Journal of Nanophotonics

Nanophotonics.SPIEDigitalLibrary.org

Green upconversion in $\text{Y}_2\text{O}_3:\text{Yb}$ nanopowder

Darja Horvat
Dušan Lazar
Janez Možina
Janez Križan
Janez Diaci
Mira Terzić

Green upconversion in $\text{Y}_2\text{O}_3:\text{Yb}$ nanopowder

Darja Horvat,^{a,*} Dušan Lazar,^b Janez Možina,^a Janez Križan,^c
Janez Diaci,^a and Mira Terzić^b

^aUniversity of Ljubljana, Faculty of Mechanical Engineering, Aškerčeva 6,
1000 Ljubljana, Slovenia

^bUniversity of Novi Sad, Faculty of Science, Trg Dositeja Obradovića 4, 2100 Novi Sad, Serbia

^cAMI d.o.o., Trstenjakova 5, 2250 Ptuj, Slovenia

Abstract. Green emission lines, in addition to the blue and the red, were observed upon 980 nm excitation in yttrium oxide (Y_2O_3) nanopowder codoped with Yb^{3+} and Tm^{3+} , synthesized by the chemical combustion method. Upconversion emission studies suggest that the number and characteristics of the green lines are influenced by the annealing temperature as well as by the $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentration ratio, opening possibilities for new customized applications. The chromaticity properties of the upconversion spectra were quantified by the Commission Internationale de l'éclairage coordinate analysis. © 2015 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JNP.9.093054](https://doi.org/10.1117/1.JNP.9.093054)]

Keywords: upconversion luminescence; optical properties; nanophosphor; fluorescence spectroscopy; Commission Internationale de l'éclairage coordinate.

Paper 15043 received Jun. 4, 2015; accepted for publication Aug. 3, 2015; published online Sep. 11, 2015.

1 Introduction

In recent years, rare earth (RE) doped nanocrystalline materials have received considerable interest due to their unique properties for the potential applications in many fields of optoelectronics, photonics, and nanobiotechnology.^{1–5} The reason for this lies in the fact that such materials are able to convert near-infrared (NIR) light into light with a shorter wavelength: ultraviolet (UV), visible, and shorter NIR.

In the upconversion (UC) processes, the characteristics of host materials play an important role. Many host materials have been developed, such as $\text{Y}_3\text{Al}_5\text{O}_{12}$,⁶ Al_2O_3 ,⁷ MgAl_2O_3 ,⁷ Gd_2O_3 ,⁸ yttrium oxide (Y_2O_3),^{9,10} and NaYF_4 ,^{1,11,12} with high UC emission efficiency. Among these materials, Y_2O_3 is a suitable host material for doping with RE ions like ytterbium (Yb^{3+}), holmium (Ho^{3+}), erbium (Er^{3+}), europium (Eu^{3+}), praseodymium (Pr^{3+}), and thulium (Tm^{3+}).

RE doped Y_2O_3 materials are promising for numerous photonics applications because of their excellent physical properties and chemical and photochemical stability, as well as high luminescence efficiency. Y_2O_3 has a high melting point (2450°C), high thermal conductivity, broad transparency range (0.2 to 8 μm), and high refractive index (~ 2).¹³ Beside this, the non-radiative relaxation rate is relatively small for RE ions in Y_2O_3 host material, which can greatly enhance the luminescence emission.^{12,14,15}

Tm^{3+} ions exhibit strong luminescence in the UV, blue, and red regions, and do not absorb 980 nm radiation. The population of the upper levels of Tm^{3+} ions can be achieved through energy transfer from a sensitizer. The studies show a significant increase in the UC yield when the host material is codoped with Yb^{3+} as a sensitizer and Tm^{3+} as an activator.^{16–18}

The absorption cross-section of Yb^{3+} ion near 980 nm is quite large, so Yb^{3+} is well equipped to actively transfer the absorbed energy to other RE codopants. Because its energy levels are resonant with the f–f transitions of many lanthanide activators (Pr^{3+} , Ho^{3+} , Er^{3+} , and Tm^{3+}), it is favorable to codepo RE ions with Yb^{3+} to increase the UC efficiency. Depending on the activators, different UC emissions can be obtained with NIR excitation.

*Address all correspondence to: Darja Horvat, E-mail: darja.horvat@fs.uni-lj.si

Several works have examined the UC emission of Yb^{3+} and Tm^{3+} doped Y_2O_3 .^{19–23} They are mainly focused on strong blue and weak red emission of Tm^{3+} ions. Up until now, the green UC region has been mentioned (535 to 560 nm) only in a few studies.^{20,24}

Here, we report efforts to enhance UC emission in the green region in $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanopowders and to improve UC luminescence characterization of these nanopowders. We analyze the influence of the annealing temperature on the existence of UC emission in the green region, for nanopowders prepared via solution combustion synthesis. The influence of the $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentration ratio on green UC lines is also discussed.

