Upconversion emission properties and un-expected white light emission from Er^{3+}/Yb^{3+} doped Gd_2O_3 nano – phosphors

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ABSTRACT

Gd_2O_3 nano-powders doped with Er^{3+} and Yb^{3+} were synthesized using the combustion method. X-ray diffraction and the scanning electron microscope techniques were used to estimate the crystalline sizes and the morphologies of the materials. The Scherer calculation were employed to estimate mean crystalline sizes. The crystalline sizes were found to be <100 nm. The down- and up-conversion emission properties of the materials have been studied using the laser spectroscopy technique. Results showed that the 1.5 μm emission of the Er^{3+} ions broadened with increasing Yb^{3+} dopant ions. The *n*-shape pumping power dependency of the up-conversion emission was observed. The formation of the new emıssion bands and the un-expected production of white light emission with increasing pumping power were observed. The color quality parameters of obtained visible emission were also measured.

Keywords: Gd_2O_3, nanophosphors, XRD, Up-conversion, white light

1. INTRODUCTION

Lanthanide doped luminescent materials have been gathering more attention of the researchers due to the up-conversion (UC) emission properties of such materials that can be engineered for wide range of applications: fluorescent labeling of biomolecules, solid state laser devices, optical sensing and imaging devices, high quality white light sources etc. [1-10]. Especially, rare earth ions (REI) activated nano-sized luminescent materials are of interest because of having optical properties distinct from those of their bulk counterparts, which are due to the change in the local environments of the REIs as a result of structural defects induced by size.

In light of above information, we synthesized Gd_2O_3 nano-powders doped with different concentrations Er^{3+} and Yb^{3+}. The effect of the dopant concentration and the crystalline size on the DC and the UC emission properties of the samples has been investigated. The X-ray diffraction (XRD) and the Scanning Electron Microscope (SEM) techniques were used to characterize samples structurally. The continuous emission DC and UC spectra of the materials were also measured to determine the spectroscopic properties of the materials. Furthermore, to the best of our knowledge, WL emission from REI doped Gd_2O_3 have been reported for the first time in this study.

2. EXPERIMENTAL

Gd_2O_3 nano-powders doped with different concentrations of Er^{3+} and Yb^{3+} were synthesized using the combustion method. The starting reagents, $Gd(NO_3)_3$ $6H_2O$, $Er(NO_3)_3$ $5H_2O$, $Yb(NO_3)_3$ xH_2O and NH_2CH_2COOH (glycine), which was used as a fuel in reaction, of an analytical grade were purchased from Sigma Aldrich and Alfa Aesar. The ratio between glycine to nitrate was kept as 0.56 [11, 12]. The appropriate amounts of the starting reagents were dissolved in minimum amount of deionized water. The solution was then transferred to a muffle furnace and quickly heated up to 500°C. Once the combustion process takes place, foamy Gd_2O_3 nano-powders were obtained. Then some of obtained powders were heat treated at 1000°C. The formulations of the samples are given in Table 1.

Bruker AXS D8 model (Cu Kα radiation) diffractometer operating at 40kV and 30 mA were used for X-ray diffraction (XRD) measurements with the scanning step of 0.01 degree in the 2θ

interval of 20°-90°. The SEM measurements were carried out using a FEI – Quanta FEG 250 model electron microscope.

Table 1. The formulations of the samples.

$Gd(NO_3)_3.6H_2O$ (mole %)	$Er(NO_3)_3.5H_2O$ (mole %)	$Yb(NO_3)_3.xH_2O$ (mole %)	Synthesis Temperature (°C)	Annealing Temperature (°C)
100	--	--	500	--
100	--	--	500	1000
94	1	5	500	--
94	1	5	500	1000
89	1	10	500	--
89	1	10	500	1000

The spectroscopic measurements were conducted using an Apollo Instruments diode laser (Model No: S30-808-6) with 805.2 nm wavelength and a CNI MDL-H-975 Model diode laser operating at 975 nm with an output power of 5W as excitation sources, a Princeton Instruments SP2500i model monochromator, and an Acton series ID441-C Model InGaAs and SI 440 detectors for the detection of luminescence in the infrared and the visible region of the spectrum, respectively. All measurements were carried out at room temperature. We were also used a Coherent FieldMaxII – TOP Model power meter to measure output power of the laser beam.

The CCT (Correlated Color Temperature), the CRI (Color Rendering Index) and the CIE – 1931 (Commission Internationale de l'éclairage) coordinates of the obtained WL emission were measured using an illuminance meter (AsenseTek Lighting Passport) to determine the quality of the emitted visible light.

