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The Effect of Metallic Ions on the Enhanced Upconversion Emission of $NaGdF_4$ Nanostructures

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Abstract - Co-doping of $NaGdF_4$ doped with Yb^{3+} and Er^{3+} with Fe^{3+} have shown to improve the intensity of upconversion emissions of green and red wavelengths. The maximum emission intensity was obtained at a Fe concentration of 0.3 mmols in the precursor and using a laser excitation at 980nm wavelength. The green emission was found to be enhanced to 10 times and red emissions was enhanced to about 3 times as compared to the intensity of the emissions without the Fe co-doping. Characterisation techniques like XRD and EDS is used to investigate the reason for this observation.

Keywords: Upconversion nanostructures, photoluminescence, metallic ion, doping

1. Introduction

There are several research findings on the improvement of luminance emission intensity on co-doping with a third ion. Co-doping of $NaGdF_4$ doped with Yb^{3+} and Er^{3+} with 7 mol% of Li^+ ions increases the luminescence intensity of green emissions by 47 fold and red emissions by 23 fold [1] and co-doping with 30 mol % Ca^{2+} improves the emission intensity by 200 times [2]; codoping with 13.5mol % of Mg^{2+} increases luminescence intensity of green and red emissions by 6 and 9 times respectively [3] (Shuwen Zhao, 2016). Similarly, in case of $NaYF_4$ doped with Yb^{3+} and Er^{3+}, co-doping with 0.5mol % of Li^+ produced green emission of 34 fold intensity and red emission of 101 fold intensity [4]; But co-doping with 10mol % Mo^{3+}, the green emission and red emissions became 6 fold and 8 fold respectively [5]; with 15mol % Cr^{3+} green emissions and red emission became 16 and 7 times [6] and with 20 mol % La^{3+}, green and red emission intensity became 7.6 and 8.1 times respectively (Junxiang Fu, 2017) and with 7mol % of Cd^{2+} total emission intensity increased 38 times [7]. Yahong Hu et al. shows that the red emission luminance intensity of $NaYF_4$:Yb^{3+}, Er^{3+} becomes 14-fold on adding 10mol % of Mo^{3+} and 24fold on adding 30mol % Fe^{3+} [8]. 20mol % co-doping with Fe^{3+} showed 7 times increase in red emission [9]. Tie Cong et al. shows that the emission intensities of green and red increased at first and then decreased with the increase of concentration of Zn^{2+} from 0 to 20 mol % [10].

2. Materials and Experimental

2.1. Materials

Gadolinium(III) nitrate hexahydrate ($Gd(NO_3)_3{\cdot}6H_2O$), ytterbium(III) nitrate pentahydrate ($Yb(NO_3)_3{\cdot}5H_2O$), erbium(III) nitrate pentahydrate ($Er(NO_3)_3{\cdot}5H_2O$), Iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$)sodium Fluoride (NaF), branched polyethylenimine (PEI) and ethylene glycol (EG) purchased from Sigma-Aldrich and deionized water was used for the synthesis of nanostructures.

2.2 Synthesis of Metallic Ions Doped $Nagdf_4$ Nanoparticles

Modified solvothermal method [11] was used in the synthesis of $NaGdF_4$ doped with Yb, Er and varied amounts of Fe. 1.6 mmol Gadolinium(III) nitrate hexahydrate, 0.38 mmol Erbium(III) nitrate pentahydrate, 0.36 mmol Ytterbium(III) nitrate pentahydrate, 0 to 0.8 mmol of Iron(III) nitrate nonahydrate and 0.7g polyethylenimine are added to into 20 mL ethylene Glycol in a three-neck round bottom flask and dispersed by stirring at room temperature. 8 mmol Sodium fluoride is added to 10 ml Ethylene Glycol and sonicated to ensure a clear solution. This solution is added to the three-neck round bottom flask dropwise while continuing to still with the help of magnetic stirrer and temperature is increased to 198 ℃ refluxing for 6

hours under nitrogen atmosphere. After the completion of the reaction, the mixture is centrifuged and washed with a 50:50 mixture of ethanol and water three times. The resulting nano structures are dried overnight at 60℃.

2.3. Characterization of Nagdf$_4$ Nanoparticles Doped With Metallic Ions

The size and morphology of nanostructures were characterized by transmission electron microscopy (TEM, Philips CM-10 operated at 80 kV). The crystal structures of NaGdF4-based nanostructures were studied by X-ray diffraction (XRD, Rigaku rotating-anode X-ray diffractometer with Co- Kα radiation). The fluorescent emission spectrum of NaGdF4-based nanostructures were measured by fluorophotometry (QuantaMsterTM 30, Horiba Canada-PTI) with an external excitation wavelength of 980 nm, 1 W.

3. Results and Discussion

Typical green (λ_{em} = 540 nm) and red (λ_{em} = 655 nm) emissions of Er^{3+} can be observed in all the samples using an excitation wavelength, λ_{ex}, of 980 nm. It is found that in most of the samples the green emission is less than 50% of red emissions.