2 Experimental

Yb - and Tm -doped Y_2O_3 nanopowders were prepared by solution combustion synthesis.²⁵ The solution of 18.38 g (192 mol %) of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.674 g (6 mol %) of $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.045 g (0.4 mol %) $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used as the reagent grade. These compounds were dissolved in a minimum amount of demineralized water. Then 7.508 g (500 mol %) of urea was added to the solution as the organic fuel. After preparation, the starting reagents were combusted with the flame burner at 500°C. The intensive exothermic reaction yielded a voluminous foamy powder. The synthesized products were annealed at two different temperatures, 1200 and 1400°C, for 2 h. All chemicals were commercially available and used in synthesis procedures without further purification.

The x-ray powder diffraction (XRD) patterns of the title nanocrystalline powder annealed at 1200 and 1400°C were collected using automatic two-circle powder diffractometer Seifert MZ IV using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm) monochromatized by the Ni β -filter. The x-ray tube was operated at 40 kV and 30 mA. Data were obtained within 2θ in the range of 10 to 120 deg, with a step of 0.02 deg/8 s.

Optical properties of $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ were studied by upconversion photoluminescence (UPL) spectroscopy. UPL spectra were obtained upon exciting the sample with a 980 nm laser diode with an incident radiation power of 1500 mW. All upconverted signals passed through an optical bandpass filter (400 to 700 nm) and were collected by an Ocean Optics USB4000 spectrometer.

3 Results and Discussion

3.1 Characterization

The recorded diffractograms of codoped Y_2O_3 samples were compared with the JCPDS file no. 41-1105 and 83-0927 for pure Y_2O_3 , as shown in Fig. 1, for the sample annealed at 1200°C. The sharp single peaks of the XRD patterns unambiguously confirm the formation of single phase compounds, which is attributable to the fact that the annealing process took place uniformly throughout the volume of the samples. All peaks match well with those of pure cubic Y_2O_3 (no peaks were observed due to dopants), thereby suggesting a highly crystalline body-cubic structure ($a = 1.06$ nm) belonging to the space group $\text{Ia}\bar{3}$ (SG206) and no structural phase transition during annealing.

The average size of the nanopowders was estimated from the linewidth of the XRD peaks using the well-known Scherrer's equation $d = -K\lambda/\beta \cos \theta$, where $K = 0.9$ is a constant related to the nanopowder shape, $\lambda = 0.154$ nm is the wavelength of the x-ray radiation used, β is the full width at half maximum (FWHM) of the diffraction peak in the XRD patterns in radians, and θ is the Bragg diffraction angle. The nine peaks [(211), (222), (400), (411), (332), (341), (431), (440), (622 nm)] have been selected for this determination. The average sizes of the nanopowders annealed at 1200 and 1400°C are 70.6 (23) nm and 74.8 (23) nm, respectively.

As the correction of the linewidths for the instrumental broadening was not included, we assume that the average nanopowder sizes are, in fact, somewhat greater than what is stated above. As the profiles of the peaks in the diffraction patterns of the samples are predominantly Gaussian, both size, D , and microstrain, ϵ , in the nanopowder were estimated by the Williamson-Hall (W-H) analysis. For a Gaussian line, the W-H relation is

Fig. 1 The x-ray diffraction patterns of $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanopowders with Y_2O_3 body-centered cubic structure with space group (206).

$$(\Gamma^2)_G \cos^2 \theta = \left(\frac{K\lambda}{D} \right)^2 + 16\epsilon^2 \sin^2 \theta, \quad (1)$$

where Γ is the FWHM, and ϵ represents the average microstrain present in the nanopowders. The plot $(\Gamma^2)_G \cos^2 \theta$ versus $16\epsilon^2 \sin^2 \theta$ yields a straight line. The size was determined from the intercept of the linear fit with the axis, and the microstrain from the slope. The sizes are $D_{\text{W-H}(1200)} = 70.5(3)$ nm and $D_{\text{W-H}(1400)} = 74.7(4)$ nm, while the microstrain is the same for both samples, i.e., $\epsilon = 1.96 \cdot 10^{-3}$, considering the uncertainty.

The grain size of the sample, which was annealed at 1400°C , was estimated based on the ratio of the half-width of the diffraction lines to those of the sample annealed at 1200°C . It was found that $D_{\text{eff}}^{1400} = (H_w^{1200}/H_w^{1400})D_{\text{eff}}^{1200} = 1.066(3) \cdot D_{\text{eff}}^{1200}$, where H_w is the FWHM. Hence, the grain is greater by 7% relative to the grain of the sample annealed at 1200°C .

