Upconversion emission in (Ln,Yb):KLu(WO$_4$)$_2$ nanocrystals for white light generation

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Abstract. Optical active lanthanides ions in double tungstates exhibit high emission cross section with low concentration quenching. Production of double tungstates nanocrystals doped with lanthanide ions is suitable for applications in white light emitters if high quantum yield is reached. In this work lanthanide doped (Ln:Yb):KLu(WO$_4$)$_2$ nanocrystals (Ln = Er, Tm, Ho) upconversion emission properties have been study after 980 nm diode laser excitation at 14-334 W/cm$^2$. From CIE chromaticity theory a possible mixture weight ratio to obtain a white light emitter powder was predicted. Luminescence under 980 nm of the (Ln:Yb):KLu(WO$_4$)$_2$ nanocrystals was study and decay times under 460 nm was measured. Reduction of the upconversion quantum yield was observed in the case of physical mixture of nanocrystals.

1. Introduction

In the last years, there has been a great interest in the development of lanthanide (Ln) doped white light emitters based in the upconversion (UC) process in which near infrared photons are converted in visible photons by a multiphoton absorption process [1]. The suitability of optical active trivalent ions Ln$^{3+}$ cations for the UC processes is due to their abundant energy levels and narrow emission spectral lines [1]. Yb$^{3+}$ is used to act as sensitizer due to its high absorption cross section, allowing the efficient excitation around 980 nm with cheap diode lasers and followed by energy transfer to other trivalent Ln ions, such as Er$^{3+}$, Tm$^{3+}$ and Ho$^{3+}$. A white light source can be tailored by mixing red-green-blue UC phosphors in proportions determined by the UC emission spectra of each phosphor at a specific chemical composition and pumping power. It is important to consider the excitation conditions of the phosphors because local high pumping induces temperature increment modifying UC emission spectra and consequently the color of the emitter [2]. Monoclinic KLu(WO$_4$)$_2$ (KLuW) host is a well-known material for laser applications. Its main advantages are the admittance of a high doping level of active
Ln$^{3+}$ ions in this host and the possibility to be highly doped with lanthanides ions, with low concentration quenching due to the relatively large Ln-Ln distances in the structure [3], and the high absorption and emission cross sections of these Ln ions in this host. In this work codoped lanthanide doped KLuW nanocrystals (NCs) were synthesized by the sol-gel modified Pechini method to obtain a red, green and blue phosphors. Emission spectra under 980 nm near infrared (NIR) radiation as a function of excitation pump power were characterized to study the UC luminescence dynamics and for calculation of CIE color coordinates.

2. Experimental

(Ln:Yb):KLuW (Ln = Ho, Er, Tm) NCs were synthesized by the modified Pechini Method [4]. Er$^{3+}$, Ho$^{3+}$, Tm$^{3+}$ atomic content was fixed to 1 at. % and Yb$^{3+}$ to 10 at. %. Analytic grade purity reagents of Er$_2$O$_3$ (99.99%), Ho$_2$O$_3$ (99.9999%), Tm$_2$O$_3$ (99.9999%), Yb$_2$O$_3$ (99.9%), Lu$_2$O$_3$ (99.9999%), were dissolved in hot nitric acid to form the nitrate precursor. We used citric acid (CA) as the chelation agent and ethylenglycol (EG) as the esterification agent. The precursors were dissolved in distilled water solution with citric acid. Ammonium tungstate (NH$_4$)$_2$WO$_4$ (99.99%) and potassium carbonate K$_2$CO$_3$ (99.99%) were added to the aqueous solution and it was fixed at 353 K under magnetic stirring during 24 h until complete dissolution. Further, EG was added to the mixture and the solution was heated at 373 K in order to remove water and generate the polymeric gel. The polymer gel was calcinated at 573 K for 3 h to eliminate the organic compounds and finally annealed at 1023 K to obtain a nanocrystalline white powder that was putted in clear glass vials, especially for UC and PL measurements.

3. Results and Discussion

Figure 1 shows the X-ray powder diffraction patterns of doped KLuW samples obtained by annealing at 1023 K for 2h. All the peaks were indexed to the monoclinic phase of KLu(WO$_4$)$_2$ with the space group C2/c by comparison with the JCPDS 54-1204 card. After annealing, single phase material was obtained indicating that doping cations were incorporated into the host lattice, as expected. The morphology was characterized for faceted and irregular shapes as showed in Figure 2. The grain size values were estimated fitting the particle size distributions obtained by contrast method. Mean particle size of 130±70, 100±30 and 90±30 nm were calculated for Er-doped, Ho-doped and Tm-doped sample respectively.

