 2-theta angles. In the absence of OH, fluoride solids are somehow volatile when heated in air. If done in air, two volatile F atoms could be replaced by one O atom (in order to keep the charge balance), and the total absence of any atom at one of those F sites could contract the unit cell and cause a shift of the observed peaks.



Fig. 1. Energy diagrams describing energy transfer during the downshifting (a) and upconversion (b) emissions in NaYF₄: Yb³⁺, Er^{3+} pumped with a 980-nm laser diode.

2.2 Downshifting and upconversion emission

Optical fluorescent spectroscopy of the emission from the synthesized phosphor powder was conducted using a 980-nm laser diode PL980P330J from Thorlabs (330-mW maximum power, quantum-well laser chip, pigtailed with a wavelength stabilizing fiber Bragg grating) as a pumping source. In all the measurements, the samples were at room temperature. Optical fluorescence spectra were taken with a Princeton Instruments 500-nm focal-length Spectra Pro (SP–2500i) imaging spectrometer/monochromator equipped with 1200 gr/mm (blazed at 500 nm) holographic diffraction grating. Downshifting spectra were recorded with an amplified InGaAs infra-red sensor, and upconversion spectra – with PI-Max 1024 HQ Digital Intensified CCD Camera system. The crystalline powder was compressed into flat pellets

using a hydraulic press. The emission measurements were made in reflectance mode using a sample chamber with the sample pellets placed approximately at an angle of 45° with respect to the optical axis of the entrance slit of the monochromator. Figure 3(a) presents the downshifting fluorescence spectra of the powder for different baking temperatures. In Fig. 3(b) the intensity of the spectral peak at 1533 nm is plotted versus the temperature. The presented data clearly indicate that the hexagonal β -phase of the host NaYF₄ (existing at the baking temperatures between 550 and 750°C) was favorable for the most efficient downshifting emission. The highest intensity was reached at the baking temperature of \leq 700°C. Figure 3(c) presents the upconversion fluorescence spectra of the phosphor powder for different baking temperatures. In Fig. 3(d) the intensities of the spectral peaks at 540 nm (green) and 656 nm (red) are plotted versus the baking temperatures between 550 and 750°C) was also favorable for the most efficient upconversion emission as for the downshifting emission. The highest intensity at the baking temperature of \leq 700°C was also favorable for the most efficient upconversion emission as for the downshifting emission. The highest intensity was reached at the baking temperature of \sim 600°C.



Fig. 2. S XRD spectrum of the synthesized powder of NaYF₄: Yb³⁺, Er³⁺ at various baking temperatures. 1 – the reference XRD spectrum (calculated line pattern – JCPDS card No. 77-2042) of NaYF₄ α –phase (cubic); 2 – XRD spectrum of the synthesized powder of NaYF₄: Yb³⁺, Er³⁺ without baking; 3 - XRD spectrum of the synthesized powder of NaYF₄: Yb³⁺, Er³⁺ baked for 1 hour at 300°C; 4 - 400 °C; 5 - 500 °C; 6 - 600 °C; 7 - 700 °C; 8 - 800 °C; 9 – the reference XRD spectrum (calculated line pattern – JCPDS card No. 28-1192) of NaYF₄ β – phase (hexagonal).

3. Preparation of nanocolloids and characterization of their size and their optical properties

3.1 Ball milling and size distribution

Ball milling of the phosphor powder was performed using a PQ-N04 Planetary Ball Mill from Across International. Two 50-ml Zirconia cups and Zirconia balls of two sizes (5-mm and 0.5-mm diameter) were used. Ball milling was done three times with each set of balls. Each cup was loaded with the balls to the 2/3 of volume, 20 mL of distilled water, and ~2 g of the powder. Alternating directions of rotation were chosen with 5-min duration of the rotation in each direction and 10-min pause between rotations (for cooling). Number of rotation cycles was 60. The speed of rotation was 50 revolutions per second. After ball milling the resulting colloid was transferred with a pipette to an open container and dried. The dry powder was washed from the walls of the container with carbon tetrachloride (CCl₄) and collected in a glass tube. One drop of oleic acid (surfactant to prevent clustering of the nanoparticles) was added. The colloid was separated from the precipitate with a pipette, filtered through a 1-µm PTFE filter and collected in a clean tube.