3.2 Upconversion

The UC spectra of $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanopowders upon 980 nm excitation were obtained in the wavelength range of 400 to 750 nm at room temperature. The spectra exhibit two major bands centered at around 485 nm (blue emission) and 660 nm (red emission), and a minor band around 550 nm (green emission), as seen in Fig. 2. As the bands are separated, we performed the Gaussian–Lorentzian deconvolution analysis dividing the UC spectra into three ranges: 400 to 510 nm, 510 to 580 nm, and 580 to 750 nm. The decomposed individual Gaussian–Lorentzian peaks for these ranges are shown in Fig. 3. The schematic diagram of the upconversion processes is shown in Fig. 4.

In the first region (400 to 510 nm), five evident UC emissions are resolved, centered at 465 nm, (transition $^1\text{D}_2 \rightarrow ^3\text{F}_4$ of Tm^{3+} ion), 477 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$), and 488 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$). The emission observed at 488 nm has the highest amplitude. For both samples, the first three peaks have the same peak positions within experimental errors.

The situation in the third region is quite different, where the wavelength ranges 580 to 750 nm and the difference in the overall emission intensity can be observed as well as a difference in the number of emission lines (Table 1). This is especially evident in the range 612 to 640 nm, where for the sample annealed at 1200°C , two emission peaks appear at 612 and 632 nm, both due to transitions $^1\text{G}_4 \rightarrow ^3\text{F}_4$ of Tm^{3+} ion. On the other hand, the sample annealed

Fig. 2 Measured upconversion spectra of $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ nanopowders annealed at 1200 and at 1400°C. The sample was excited at 980 nm.

at 1400°C has an emission peak at 632 nm, also due to the transition $^1\text{G}_4 \rightarrow ^3\text{F}_4$. Interestingly, the next positions of emission peaks 653, 665, 673, 686, and 697 nm for both samples are identical, taking into account the experimental errors.

Compared to the emissions in the blue and the red regions, the intensity peaks in the green region (510 to 580 nm) are considerably smaller. These weak UC emissions are the results of the energy transfer $^1\text{D}_2 \rightarrow ^3\text{H}_5$ of Tm^{3+} ions. The reason for the low intensity is the very small cross-energy transfer rate of $^1\text{D}_2 \rightarrow ^3\text{H}_5$ transitions.²⁷ For the sample annealed at 1200°C, we found two green UC lines (525 and 546 nm). These results are in good agreement with data reported by Mishra et al.²⁴ for $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$, synthesized by the combustion technique and annealed at 1200°C (Table 1). They observed two UC emissions (530 and 555 nm), for ytterbium versus thulium concentration ratio ($\text{Yb}^{3+}/\text{Tm}^{3+}$) of 5. The difference in the position of the green lines between our data and the data from Mishra et al.²⁴ can be attributed to the different $\text{Yb}^{3+}/\text{Tm}^{3+}$ ratio. For the sample annealed at 1400°C, four UC emission lines were found (524, 538, 550, and 564 nm). The green emission band for the sample annealed at 1200°C is significantly weaker. The weak emissions in the green region were also reported in different host codoping with Yb^{3+} and Tm^{3+} ions (in Ref. 28 at 574 nm, in Ref. 12 at 514 nm, and in Ref. 29 at 511 nm).

In the literature, several ways are described explaining how the $^1\text{D}_2$ level of Tm^{3+} ions in different host materials is populated.^{30–32} Some controversy exists about the possibility of the population of the $^1\text{D}_2$ level via a fourth nonresonant transfer of energy from Yb^{3+} ion to Tm^{3+} ion in the $^1\text{G}_4$ level. The phonon-assisted energy transfer probability is governed by the energy-gap law $W = W_0 \exp(-k\Delta E)$, where W_0 is the energy transfer probability when the zero phonon lines overlap, k is the material constant determined by the characteristics of the host material that surrounds the optically active ions, and ΔE is the energy gap between the electronic levels of the donor and acceptor ions.³² The population of the $^1\text{D}_2$ level is a result of the energy transfer $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^1\text{G}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}) + ^2\text{F}_{7/2}(\text{Yb}^{3+})$. These transitions occur with little probability due to large energy mismatch ($\sim 3500 \text{ cm}^{-1}$) between Yb^{3+} ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) and Tm^{3+} ($^1\text{G}_4 \rightarrow ^1\text{D}_2$).^{3,24,30,32} Due to this, the intensities of the lines arising from $^1\text{D}_2$ should be very small. Contrary to this, it was reported for fluorescence transitions $^1\text{D}_2 \rightarrow ^3\text{H}_6$, the $^1\text{D}_2$ level of Tm^{3+} is not populated via the fourth photon from Yb^{3+} via energy transfer to $^1\text{G}_2$.^{23,33}

On the other hand, a cross-relaxation process may alternatively play an important role in population of the $^1\text{D}_2$ level of Tm^{3+} ions. According to data from the literature, the energy transfer between Tm^{3+} ions can take several possible routes:^{3,19,23,24,26,30}

Fig. 3 Deconvolution of upconversion spectra for $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ annealed at 1400°C : (a) blue region, wavelength 400 to 520 nm, (b) green region, wavelength 510 to 580 nm, and (c) red region, wavelength range 600 to 750 nm.