![Figure 1. X-ray powder diffraction pattern of the synthesized doped KLuW NCs. JCPDS 54-1204 of KLu(WO$_4$)$_2$ is presented for comparison.](image1)

![Figure 2. TEM micrographs of 1 at.% Ho 10 at.% Yb KLuW nanocrystals.](image2)
Figure 3 shows the 980 nm excited UC emission spectra in the range of 450-725 nm, of Yb, Ln-doped nanocrystals and the observed emission bands labelled with the corresponding electronic transition in Er$^{3+}$, Ho$^{3+}$ and Tm$^{3+}$ ions. UC emission intensities ($I_{UC}$) versus power excitation ($I_0$) follow the proportionality $I_{UC} \propto (I_0)^n$ [5] as it shows in the log-log graphs in Figure 4. The calculated $n$ slope values for each emission band corresponds to the number of photons involved in the upconversion process. In that way upconversion dynamics corresponds to previous descriptions reported for Er:KYbW [6] and Ho:Tm:Yb:KLuW nanocrystals [7]. The experimental emission decay times under 460 nm excitation were evaluated by proposed model by Inokuti and Hirayama [5]. Table 1 summarizes the measured decay times from photoluminescence decay time curves of Ln-doped NCs.

**Figure 3.** NIR to visible UC luminescence spectra of codoped KLuW NCs at 74 W/cm$^2$ excitation power.

**Figure 4.** Integrated intensities versus excitation power density. The emissions correspond to 475 nm (squares), 540 nm (circles) and 650 nm (up triangles).

UC emitted colors have been quantified in terms of the CIE 1931 color diagram [8,9]. The dependence of CIE coordinates for different power density values for 1 at. % Ln, 10 at. % Yb:KLuW nanocrystals (Ln = Er, Ho, Tm) is shown in Figure 5. UC emitted colors are visible by the naked eye as shown in the inset pictures in Figure 5. Chromaticity coordinates are near the boundary, which means high color purity. The dominant wavelength and color purity were calculated for different values of excitation power density and they are listed in Table 2. Restricted excitation power density of Yb, Er-doped nanocrystals in Table 2 was a consequence of the observed saturation of the CCD detector under the fixed setup, for the Er$^{3+}$ $^2$H$_{11/2}$, $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$ green emission.

**Table 1.** Summary of measured decay times for 1 % Ln$^{3+}$ doped 1 % Ln 10 % Yb:KLuW nanocrystals after 460 nm excitation.

| Emitting State | $\lambda_{EM}$ [nm] | $\tau$ [±1 µs] |
|---------------|-----------------|--------------|
| Er$^{3+}$     | $^4$H$_{11/2}$, $^4$S$_{3/2}$ | 550 | 9 |
|               | $^4$F$_{9/2}$   | 660 | 5 |
|               | $^4$I$_{15/2}$  | 800 | 11 |
| Ho$^{3+}$     | $^5$S$_2$       | 540 | 5 |
|               | $^5$F$_{5}$     | 650 | 7 |
| Tm$^{3+}$     | $^3$G$_4$       | 475 | 76 |
|               | $^3$H$_4$       | 800 | 137 |

**Table 2.** Chromaticity properties of 1 at. % Ln, 10 at. % Yb:KLuW (Ln = Er, Ho, Tm) nanocrystals

| Active Ion | Excitation power density [W/cm²] | Dominant wavelength [nm] | Color purity [%] |
|-----------|---------------------------------|--------------------------|-----------------|
| Er$^{3+}$ | 15-100                          | 547 - 540                | 96 – 97         |
| Ho$^{3+}$ | 50 – 250                        | 574 - 563                | 96 – 97         |
| Tm$^{3+}$ | 50 – 250                        | 473 - 472                | 84 – 87         |
Figure 5. Chromaticity diagram for 1 at. % Ln, 10 at. % Yb:KLuW (Ln= Er, Ho, Tm) nanocrystals for excitation power densities in the range 10-250 W/cm², in the indicated arrow direction.

Figure 6. Chromaticity diagram for the mixture of 1 % Ho, 10 at. % Yb:KLuW and 1 at. % Tm, 10 at. % Yb: KLuW nanocrystals, with $a_{Tm}^2:a_{Ho}=1:4$. Symbol size is proportional to excitation power density, from 94 to 354 W/cm². Simulated data (circles), experimental data (squares).