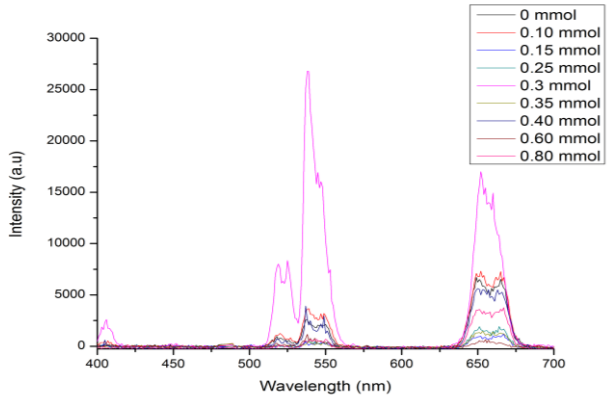

Figure 1. Upconversion luminescence properties of NaGdF4 doped without/ with Yb^{3+}, Er^{3+} and Fe^{3+} (0-0.8 mmol) under 980nm excitation wavelength (λ_{ex}).

As compared to the rest of the emission graphs, sample containing 0.3 mmol Fe has higher green to red ratio and overall higher intensity of emissions. The green emission is enchanced to about 10 times and the red emission is enchanced to about 3 times at this iron concentration.

Erbium content is seen to be minimum in 0.3 mmol Fe containing sample. Previous studies also suggest that higher Er3+ results in lower upconversion intensity due to quenching effect [12]. This explains the highest overall intensity of emission for sample containing 0.3 mmol Fe.

The intensity of upconversion emission is known to be directly proportional to the n th power of input power, with n being the average number of photon absorption resulting in the emission [13].

$$I \approx P^n \quad (1)$$

Where I is the intensity, P the laser power and n the number of photons absorbed for emission of one photon. The value of n gives the number of photons involved in the emission of particular wavelength peaks.

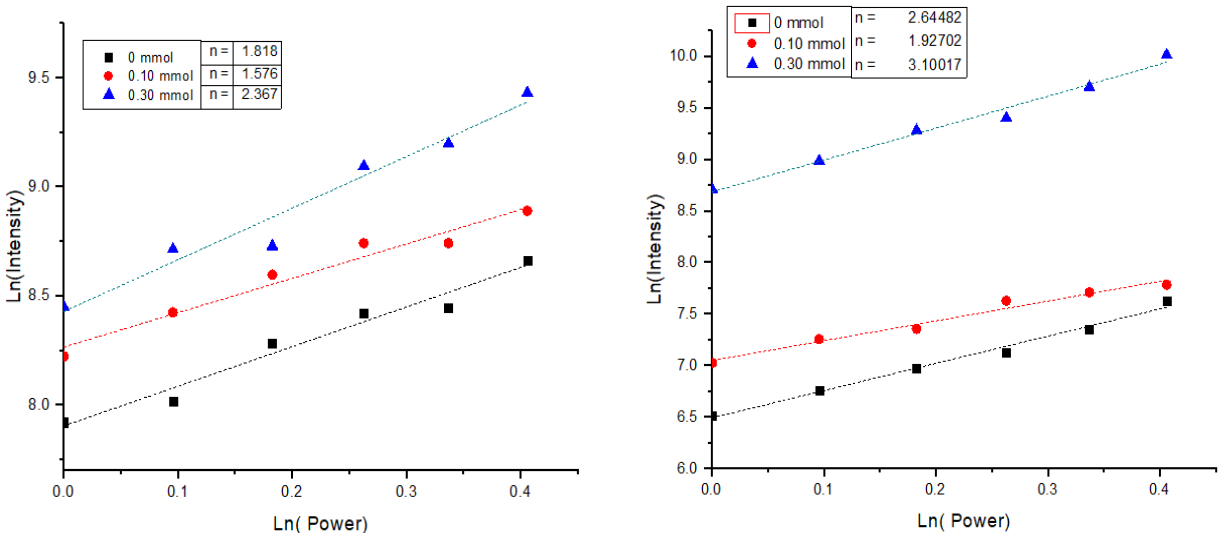

Figure 2. Log intensity vs log power plot for different precursor iron content from 0mmol to 0.3mmol of (a) red peak (650nm) and (b) green peak (537nm)

The red emission is found to be the result of the following transitions utilizing two photons Yb3+ (2F5/2 → 2F7/2) and Er3+ (4I15/2 → 4I11/2), Er3+ (4I11/2 → 4I13/2) and Yb3+ (2F5/2 → 2F7/2) and Er3+ (4I13/2 → 4I9/2). The green emisssions are result of Yb3+ (2F5/2 → 2F7/2) and Er3+ (4I15/2 → 4I11/2) and Yb3+ (2F5/2 → 2F7/2) and Er3+ (4I11/2 → 2H11/2). This is two photon emission. But at higher power Yb3+ (2F5/2 → 2F7/2) and Er3+ (4F9/2 → 2H9/2) or Yb3+ (2F5/2 → 2F7/2) and Er3+ (4I9/2 → 2H9/2) followed by non radiative transition Er3+ (2H9/2 → 2H11/2) also can result in green emissions (F.Song, 1999). This explains the possibility of value n =3 (Figure 22).