3. RESULTS

3.1.Structural Characterization

XRD patterns of Er^{3+}, Yb^{3+} co-doped Gd_2O_3 samples are presented in Figure 1. The Joint Committee of Powder Diffraction Standards (JCPDS) database used to identify the phase formations of the samples. The non-annealed samples resemble an amorphous structure encompassing a monoclinic phase well matching with the standard reference data having the card number of 00-043-1015. However, as the samples annealed at 1000°C, cubic phase with the card number 01-086-2477 dominates. Scherer Method was used to estimate mean crystalline sizes of the nano-powders.

$$d_{hkl} = \frac{K.\lambda}{\beta.cos\theta}$$

The representative SEM image of the G100-1000 nano-powders is given in Figure 2. The micrograph of the sample shows the agglomerated nano-powders with spherical morphology are relatively uniform and have average diameters of ~100 nm.

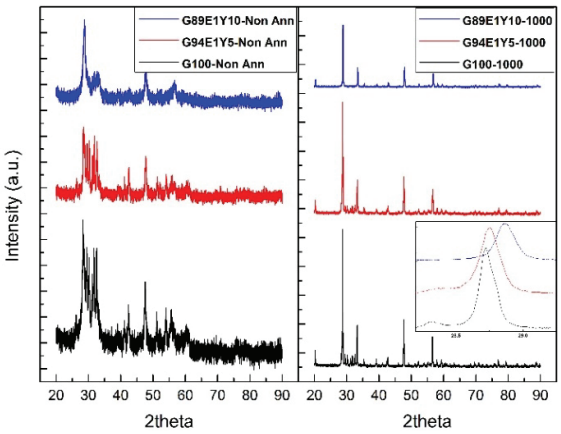

Figure 1. XRD patterns of the samples studied (inset is the shift of the peak position by increasing dopant concentration).

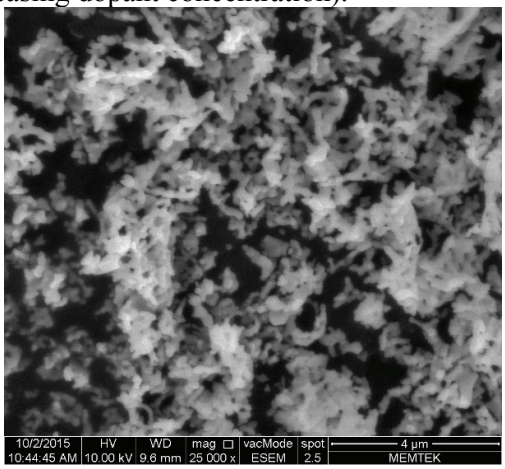

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Figure 2. Representative SEM image of the G100-1000 sample.

3.2.Spectroscopic Characterization

Down-conversion (DC) Emission

The DC emission spectra of the samples with corresponding transitions are given in Figure 3. The measurements of DC spectra were conducted at room temperature and in the 850 – 1700 nm wavelength range under 805.2 nm diode laser excitation. The DC emission spectra of the materials consist of two groups of emission bands located around 1000 nm and 1550 nm which are originated from $^4I_{11/2}$ and $^4I_{13/2}$ to $^4I_{15/2}$ transitions of Er^{3+} and $^4F_{5/2}$ to $^4F_{7/2}$ transition of Yb^{3+}. It was noted from Figure 3 that the general aspects of the spectra of the samples are same for different Yb^{3+} dopant concentrations.

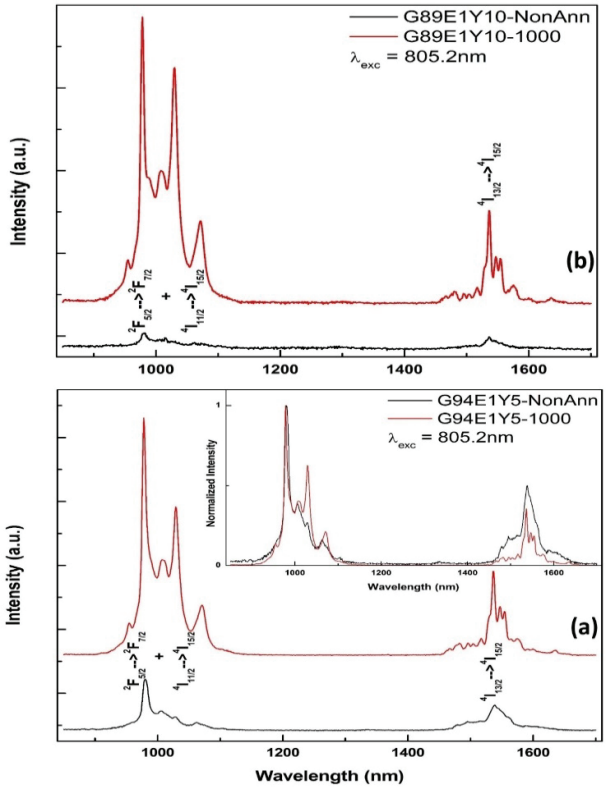

Figure 3. Room temperature DC spectra of the (a) G94E1Y5 (both non-annealed and annealed) (inset is the DC spectral shape change from monoclinic to cubic Gd_2O_3) and (b) G89E1Y10 (both non-annealed and annealed) samples under 805.2 nm excitation.