Table 1 Emission bands and transitions in $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanopowder.

This work			Reference 26		Reference 24		Reference 20	
Excitation (nm)	980		980		976		976	
	Tm ³⁺ (0.4 mol%) Yb ³⁺ (6.0 mol%)		Tm ³⁺ (0.2 mol%) Yb ³⁺ (3.0 mol%)		Tm ³⁺ (0.5 mol%) Yb ³⁺ (2.5 mol%)		Tm ³⁺ (0.5 mol%) Yb ³⁺ (3.0 mol%)	
Annealed at	1200°C	1400°C	880°C		1200°C		800°C; 1200°C	
Transition	Peak position (nm)		Transition	Peak position (nm)	Transition	Peak position (nm)	Transition	Peak position (nm)
			¹ I ₆ → ³ H ₆	298	¹ I ₆ → ³ H ₆	300	¹ I ₆ → ³ H ₆	301
					¹ I ₆ → ³ F ₄	346		
			¹ D ₂ → ³ H	364	¹ D ₂ → ³ H ₆	364	¹ D ₂ → ³ H ₆	368
			¹ I ₆ → ³ H ₅	391	¹ I ₆ → ³ H ₅	394	¹ I ₆ → ³ H ₅	394
¹ D ₂ → ³ F ₄	465	465			¹ D ₂ → ³ F ₄	467	¹ D ₂ → ³ F ₄	466
¹ G ₄ → ³ H ₆	477	477			¹ G ₄ → ³ H ₆	478 to 490		
	488	488	¹ G ₄ → ³ H ₆	489			¹ G ₄ → ³ H ₆	491
¹ D ₂ → ³ H ₅	525	524			¹ D ₂ → ³ H ₅	530		
		538						
	548	550				555		
		563						
¹ G ₄ → ³ F ₄	613							
	627	628			¹ G ₄ → ³ F ₄ ³ F _{2,3} → ³ H ₆	610 to 710		
	654	654					¹ G ₄ → ³ F ₄	658
	666	666						
³ F _{2,3} → ³ H ₆	675	675					³ F ₂ → ³ H ₆	679
	686	686						
	697	697						
							¹ D ₂ → ³ F ₃	777
					¹ G ₄ → ³ H ₅	760	¹ G ₄ → ³ H ₅	798
			³ F ₄ → ³ H ₆	813			³ H ₄ → ³ H ₆	817
					³ H ₄ → ³ H ₆	850		

$^3\text{H}_4(\text{Tm}^{3+}) \rightarrow ^3\text{F}_4(\text{Tm}^{3+}), ^1\text{G}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}),$
 $^1\text{G}_4(\text{Tm}^{3+}) \rightarrow ^3\text{F}_4(\text{Tm}^{3+}), ^3\text{H}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}),$
 $^3\text{F}_2(\text{Tm}^{3+}) \rightarrow ^3\text{H}_6(\text{Tm}^{3+}), ^3\text{H}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}),$
 $^1\text{G}_4(\text{Tm}^{3+}) \rightarrow ^3\text{H}_6(\text{Tm}^{3+}), ^3\text{F}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}),$
 $^3\text{F}_4(\text{Tm}^{3+}) \rightarrow ^3\text{H}_6(\text{Tm}^{3+}), ^1\text{G}_4(\text{Tm}^{3+}) \rightarrow ^1\text{D}_2(\text{Tm}^{3+}).$

The population of the $^1\text{D}_2$ increases with increasing Tm^{3+} concentration. This causes a decrease in $^1\text{G}_4$ and other levels' populations. In this work, the ratio of $\text{Yb}^{3+}/\text{Tm}^{3+}$

Fig. 4 Schematic diagram of the upconversion processes and simplified energy level diagrams for the Yb^{3+} , Tm^{3+} codoped Y_2O_3 .

concentration was 15, while in the work of Mishra et al.,²⁴ it was 5 and the annealing temperature was 1200°C.