For the calculation of a white light emitter, we have defined a sub-space base in the color $X_{XYZ}$ space which is formed by linear combination of the tristimulus functions obtained for each sample expressed as vectors $(X_i, Y_i, Z_i)$ where $i$ indicates the dopant cation Er$^{3+}$, Tm$^{3+}$ or Ho$^{3+}$. In this sub-space any vector is expressed as,

$$\mathbf{X} = \begin{bmatrix} X_{Er} \\ Y_{Er} \\ Z_{Er} \end{bmatrix}, \mathbf{X}_{Tm} = \begin{bmatrix} X_{Tm} \\ Y_{Tm} \\ Z_{Tm} \end{bmatrix}, \mathbf{X}_{Ho} = \begin{bmatrix} X_{Ho} \\ Y_{Ho} \\ Z_{Ho} \end{bmatrix}$$

$$a_i = \begin{bmatrix} a_{Er} \\ a_{Tm} \\ a_{Ho} \end{bmatrix}$$ (1)

where the $a_i$ coefficients determine the relative intensity of each $(X_i, Y_i, Z_i)$ vector in the linear combination. Here we suppose that each $a_i$ coefficient corresponds experimentally to relative doping concentration of sample doped with cation $i$ in the mixture. Chromaticity coordinates were calculated by application of the normalization condition $X+Y+Z=1$.

In the mixture of Yb,Ln-doped nanocrystals, a reduction of the total Ln$^{3+}$ to Yb$^{3+}$ ratio is realized, and therefore a proportional quenching of the UC emission could be expected. The excitation is produced through Yb$^{3+}$ ions. Individual samples of nanocrystals have the same 1 at. % Yb$^{3+}$ content, in consequence, the mixture has 1 at. % Yb$^{3+}$ content. Before mixture the total Tm-to-Yb (Ho-to-Yb) ratio is 1/10 (1/10). After a mixture with the relative molar $a_{Tm}^2:a_{Ho}=1:4$, it changes to 0.2/10 (0.8/10), so we expect an intensity of 20 % (80 %) in comparison with the corresponding emissions in the Ln,Yb:KLuW samples. Figure 3 shows the UC emission spectra for mixture at low excitation power. As the intensities are reduced after mixture, and the UC quantum yield is proportional to the emission UC intensity we can indicate that quantum yield is reduced after physical mixture of nanocrystals.

For the larger quenching of the Tm$^{3+}$ $^1G_4\rightarrow^3H_6$ blue emission, we propose a self-absorption process of this radiation through the Ho$^{3+}$ $^3F_{2,3}$ multiplet. The temperature can play an important role by
modifying the UC efficiency of each emission. However interactions between Yb, Ho-doped and Yb, Tm-doped nanocrystals cannot be discarded. The UC process is nonlinear in nature and tailoring of a UC white light emitter by mixture of powders does not follow a simple addition of the spectra of each powder.

The chromaticity coordinates for the mixture of Yb, Ho-doped and Yb, Tm-doped nanocrystals start moving across the upper part of the white region in the chromaticity diagram in Figure 6, from the yellow to the blue region, as the power density increases in the 94-354 W/cm² range. Simulated data only coincide in following the direction path traced by experimental chromaticity coordinates. In the 94-354 W/cm² power density range, deviations of the simulated chromaticity coordinates correspond to a large contribution of the Tm³⁺ 1G₄→3H₆ blue emission at low power excitation and the saturation of this emission at high power excitation. These phenomena are not observed in the UC emission spectra of the nanocrystals mixture, indicating that there is an energy interaction between Yb, Ho- and Yb, Tm-doped nanocrystals for the UC process and the proposed model cannot explain these results.

4. Conclusions

1 at. % Ln:10 at. %Yb:KLu(WO₄)₂ (Ln=Er, Tm, Ho) nanocrystals with ~100 nm particle size have been prepared by the modified Pechini method, with monoclinic C2/c crystalline phase. Chromaticity coordinates and tristimulus functions were calculated from excitation power dependence of the upconversion spectra. A white light emitter was predicted for a physical mixture of 1 at. % Tm³⁺, 10 at. % Yb³⁺ KLu(WO₄)₂ and 1 at. % Ho³⁺, 10 at. % Yb³⁺ KLu(WO₄)₂ in the 1:4 ratio. Comparison with a physical mixture of nanocrystals shows partial approximation for excitation power densities below 74 W/cm². The upconversion quantum yield was reduced after physical mixture of nanocrystals showing that resulting spectra of a mixture of upconversion emitting powders does not match simple addition of the spectra of each emitting powder.

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