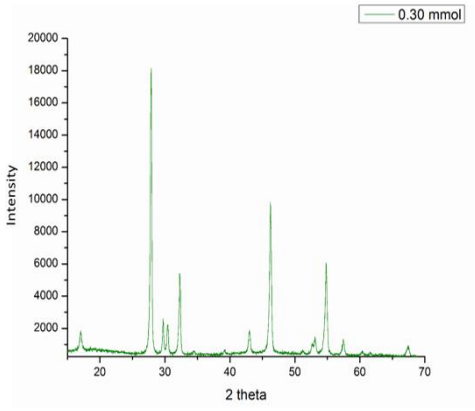

Figure 3. XRD spectra of NaGdF4 doped with Yb3+, Er^{3+} and Fe^{3+} (0.3 mmol)

Samples expect 0.3 mmol Fe is found to be cubic lattice structure. 0.3mmol Fe is found to be a mixture of cubic and hexagonal lattice structure. NaGdF4 doped with Yb3+, Er3+ and Fe3+ with hexogonal shaped lattice is found to have higher green emission compared to red emission [14] (Parthiban Ramasamy, 2013). Doping of Iron can induce phase changes.

3. CONCLUSION

Upconversion nanostructures with optical and magnetic properties were prepared using solvothermal process. The lower external magnetic field applied did not show considerable influence of optical properties of the UCNP. Co-doping with Iron is found to influence the optical emission of NaGdF4 doped with Yb3+, Er3+. The higher iron content in the nanostructure resulted in higher over all emissions, higher green to red ratio compared to the rest of the samples and have shown transition in crystal structure from pure cubic to a mixture of cubic and hexogonal lattice structures. The maximum emission intensity was obtained at a Fe concentration of 0.3 mmols in the precursor and using a laser excitation at 980nm wavelength. The green emission was found to be enhanced to 10 times and red emissions was enhanced to about 3 times as compared to the intensity of the emissions without the Fe co-doping.

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References

[1] Qian Cheng, J. S. (2012). Enhanced upconversion emission in Yb3+ and Er3+ codoped NaGdF4 nanocrystals by introducing Li+ ions. *Nanoscale*, 779–784.

[2] Lei Lei, D. C. (2014). Highly Intensified Upconversion Luminescence of Ca2+-doped Yb/Er:NaGdF4 Nanocrystals Prepared by a Solvothermal Route. *Asian Journal of Chemistry*, 728 – 733.

[3] Shuwen Zhao, W. L. (2016). Enhanced upconversion luminescence and modulated paramagnetic performance in NaGdF4:Yb, Er by Mg2+ tridoping. *The Royal Society of Chemistry*, 81542–81551.

[4] Xiuwen Wang, †. X. (2013). Comprehensive Studies of Li+ Effect on NaYF4:Yb/Er Nanocrystals:Morphology, Structure, and Upconversion Luminescence. *Royal Society of Chemistry*, 1-3.

[5] Dongguang Yin, C. W. (2014). Enhancing upconversion luminescence of NaYF4:Yb/Er nanocrystals by Mo3+ doping and their application in bioimaging. *The Royal Society of Chemistry*, 12037–12043.

[6] Chuanying Wang, X. C. (2015).. *Journal of Alloys and Compounds 649* , 196-203

[7] Cong, T., Ding, Y., Yu, X., Mu, Y., Hong, X., & Liu, Y. (2017). Upconversion luminescence enhancement in NaYF4: Yb3+, Er3+ nanoparticles induced by Cd2+ tridoping. *Materials Research Bulletin* , 151–155.

[8] Yahong Hu, X. L. (2015). Enhancement of the red upconversion luminescence in NaYF4:Yb3+, Er3+ nanoparticles by the transition metal ions doping. *Ceramics International*, 4545–14553.

[9] Jing Tang, L. C. (2015). Selectively enhanced red upconversion luminescence and phase/size manipulation via Fe3+ doping in NaYF4:Yb,Er nanocrystals. *Nanoscale*, 14752- 14759.

[10] Tie Cong, Y. D. (2016). Synthesis and optical properties of Zn2+ doped NaYF4: Yb3+, Er3+upconversion nanoparticles. *Materials Letters*, 59–62.

[11] Longyi Chen, W. H. (2017). Special properties of luminescent magnetic NaGdF4:Yb3+, Er3+ upconversion nanocubes with surface modifications. *The Royal Society of Chemistry*, 26770–26775.

[12] F.Song, M. S. (1999). Effect of Erbium Concentration on Upconversion Luminescence of Er:Yb:phosphate Glass Exited by InGaAs Laser Diode. *S PI E*, 1822188.

[13] M. Pollnau, D. R. (n.d.). Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems.

[14] Parthiban Ramasamy, P. C. (2013). Enhanced upconversion luminescence in NaGdF4:Yb,Er nanocrystals by Fe3+ doping and their application in bioimaging. *Nanoscale,*, 8711–8717.