Up-conversion (UC) Emission Properties

The UC spectra of the materials were collected under excitation of 975 nm diode laser in the 400 – 800 nm wavelength range at room temperature. The UC spectra of the materials are given in Figure 4 with corresponding transitions as a function of pumping excitation power. The strong visible UC emission in the green and red spectral regions were observed for the phosphors which are localized at around 520 nm, 540 nm and 650 nm associated with the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. The up-converted emissions are induced by photon transitions via excited state absorption. It is seen that the intensities of the UC emission bands of all samples increase up to certain point, then, started to decrease with increasing pumping power. The detailed comparison of the UC spectra of the monoclinic and mostly-cubic Gd_2O_3 samples also show that the shape of the bands vary, which is an indication of the different crystal structures

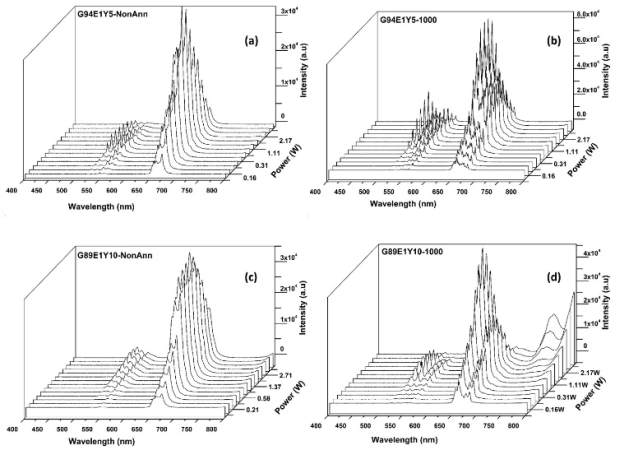

Figure 4. The pumping power dependence of the UC spectra of the (a) G94E1Y5-NonAnn, (b) G94E1Y5-1000, (c) G94E1Y10-NonAnn and (d) G94E1Y10-1000 samples under 975 nm excitation.

Another interesting finding of the present work is the formation of some new bands located at yellow and red-infrared region of the spectra, which were observed for 1% Er and 10 % Yb co-doped samples. The formation of the new bands was attributed to the generation of the white light (WL) emission which is the result of increasing surface temperature of the sample due to the laser

heating [13-17]. The yellowish WL emission from the sample was clearly seen by naked eye. The formation of the WL emission was only observed in highly doped samples (1% Er + 10%Yb). This fact is related to the effect of dopant concentration on the WL emission, which was already discussed in our earlier works [13-15]. The increasing amount of dopant ions makes the WL emission formation easier and it can be obtained even at lower excitation pumping powers. The formation of the WL emission cannot be ascribed to an overlap of sharp emission bands, or broadening of the emission bands caused by the laser induced heating of the materials. Because, the emission band structure is always present even at higher pumping powers. The spectrum of the WL emission is given in Figure 5 together with color quality parameters which were measured using illuminance meter.

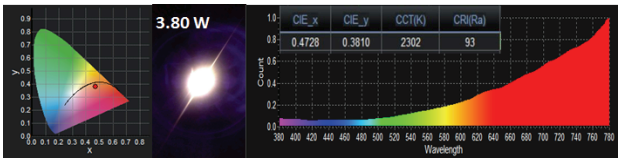

Figure 5. White light spectrum, CIE coordinates, CCT and CRI values measured using illuminance meter.

4. Conclusion

The un-doped and Er^{3+} and Yb^{3+} co-doped Gd_2O_3 nano-powders were synthesized using the combustion method. The structural characterization of the materials showed that the particles are in nano-size and two phases of the Gd_2O_3, monoclinic for non-annealed and cubic for annealed samples, were occurred. The spectroscopic characterization of the materials were performed by measuring the infrared DC and visible UC emission spectra. The results indicated that powders have enough strong emission even if they are in nano-size. The change of the spectral shape from one crystal phase to another was clearly observed. Some interesting behavior of the UC emission such as formation of the new emission bands and *n*-shape power dependence of the UC emission intensity were observed, and plausible explanations were made. It was shown that the UC emissions are poor in color quality parameters but they found to be enhanced with the formation of WL emission and approach to those of incandescent lamp which is still unmatched with respect to its color quality.

5. REFERENCES

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