VISIBLE UPCONVERSION IN RARE-EARTH ION-DOPED $NaYF_4$ CRYSTALS AND NANOCOLOIDS

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ABSTRACT

Nano-colloids and nano-crystals doped with ions of rare-earth elements have recently attracted a lot of attention in the scientific community. This attention is due to unique physical, chemical and optical properties particularly attributed to nanometer size of the particles. They have great potential of being used in applications spanning from new types of lasers, especially blue and UV ones, phosphorous display monitors, optical communications, and fluorescence imaging. In this paper we investigate the infrared-to-visible upconversion luminescence in crystalline powder and nano-colloids. The photonic crystal fiber was filled with nano-colloids. The phosphors were prepared by using simple co-precipitation synthetic method. The initially prepared phosphors had very weak or no fluorescence signals. The fluorescence significantly increased after the phosphors were annealed at a temperature of 600^0C. Nano-colloids of the phosphors were prepared in methanol as a solvent and later were utilized as laser filling medium in photonic crystal fibers. Under 980 nm laser excitation, ytterbium and erbium co-doped $NaYF_4$ phosphor showed very strong upconversion signals at 408 nm, 539 nm and 655 nm, the ytterbium and holmium co-doped $NaYF_4$ phosphor showed strong upconversion at 540 nm, 646 nm and 751 nm and the ytterbium and thulium co-doped $NaYF_4$ phosphor showed strong upconversion at 376 nm, 476 nm, 647 nm, 689 nm and 802 nm. The reported nano-colloids are good candidates for fluorescent biosensing applications and also as a new laser filling medium in fiber lasers.

Keywords: crystals, nano-colloids, rare-earth

In general, efficient hosts for energy upconversion are based on materials with low phonon energies which minimize the non-radiative multiphonon relaxation process of the dopant [1-2]. The most efficient up-conversion materials known today are based on fluorides which are doped with Yb^{3+} and Er^{3+} or Yb^{3+} and Ho^{3+} or Yb^{3+} and Tm^{3+}. Hexagonal-phase $NaYF_4$ (β-$NaYF_4$) crystals has been reported to be the most efficient host material for upconverting rare-earth ions due to the low phonon energy of the crystal lattice [1-2].

INTRODUCTION

Many rare earth doped materials of different compositions, shapes and size distribution have been prepared by various synthetic methods such as chemical vapor deposition, sol-gel process, micro-emulsion techniques, gas phase condensation methods, hydrothermal methods and laser ablation. In this present work $NaYF_4$ crystals co-doped with trivalent rare-earth ions were synthesized using simple solution based technique in the presence of Na_2-ethylenediaminetetraacetic acid (EDTA).

After annealing at a temperature of 400°C or 600°C very strong upconversion fluorescence could be observed by the naked eye. The Er^{3+}, Yb^{3+} co-doped crystals, Ho^{3+}, Yb^{3+} co-doped crystals and the Tm^{3+}, Yb^{3+} co-doped crystals were capable of upconverting NIR light from a 980 nm diode laser into blue, green, red and UV fluorescence.

The synthesis did not require any sophisticated equipment or complicated procedures. The synthesized upconversion phosphors could be excited with inexpensive commercial 980 nm laser diodes. This dramatically increases their commercial potential [3-4].

RESULTS & DISCUSSION

In all the measurements, the samples were at room temperature. Optical fluorescent spectra were taken with the Princeton Instruments 500-mm-focal-length Spectra Pro (SP – 2500i) imaging spectrometer equipped with 1200 gr/mm blazed at 500 nm holographic diffraction grating, R929 photomultiplier tube, and PI-Max 1024HQ Digital Intensified CCD Camera system. The microcrystalline powders were pressed into flat disks to obtain the emission spectra. The emission measurements were collected using a sample chamber with the sample placed at 45° with respect to the input optical axis of the spectrometer. The emission spectra of nano-colloid samples were conducted using a 10 mm thick glass fluorometric cuvettes mounted inside the sample chamber of the spectrometer.