Fig. 3. Optical emission from the powder of NaYF₄: Yb³⁺, Er³⁺ (excited with a 980-nm laser diode) versus the baking temperature: (a) downshifting emission spectra; (b) downshifting emission intensity at the 1533-nm spectral peak versus the baking temperature; (c) upconversion emission spectra; (d) emission intensity at the 540-nm (green) and 656-nm (red) spectral peaks versus the baking temperature.

The size of the nanoparticles of the colloid was measured using two techniques: dynamic light scattering (DLS) and atomic force microscopy (AFM). Figure 4(a) presents the results of the DLS size measurement with a Zetasizer 90 instrument from Malvern Instruments. According to the DLS measurement results, the colloid was dominated by the particles with an average size (diameter) of (122 ± 14) nm. Small portion of the colloid was made up of the

particles of a size between 1 and 2 nm. In order to conduct the AFM scan, the colloid was spin cast on the fresh (after peeling off the top layer) surface of a mica substrate. The solvent was dried out. AFM scan was conducted using the tapping mode. AFM image of the nanoparticles is presented in Fig. 4(b). The histogram of the statistical distribution of size of the nanoparticle (average effective diameter, assuming the particles are round shaped) is presented in Fig. 4(c). The average size was determined as (133 ± 35) nm, in agreement with the DLS data.

3.2 X-ray diffraction spectrum

Figure 4(d) presents the XRD spectrum of the phosphor nanopowder dried in open air at room temperature after ball milling. The spectrum was taken with a Bruker D2 Phaser X-ray diffractometer. The diffraction peaks correspond to the hexagonal β -phase of NaYF₄ (Fig. 2) meaning that the crystalline phase of the phosphor did not change after ball milling. Widening of the diffraction peaks (with partial overlapping of the adjacent peaks) is in the agreement with the reduction of the size of the phosphor particles from microns to a hundred nanometers after ball milling.



Fig. 4. Size of the ball-milled nanoparticles of NaYF₄: Yb³⁺, Er³⁺, and their X-ray diffraction properties. (a) Size distribution of the nanocolloid in CCl₄ obtained using the dynamic light scattering (DLS) measurement (Zetasizer 90). Solid and dashed lines correspond to two sets of measurement data. (b) AFM image of the nanoparticles dispersed on a mica substrate. (c) Histogram of the size (average diameter) distribution of the nanoparticles obtained from the AFM image analysis. (d) XRD spectrum of the ball milled nanopowder of NaYF₄: Yb³⁺, Er³⁺. The arrows and associated indices mark the positions of the calculated diffraction peaks of the computed line pattern of NaYF₄ hexagonal β –phase (JCPDS card No. 77-2042) also presented in Fig. 2.

3.3 Downshifting and upconversion emission from the nanocolloids

The dry ball-milled nanopowder was again suspended in carbon tetrachloride at a proportion of 1 g solids per 8 mL liquids. Carbon tetrachloride was selected because of its low optical

absorption in the infra-red region around the peak of the downshifting emission of the phosphor (~1530 nm). The colloid was sonicated in an ultrasonic bath for 60 min and left overnight to settle. Then the colloid was separated from the precipitate with a pipette, filtered through a 1- μ m PTFE filter and collected in a 10-mm-thick fluoroscopic cuvette. Figure 5(a) presents the image of a fluoroscopic cuvette filled up with the nanocolloid. The photograph was taken with an iPhone 6 camera at dimmed room light. One can see clearly rather bright trace of the visible upconversion emission produced by the focused beam (300-mW power) from a 980-nm laser diode (PL980P330J from Thorlabs) propagating through the nanocolloid. The downshifting and upconversion emission from the nanocolloid was collected with the tip of a multimode fiber placed against the wall of the cuvette close to the trace and transmitted to the entry slit of the Princeton Instruments Spectra Pro (SP–2500i) imaging spectrometer for analysis. The spectra are presented in Figs. 5(b) and 5(c). They are similar to the spectra of the initial phosphor powder (Fig. 3).



Fig. 5. Optical emission from the ball-milled nanocolloid: (a) Photograph (taken with the digital camera of iPhone 6) of a 10-mm-thick fluoroscopic cuvette with the nanocolloid of NaYF₄: Yb³⁺, Er^{3+} in CCl₄ prepared by ball milling. The streak of visible light inside the cuvette is the upconversion emission generated by a 980-nm laser beam propagating from the right to the left through the cuvette. (b) Spectrum of downshifting emission of the nanocolloid of NaYF₄:Yb³⁺, Er^{3+} in CCl₄. (c) Spectrum of upconversion emission of the nanocolloid.