To better understand the UC mechanisms of Tm^{3+} and Yb^{3+} ions which lead to green emission lines in the Y_2O_3 matrix, we compare the emission UC intensity of different emission bands (Fig. 5). The data were integrated numerically. The integrated area, A , of blue transitions ($^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$) is somewhat higher ($\sim 6\%$) for the sample annealed at 1400°C compared with the sample annealed at 1200°C. Unlike the blue emission band, a significantly higher increase in ratio for emission intensity, A_{1400}/A_{1200} , is observed for the red ($\sim 80\%$) and the green ($\sim 60\%$) emission lines.

With higher annealing temperature, the integrated intensity ratio of red to green emission bands A^r/A^g increases from 9.8 to 11. The red and the green emission intensities are proportional to the population of the $^1\text{G}_4/{}^3\text{F}_{2,3}$ and $^1\text{D}_2$ states, respectively. An increase in ratio indicates that

Fig. 5 Integrated upconversion intensity of $\text{Y}_2\text{O}_3:\text{Yb, Tm}$ of the blue, green, and red regions for two annealing temperatures (1200 and 1400°C).

$^1\text{D}_2$ and $^3\text{F}_{2,3}$ states were populated more efficiently than the $^1\text{D}_2$ state for the sample annealed at a higher temperature.

In contrast to A^r/A^g , the ratio of blue to green emission bands, A^b/A^g , significantly decreases with increasing annealing temperature from 38 to 25. Both the blue and the green emission intensities depend on the population $^1\text{D}_2$ (line 465 nm). Moreover, the blue emission depends on the population of the $^1\text{G}_4$ state. On the other hand, the contribution of the line at 465 nm to total emission from transition $^1\text{D}_2 \rightarrow ^3\text{F}_4$ in the blue bands is small and slightly changed (from 1 to 1.24%) with a rise in the annealing temperature. This indicates that the $^1\text{D}_2$ state became more populated than the $^1\text{G}_4$ state for the sample annealed at a higher temperature. Due to this, with higher annealing temperature, the intensity of the green emission from transition $^1\text{D}_2 \rightarrow ^3\text{H}_5$ increases more and the blue emission from $^1\text{G}_4 \rightarrow ^3\text{H}_6$ increases only slightly.

To identify the number of photons n , which are required to populate the upper emitting state for the green emission process under unsaturated conditions, the dependence of UC fluorescence intensity on incident pump power is studied. The dependence of UC fluorescence intensity, I_{up} , on incident pump power, P , can be obtained according to the relation¹⁷

$$I_{up} \propto P^n.$$

Hence, the number of photons, n , can be estimated from the slope of the line $\ln(I_{up})$ versus $\ln(P)$. The linear least squares fit approach was used to obtain these slopes. The results for selected emission bands for the two samples are presented in Fig. 6.

The slopes for the sample prepared at a higher temperature (1400°C) are somewhat greater than the slopes for the sample prepared at the lower temperature (1200°C). This difference is most pronounced ($\sim 20\%$) for the band at 654 nm. The values for this line are 3.8 ± 0.3 (1200°C) and 4.57 ± 0.13 (1400°C). Taking into account the uncertainty, the obtained data for the slope indicate that four (1200°C) and five (1400°C) photons are necessary to populate the $^1\text{G}_4$ state. The blue line at 488 nm shows less dependence on the annealing temperature. The calculated values are 4.12 ± 0.29 (1200°C) and 4.43 ± 0.27 (1400°C), indicating that four (possibly five) photons are involved to generate this UC line. To our knowledge, such values for slope have not been reported in the literature for $\text{Y}_2\text{O}_3:\text{Yb,Tm}$, or for any other host doped with Yb^{3+} and Tm^{3+} ions. Usually, the blue and the red UC emission lines are reported to be realized via two to three photons.^{9,24,29}

Interestingly, the green band also shows a deviation from the data in the literature. A fourth energy transfer has been proposed to populate the $^1\text{D}_2$ level.²⁴ For the weak green UC emission line at 511 nm detected in a different host (NaYF_4 ; with $\text{Yb/Tm} = 60$), it was found that four photons are involved in its generation.³⁴ Here, the power dependence gives smaller values:

Fig. 6 The variation of upconversion emission intensity with laser pump power for $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ nanopowders excited at 980 nm for various emission bands for two samples prepared at two different annealing temperatures.