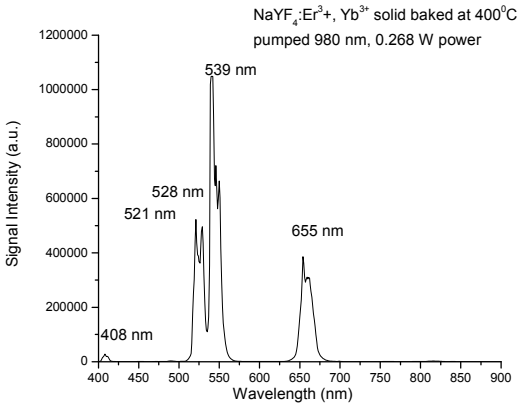

Fig. 1 Emission Spectra of $NaYF_4$: Er^{3+}, Yb^{3+}

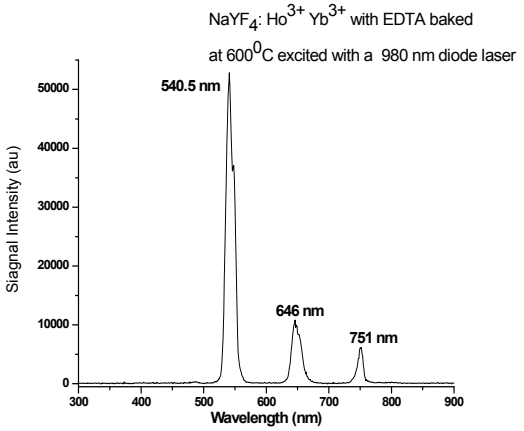

Fig. 2 Emission Spectra of $NaYF_4$: Ho^{3+}, Yb^3

We saw five emission peaks for Er^{3+}, Yb^{3+}:$NaYF_4$ crystals at 408 nm, 521 nm, 539 nm, 655 nm and 816 nm, which are assigned to $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions of erbium respectively (Fig. 1 excitation with 980-nm laser diode). We saw emission peaks for Ho^{3+}, Yb^{3+}:$NaYF_4$ crystals at 541 nm, 646 nm, 751 nm and 376 nm, which are assigned to $^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, $^5I_4 \rightarrow {}^5I_8$, and $^1D_2 \rightarrow {}^3H_6$ transitions respectively (Fig. 2; 980-nm excitation). The Ho^{3+}, Yb^{3+}:$NaYF_4$ nano-colloid was also excited with an argon ion laser; we obtained emissions peaks at 369 nm, 549 nm, 708 nm, 757 nm and 866 nm. We also saw emission peaks for Tm^{3+}, Yb^{3+}:$NaYF_4$ crystals at 476 nm, 646 nm, 696 nm and 803 nm, which are assigned to $^1G_4 \rightarrow {}^3H_6$, $^3F_2 \rightarrow {}^3G_6$, $^3F_3 \rightarrow {}^3H_6$ and $^3F_4 \rightarrow {}^3H_6$ transitions respectively (Figs. 3 and 4; 980-nm laser excitation).

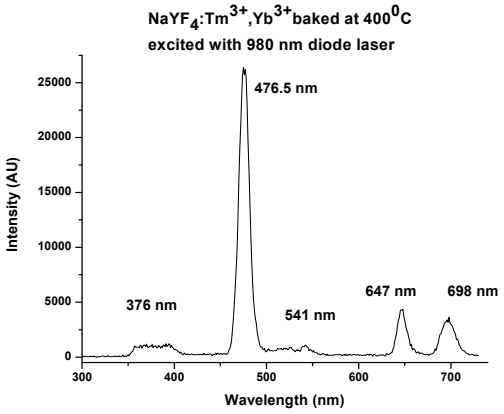

Fig. 3 Emission Spectra of $NaYF_4$: Tm^{3+}, Yb^{3+}

Recently, there have been attempts to design a laser medium by filling micro-structured optic fibers with solutions of fluorescent materials [5]. We have filled the micro-structured fibers with nano-colloids of