4. Capillary optical amplifier

The ball-milled nanocolloid was investigated as the gain medium of a capillary optical light guide amplifier. The dry ball-milled nanopowder was suspended in refractive index matching liquid 1057B from Cargille Laboratories (refractive index 1.551 at 1550 nm) at a proportion of 1 g solids per 30 mL liquids. The solution was sonicated for 180 min and left to precipitate for 24 hours. The nanocolloid was collected from the top of the solution (in order to avoid any precipitates) and filtered through a 1- μ m filter. The filtered nanocolloid was used to fill a capillary tube made of fused silica (refractive index 1.449 at 1550 nm) with an inner diameter of 150 μ m.

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The block diagram of the experimental setup used to investigate the optical amplifier is presented in Fig. 6. Pump radiation (980-nm wavelength) from a laser diode (PL980P330J from Thorlabs) was mixed up with a pulsed 1550-nm optical signal in an optical fiber wavelength-division multiplexer (WDM) and injected via a single-mode 1550/980-nm fiber (SM980-5.8-125 from Thorlabs) in the nanocolloid-filled capillary light guide. The other end of the light guide was coupled with a multi-mode fiber. The output signal was analyzed either with a digital oscilloscope or with an optical spectrum analyzer (OSA) MS9740A from Anritsu.



Fig. 6. Block-diagram of the experimental setup to investigate the nanocolloid-filled capillary optical light guide amplifier.

Figure 7(a) presents the image of a 7-cm-long amplifier with the pump radiation (200-mW power) injected. Bright visible upconversion radiation emanating from the capillary light guide conveniently indicates the interaction between the pump radiation (being confined within the capillary light guide due to the total internal reflection) and the gain nanocolloid medium inside the tube. The decay of the upconversion emission also represents the loss of the power of the pump radiation propagating through the light guide. Oscillogram in Fig. 7(b) presents a typical input pulsed signal (at 1550-nm wavelength) amplified by the continuous pump of a relatively low power of 4.2 mW (after the pump starts exceeding 50-mW it becomes more and more consumed by the competing upconversion process). The amplifier gain coefficient G was defined here similarly to [2] as $G = 1/L \times Log(I/I_0')$, where L is the length of the light guide, I is the amplitude of the amplified signal, and $I_0' = I_0 \times 10^{|\alpha|L}$ (I_0 is the output signal intensity without pumping and α is the loss coefficient of the light guide). Based on the photometry of the light scattered from the light guide, α was estimated to be approximately -0.028 cm⁻¹. The gain coefficient could thus be determined as $G = 1/L \times Log(I/I_0) - \alpha$. Coefficient G plotted versus pump power (for 0.04 mW amplitude of the input pulses) is presented in Fig. 7(c). Flattening the gain that follows the increase of the pump power is expected since a large pump power will cause a severe depletion of the ground state (see Fig. 1(a)) leading to reduced absorption and pumping rate [2, 19]. This phenomenon, referred to as pump saturation, prevails in all threelevel systems where the lower gain state is the ground state, which by definition must be at

least 50% depleted simply to contain a population inversion. The fact that the gain flattening starts at relatively low (comparing to [2]) pump power could be related to the onset of the competing process of upconversion emission (which has, as a two-photon effect, the intensity proportional to the square of the pump power). This would require a further investigation going beyond this paper. Gain plotted against the amplitude of the input pulsed signal is presented in Fig. 7(d). The gain behavior for two pump powers (4.2 and 18 mW) is typical for Er-doped fiber amplifiers [19]. The gain remains flat for an input power of less than 15 dB (0 dB corresponds to 0.016 mW). Then the gain starts gradually falling off as the system experiences gain saturation. This arises from significant depletion of the upper state population of Er^{3+} ion [Fig. 1(a)] by the high rate of the simulated emission. The reported experimental results point to the possibility of realization of a capillary light guide laser (compatible with fiber optics hardware) employing a similar ball-milled nanocolloid gain media.



Fig. 7. Nanocolloid-filled capillary optical light guide amplifier: (a) The photo of the amplifier with the pump radiation injected from the left. The bright visible light is the upconversion radiation from by the nanocolloid. (b) Oscillogram of the input pulsed signal (1550-nm wavelength, 0.04-mW amplitude) after passing the amplifier with the pump off (black graph 1) and the 4.2-mW pump (blue graph 2). (c) The gain versus the pump power. The amplitude of the input pulsed signal is 0.04 mW. (d) The gain versus the amplitude of the input pulsed signal at 4.2-mW (blue circles) and 18.0-mW (black triangles) pump.