3.0 ± 0.8 (1200°C) and 3.14 ± 0.27 (1400°C) (Fig. 6). There is evidently a higher uncertainty in the slope for the sample annealed at 1200°C, arising from the nonlinear fitting/deconvolution process to identify the green lines, which are less intense compared with the intensity of green lines in the sample annealed at 1400°C. This indicates that three photons are involved in the pump process for the $^1\text{D}_2$ state of the Tm^{3+} ion. Stecher et al.³⁴ observed a smaller number of photons (two) for the 511 nm line in $(\text{Na})\text{LaF}_3:\text{Yb, Tm}$ (with $\text{Yb}/\text{Tm} = 40$). We believe that the $^1\text{D}_2$ level of Tm^{3+} is populated by the four photon process, but the rapid nonradiative relaxation to the level $^1\text{G}_4$ appears to reduce the number of photons involved in the green emission. At the same time, this process contributes to the increased population of the level $^1\text{G}_4$. Hence, four/five photons participate in generating the red and the blue bands. The described behavior can be attributed to the combined effects of the improved nanopowder crystallinity (effect of annealing temperature), Yb/Tm ratio (i.e., concentration of dopant ions), crystal structure, and host materials.

Mechanisms responsible for populating the $^1\text{D}_2$ state are the cross-relaxation processes in the $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanopowder. The results show that these processes become more pronounced for the higher annealing temperature and higher $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentration ratios leading to increased green UC emission ($^1\text{D}_2 \rightarrow ^3\text{H}_5$).

Annealing of the $\text{Y}_2\text{O}_3:\text{Yb, Tm}$ nanopowder at 1400°C was reported only in the work Giri et al.,³⁵ but no green band was mentioned, although the ratio $\text{Yb}^{3+}/\text{Tm}^{3+} = 5$ is the same as in the work of Mishra et al.²⁴ One of the possible reasons may be that with increasing annealing temperature, the average nanopowder size is increased.

3.3 Chromaticity Properties of Upconversion Emission

The chromaticity properties of UC emission have been quantified in terms of the The Commission Internationale de l'éclairage (CIE) 1931 chromaticity diagram.^{36,37} The CIE coordinates depending on the annealing temperature (1200 and 1400°C), as well as on the pump excitation powers from 500 to 1000 mW were determined. The variation in CIE color on the annealing temperature is evident and is shown on the CIE chromaticity diagram (Fig. 7).

Fig. 7 The Commission Internationale de l'éclairage chromaticity diagram of upconversion emission spectra of $\text{Y}_2\text{O}_3:\text{Yb, Tm}$ nanopowder for samples annealed at 1200°C (○) and 1400°C (□) under laser excitation at 980 nm for different incident radiation powers (500 to 1000 mW).

This behavior suggests that nanopowder size has a significant influence on its UC emission color.

The chromaticity coordinate for the nanopowder sample annealed at 1200°C lies in the pink and the orange-pink region of the CIE diagram. On the other hand, the sample annealed at 1400°C lies closer to white light and partly in the yellow region, although with a decrease in pump excitation power, the UC intensity decreases and there is no change in the peak positions of all emission bands. The obtained results show that the UC emission color of $\text{Y}_2\text{O}_3:\text{Yb},\text{Tm}$ can be tuned by the introduction of the green UC line, which can be achieved by changing the annealing temperature (nanocrystal size), the $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentration ratio, and the incident laser power.

4 Conclusion

The analysis of green UC emission lines in $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ nanopowders prepared by solution combustion synthesis showed that the annealing temperature has an important influence on the UC emission spectra. Increasing the annealing temperature for 200°C resulted in $\sim 7\%$ greater nanopowder average size, while the number of emitting green lines doubled and the integrated emission intensity increased by 60%. Another factor influencing the shape and intensity of the green lines is the $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentration ratio.

The impact of different influencing factors on the UC spectra is quantified and characterized by the chromaticity coordinate in the CIE diagram.

With this knowledge, custom design of the UC emission spectra is possible and the use of $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ nanopowder shows a promising potential for different but related applications, such as biolabeling, white light sources, back lighting, three-dimensional displays, etc.

Acknowledgments

This work has been done within the projects MESTD RS OI 171020, Bilateral Project Serbia–Slovenia #651-03-1251/2012-09/03, project MESTD RS III 45008 as part of the development of new materials in nanotechnology, and project BI-RS/12-13-003 (SLO Research Agency).