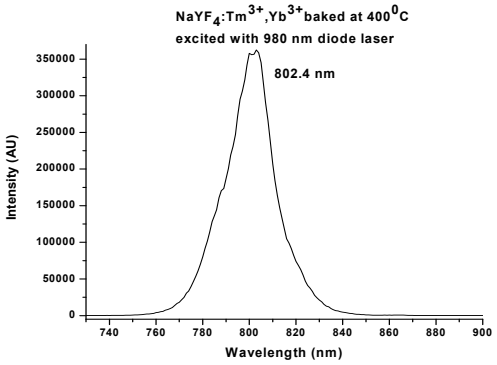

Fig. 4 Emission Spectra of $NaYF_4$: Tm^{3+}, Yb^{3+}

Er^{3+}, Yb^{3+}:$NaYF_4$. The nano-colloid was driven in the holes of the fiber by capillary forces[4]. After the solvent had dried out, particles of Er^{3+}, Yb^{3+}:$NaYF_4$ were dispersed along the inner walls of the holes of the fiber. Radiation from an external 980-nm pumping laser could be concentrated in the holes of the fiber and excited the ions of rare-earth in the nano-particles thus potentially producing laser effect in the fiber. The prepared $NaYF_4$: Er^{3+}, Yb^{3+} nanocolloids was filled in micro structured (holey) optical fiber HC19-1550-01 from Crystal-Fibers. Micro structured fibers guided light in a hollow core, surrounded by a micro structured cladding formed by a periodic arrangement of air holes in silica. This fiber had a center wavelength of 1570 nm and core diameter of 20 $\pm$ 2 μm. The core was formed by removing 19 hexagonal cell units, diameter of the holey region was 73 μm and the diameter of the silica cladding was 115 μm. The total length of the used fiber was 30 cm while the nano-colloid was driven in the 25-50-mm segment. The movement of the nano-colloid filler in the direction from the end of the fiber immersed in the nano-colloid was observed when the pump laser beam was "ON. Radiation from a diode laser of 980 nm wavelength was injected in the opposite end of the fiber and a strong emission was observed from the core region of the fiber filled with the nano-colloid. Fig. 5 shows the optical spectrum of the emission coming from the free end of the fiber. The spectrum features peaks at 540 nm, 654 nm and 840.5 nm which can be attributed to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions respectively. The power of this 654-nm radiation was measured to be approximately 0.1% of the power of the pump radiation that passed through the fiber.

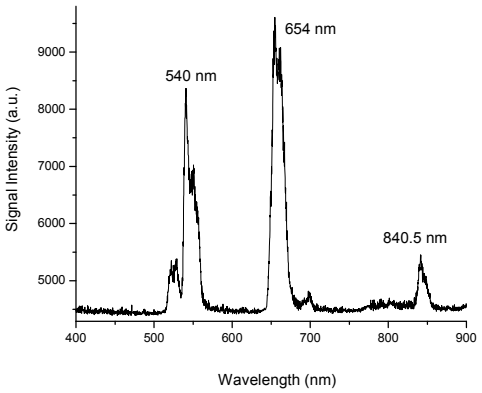

Fig. 5 $NaYF_4$: Er^{3+},Yb^{3+}nano-colloid insideHC19-1550-01 photonic crystal holy fiber pumped with 980 nm laser

CONCLUSIONS

A highly efficient hexagonal-phase $NaYF_4$ (β-$NaYF_4$) co-doped with trivalent ions was synthesized in the form of microcrystalline powder and nano-colloid. The fiber arrangement of optically pumped laser/amplifier containing the nano-colloid was able to produce 540 nm, 654 nm and 840.4 nm emissions with a pump-emission power efficiency of 0.1% when pumped with 980 nm single mode diode laser. The co-doped sodium yttrium fluoride crystals and nano-colloids were demonstrated to be good candidates for fluorescent applications and also as a new laser filling media for fiber lasers and amplifiers.

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