5. Additional considerations with regard to material selection

Compound NaYF₄: Yb³⁺, Er³⁺ is not the best gain medium for a nanocolloid optical amplifier at 1550 nm at least due to a significant portion of the pump energy being consumed by the upconversion process. Other materials would be more suitable for the task [20, 21]. There were two reasons for choosing NaYF₄: Yb³⁺, Er³⁺ in this work. First, the phosphor was previously used as a nanocolloid gain medium in the free-space configuration of an optical

amplifier [2]. The data of the previous study could thus be used as the basis for comparison and analysis of the results of this work. Second, intense visible upconversion emission made it technically easier to handle the nanocolloid while filling it in the capillary tube and coupling the optical fibers carrying the pump and signal radiation with the light guide. Once the capillary tube was filled with the nanocolloid, it could be illuminated from the side with a 980-nm laser diode. Any discontinuity of the filler would be detected with bare eyes as the absence of the visible upconversion light emitted from the illuminated spot. Also, the easily observable and measurable decay of the upconversion radiation was used to estimate the losses of the IR radiation. Interruption or weakening of the upconversion light in the point of coupling would similarly indicate coupling disruption.

The optical amplification does generally work in the gain media doped with Er^{3+} only, but co-doping with Yb³⁺ sensitizer ions improves the gain. The ytterbium ions can efficiently absorb pump radiation at 980 nm, and then transfer the energy to erbium ions in the groundstate, bringing them into the ${}^{4}I_{11/2}$ state [Fig. 1(a)]. From that level, the ions are quickly transferred into the laser level ${}^{4}I_{13/2}$, so that energy transfer back to ytterbium is suppressed. Erbium–ytterbium-doped media are frequently used for optical fiber amplifiers and short fiber lasers [22, 23]. Typically, the optimal doping rate of Yb³⁺ goes up to 20 times that of Er^{3+} [22]. In case of NaYF₄: Yb³⁺, Er^{3+} with the optimal doping rate of Er^{3+} being 2% [2], the doping rate of Yb³⁺ is typically between 10% and 20% [2, 24]. The phosphor used in this work had a doping rate of Er^{3+} and Yb³⁺ of 2% and 10% respectively (see Sub-section 2.1). At 10% ytterbium the green portion of the upconversion fluorescence (more visible by human eyes) came up brighter and made handling the nanocolloid filler in the capillary tube easier.

Further reduction of the size of the nanoparticles below 100 nm (requiring significantly longer time of ball milling) resulted in the drop of the gain. This was previously explained as weakening of the sensitizer-to-activator energy transfer in the ball-milled nanoparticles of NaYF₄: Yb³⁺, Er³⁺due to the surface compositional segregation of Er³⁺ and Yb³⁺ dopant ions after prolonged ball milling [15]. The gain drop (linked to the loss of the efficiency of the energy conversion of the pump power) could be also explained by the rapidly diminishing average number of the dopant ions in each nanoparticle (inversely proportional to the cube of the particle diameter) [25]. The efficiency of the energy conversion of the pump in the phosphor nanopowder with an average diameter of the particles of ~40 nm could be as low as 1% of that in the bulk material [26].

6. Conclusion

A conceptual prototype capillary optical light guide amplifier (compatible with fiber optics hardware) using a ball-milled nanocolloid of NaYF₄: Yb³⁺, Er³⁺ as a filler was successfully demonstrated. A 7-cm-long device was capable of amplifying a pulsed optical signal in communication C-band (1525 to 1565 nm) ten times at a moderate pump power of approximately 4 mW (980-nm wavelength). The nanocolloid gain medium was prepared by the physical method of pulverization of a phosphor powder with a high-speed planetary ball mill. The optical emission properties of the initial powder synthesized with the wet process depended strongly on the post-synthesis baking conditions in open air. The most favorable for reaching intensive downshifting and upconversion emission was a baking temperature within range 550 to 750°C resulting in the dominant β - (hexagonal) crystalline phase of the fluoride host NaYF₄. Ball milling of the powder in water produced nanoparticles with a size of approximately 120-135 nm that after drying could be transferred to different liquids (carbon tetrachloride or an index matching liquid) with the optical (optical spectra of the downshifting and upconversion emission) and crystalline properties of the initial powder preserved. The results imply that RE-doped colloids of nanocrystals prepared by ball-milling represent a new family of liquid gain media that are advantageous over dye solutions as well as colloidal quantum dots due to their high photostability and low toxicity.

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