References

1. M. Nyk et al., “High contrast in vitro and in vivo photoluminescence bioimaging using near infrared to near infrared up-conversion in Tm^{3+} and Yb^{3+} doped fluoride nanophosphors,” *Nano Lett.* **8**, 3834–3838 (2008).
2. M. Godlewski et al., “Nanoparticles doped with TM and RE ions for applications in optoelectronics,” *Opt. Mater.* **31**, 490–495 (2009).
3. G. Chen et al., “Light upconverting core-shell nanostructures: nanophotonic control for emerging applications,” *Chem. Soc. Rev.* **44**, 1680–1713 (2015).
4. A. Podhorodecki et al., “Multicolor light emitters based on energy exchange between Tb and Eu ions co-doped into ultrasmall $\beta\text{-NaYF}_4$ nanocrystals,” *J. Mater. Chem.* **22**, 5356–5361 (2012).
5. S. Gai et al., “Recent progress in rare earth micro/nanocrystals: soft chemical synthesis, luminescent properties, and biomedical applications,” *Chem. Rev.* **114**, 2343–2389 (2014).
6. M. Lawrence, H. Zhao, and L. Ganippa, “Gas phase thermometry of hot turbulent jets using laser induced phosphorescence,” *Opt. Express* **21**, 12260–12281 (2013).
7. J. Križan et al., “Synthesis and fluorescent properties of chromium-doped aluminate nanopowders,” *Acta Chim. Slov.* **59**(1), 163–168 (2012).
8. Y. Jia et al., “Upconverted photoluminescence in Ho^{3+} and Yb^{3+} codoped Gd_2O_3 nanocrystals with and without Li^+ ions,” *Luminescence* **26**, 259–263 (2011).
9. F. Vetrone et al., “A spectroscopic investigation of trivalent lanthanide doped Y_2O_3 nanocrystals,” *Nanotechnology* **15**, 75–81 (2004).
10. B. K. Gupta et al., “Synthesis and characterization of ultra-fine $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors for luminescent security ink applications,” *Nanotechnology* **21**, 055607 (2010).

11. W. H. Zhang, F. Ding, and S. Y. Chou, "Large enhancement of upconversion luminescence of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystal by 3D plasmonic nano-antennas," *Adv. Mater.* **24**, OP236–OP241 (2012).
12. J. Zhao et al., "Single-nanocrystal sensitivity achieved by enhanced upconversion luminescence," *Nat. Nanotechnol.* **8**, 729–734 (2013).
13. T. S. Atabaev, Y. H. Hwang, and H. K. Kim, "Color-tunable properties of Eu^{3+} - and Dy^{3+} -codoped Y_2O_3 phosphor particles," *Nanoscale Res. Lett.* **7**, 556 (2012).
14. Y. Guyot et al., "Luminescence properties of Y_2O_3 single crystals doped with Pr^{3+} or Tm^{3+} and codoped with Yb^{3+} , Tb^{3+} or Ho^{3+} ions," *Opt. Mater.* **5**, 127–136 (1996).
15. F. Vetrone et al., "Effect of Yb^{3+} codoping on the upconversion emission in nanocrystalline $\text{Y}_2\text{O}_3:\text{Er}^{3+}$," *J. Phys. Chem. B* **107**, 1107–1112 (2003).
16. F. Auzel, "Up-conversion and excited state absorption in laser crystals and glasses: advantages and disadvantages," in *Nonlinear Spectroscopy of Solids: Advances and Applications*, B. Baldassare, Ed., pp. 531–553, Plenum Press, New York (1994).
17. F. Auzel, "Upconversion and anti-Stokes processes with f and d ions in solids," *Chem. Rev.* **104**, 139–173 (2004).
18. J. Zhang et al., "Mechanisms and concentrations dependence of up-conversion luminescence in $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped oxyfluoride glass-ceramics," *Phys. Lett. A* **337**, 480–486 (2005).
19. T. Li et al., "Ultraviolet upconversion luminescence in $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanocrystals and its application in photocatalysis," *J. Mater. Sci.* **46**, 2882–2886 (2011).
20. R. S. Yadav, R. K. Verma, and S. B. Rai, "Intense white light emission in $\text{Tm}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{Y}_2\text{O}_3\text{--ZnO}$ nano-composite," *J. Phys. D Appl. Phys.* **46**, 275101 (2013).
21. Q. Lü et al., "Experimental study on the surface modification of $\text{Y}_2\text{O}_3:\text{Tm}^{3+}/\text{Yb}^{3+}$ nanoparticles to enhance upconversion fluorescence and weaken aggregation," *Nanotechnology* **19**, 145701 (2008).
22. C. B. Zheng et al., "Upconversion emission from amorphous $\text{Y}_2\text{O}_3:\text{Tm}^{3+}/\text{Yb}^{3+}$ prepared by nanosecond pulsed laser irradiation," *Chem. Phys. Lett.* **509**, 29–32 (2011).
23. X. Chen and Z. Song, "Study on six-photon and five-photon ultraviolet upconversion luminescence," *J. Opt. Soc. Am. B* **24**, 965–972 (2007).
24. K. Mishra, N. K. Giri, and S. B. Rai, "Preparation and characterization of upconversion luminescent $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped Y_2O_3 nanophosphor," *Appl. Phys. B* **103**, 863–875 (2011).
25. M. S. Rabasović et al., "Characterization and luminescent properties of Eu^{3+} doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanopowders," *J. Alloys Comp.* **622**, 292–295 (2015).
26. G. Y. Chen, G. Somesfalean, and Z. G. Zhang, "Ultraviolet upconversion fluorescence in rare earth-ion-doped Y_2O_3 induced by infrared diode laser excitation," *Opt. Lett.* **32**, 87–89 (2007).
27. X. Chen et al., "Multiphoton near-infrared quantum cutting luminescence phenomena of Tm^{3+} ion in $(\text{Y}_{1-x}\text{Tm}_x)_3\text{Al}_5\text{O}_{12}$ powder phosphor," *Opt. Express* **21**, A829–A840 (2013).
28. G. Wang et al., "Intense ultraviolet upconversion luminescence from hexagonal $\text{NaYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}$ microcrystals," *Opt. Express* **16**, 11907–11914 (2008).
29. H. Qiu et al., "Enhanced upconversion luminescence in $\text{Yb}^{3+}/\text{Tm}^{3+}$ -codoped fluoride active core/active shell/inert shell nanoparticles through directed energy migration," *Nanomaterials* **4**, 55–68 (2014).
30. N. K. Giri et al., " $\text{SrAl}_4\text{O}_7:\text{Tm}^{3+}/\text{Yb}^{3+}$ nanocrystalline blue phosphor: structural, thermal and optical properties," *Appl. Phys. B* **99**, 271–277 (2010).
31. I. Etchart et al., "Oxide phosphors for light upconversion; Yb^{3+} and Tm^{3+} co-doped Y_2BaZnO_5 ," *J. Appl. Phys.* **109**, 063104–063107 (2011).
32. M. Ma et al., "Intense ultraviolet and blue upconversion emissions in $\text{Yb}^{3+} - \text{Tm}^{3+}$ codoped stoichiometric $\text{Y}_7\text{O}_6\text{F}_9$ powder," *Phys. B* **406**, 3256–3260 (2011).
33. V. Lojpur et al., "Up-conversion luminescence in Ho^{3+} and Tm^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Yb}^{3+}$ fine powders obtained through aerosol decomposition," *Opt. Mater.* **35**, 38–44 (2012).
34. J. T. Stecher, A. B. Rohlfiing, and M. J. Therien, "One-pot solvothermal synthesis of highly emissive, sodium-codoped, LaF_3 and BaLaF_5 core-shell upconverting nanocrystals," *Nanomaterials* **4**, 69–86 (2014).

35. N. K. Giri, K. Mishra, and S. B. Rai, "Upconversion based tunable white-light generation in $\text{Ln}:\text{Y}_2\text{O}_3$ nanocrystalline phosphor ($\text{Ln} = \text{Tm}/\text{Er}/\text{Yb}$)," *J. Fluoresc.* **21**, 1951–1958 (2011).
36. "Colorimetry," 3rd ed., E. C. Carter et al., Commission Internationale de l'Eclairage, CIE Publication 15:2004, ISBN 3-901-906-33-9, Vienna, Austria (2004).
37. J. Schanda, *Colorimetry: Understanding the CIE System*, 1st ed., John Wiley and Sons, New York (2007).

Darja Horvat received her PhD in 2005 from the Faculty of Mechanical Engineering, University of Ljubljana, where she is employed as a teaching assistant of physics. The focus of her research is in the fields of optodynamics in liquids and laser ultrasonics, applied also to the analysis and characterization of materials.

Dušan Lazar is an associate professor of physics at the University of Novi Sad. He received his PhD degree in solid-state physics from the University of Novi Sad in 1993. He is the author of more than 70 journal articles and has written one book and two workbooks. His current research interests include powder diffraction.

Janez Možina received his PhD in 1980 from the Faculty of Mechanical Engineering, University of Ljubljana, where he is currently a professor of physics and laser engineering. His research areas include optodynamics, laser metrology, and laser materials processing. He is credited with more than 150 peer-review papers in peer-reviewed journals.

Janez Križan has worked in the field of industrial automation of technological processes for 35 years. He graduated in 1977 from the Faculty of Mechanical Engineering, University of Ljubljana, with a focus on cybernetics and automation, and received his PhD in 2012 at the same faculty. The topic of his PhD thesis was fluorescence thermometry, including the development of processes for the synthesis of nanopowder materials.

Janez Diaci is a professor of mechatronics and laser engineering at the Faculty of Mechanical Engineering, University of Ljubljana, where he received his PhD in 1990. His research interests include mechatronics, optomechatronics, laser systems, and diagnostics of laser manufacturing processes.

Mira Terzić is a professor at the University of Novi Sad. She received her PhD in physics at the University of Ljubljana in 1989. She is the coauthor of more than 90 scientific publications, a scientific book, and several university textbooks. The focus of her research is in time-resolved laser-induced fluorescence and nanophotonics.