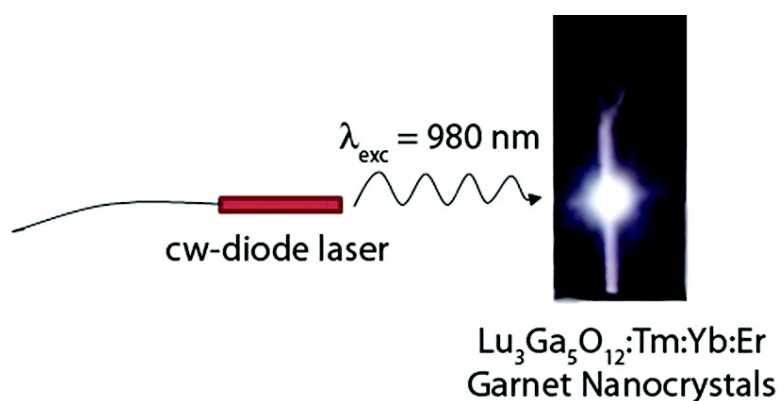


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# Bright White Upconversion Emission from $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -Doped $\text{Lu}_3\text{Ga}_5\text{O}_{12}$ Nanocrystals

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We report the synthesis of  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals prepared by a simple sol–gel method exhibiting bright white light following excitation with lower energy near-infrared light ( $\lambda_{\text{exc}} = 980$  nm) via an upconversion process. The combination of upconverted blue (from  $\text{Tm}^{3+}$ ), green, and red (from  $\text{Er}^{3+}$ ) emissions resulted in the white luminescence, which is intense and visible to the naked eye at a laser power less than 30 mW (3.4 W/cm<sup>2</sup>). The calculated Commission internationale de l'éclairage (CIE) color coordinates, which is the standard reference for defining colors, fall well within the white region and shift only slightly with the incident laser powers indicating that the material might be promising for the development of devices such as white light lasers and LEDs.

## 1. Introduction

Research on nanoscale materials is rapidly increasing due to their potential applications in the development of state-of-the-art technologies. Among the various nanoscale materials, trivalent lanthanide ( $\text{Ln}^{3+}$ )-doped luminescent materials are particularly attractive both from a fundamental and a practical viewpoint mainly due to their unique optical properties arising from the intra 4f transitions.<sup>1,2</sup> These inner 4f electrons are well-shielded by the outer 5s and 5p orbitals giving rise to strong and sharp emissions (due to weak interactions with the host lattice). These characteristics make them an interesting alternative to quantum dots in the development of optoelectronic devices such as field emission and plasma displays, electroluminescent devices, as well as biological applications.<sup>3–5</sup> The lanthanide ions, more importantly, can undergo a process known as upconversion (UC) where they can convert low energy near-infrared (NIR) radiation to higher energies such as visible and/or UV.<sup>6,7</sup> Upconversion in  $\text{Ln}^{3+}$ -doped materials is typically a two-step process where an NIR photon excites the ion from the ground-state to an intermediate state, which possesses a long lifetime. Consequently, a second incoming NIR photon excites the ion from that intermediate state to the upper emitting state. Using different combinations of  $\text{Ln}^{3+}$  ions at different concentrations one may tailor the visible emission wavelengths obtained following excitation with the low energy NIR radiation to obtain almost any desired visible emission. The generation of white light using this process could be particularly interesting.

Sources of white light materials find applications in flat panel display backlights, in addition to their importance in the development of efficient white-LEDs, which are quite promising replacements for existing incandescent and fluorescent bulbs.<sup>8</sup> The advantage of developing materials that can be excited with commercially available NIR diode lasers, which produce white light via the process of upconversion and possessing a degree of brightness comparable to those excited conventionally using UV light, can eliminate photodegradation caused by the high energy photons.<sup>9</sup> Although, there are many papers published in the literature in which white light has been observed, white light via upconversion from  $\text{Ln}^{3+}$ -doped materials is limited. Bright white light through UC has been observed from thin films made via sol–gel matrices incorporated with  $\text{Ln}^{3+}$ -doped nanoparticles.<sup>10</sup> The individual  $\text{Ln}^{3+}$  ions responsible for blue, green, and red emission ( $\text{Tm}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Eu}^{3+}$ ) were doped in  $\text{LaF}_3$  nanoparticles and subsequently incorporated in  $\text{SiO}_2$  and  $\text{ZrO}_2$  sol–gel matrices.  $\text{Ln}^{3+}$ -doped sesquioxides ( $\text{Y}_2\text{O}_3$ ) and molybdates ( $\text{Gd}_2(\text{MoO}_4)_3$ ) have also been reported as white light sources,<sup>11,12</sup> where the former was synthesized utilizing a precipitation method and the latter by a combustion method. Despite these reports there is a continuous demand for new and efficient white light materials for advanced technological applications. Among other classes of photonic materials, garnets are superior hosts for the lanthanide ions. In particular, aluminum and gallium garnets doped with luminescent rare-earth ions are interesting materials for many optical devices, such as high-power lasers<sup>13</sup> or optical waveguides.<sup>14,15</sup> We have previously shown that nanocrystalline  $\text{Er}^{3+}$ -doped gadolinium gallium garnet ( $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Er}^{3+}$ ) shows much higher luminescent intensities than binary oxide nanocrystals such as  $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ <sup>16,17</sup> and thus our motivation to study garnet hosts for the production of white light. Furthermore, it has been shown that the luminescent intensities of many Lu-based compounds

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are significantly higher than corresponding yttrium (Y) or gadolinium (Gd) based compounds.<sup>18,19</sup>

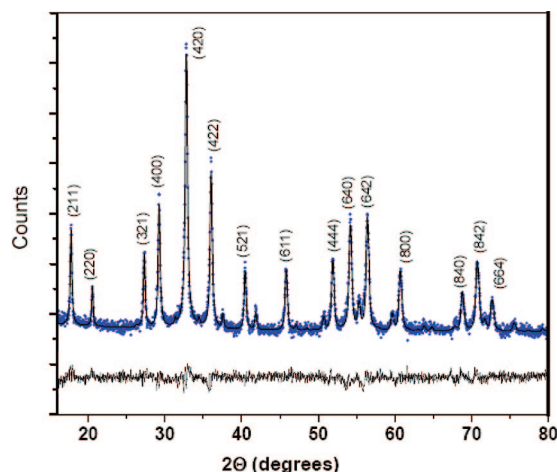
In this communication, we report the observation of strong white light obtained from  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals prepared by a simple sol-gel method. The blue component of the upconverted white light is obtained from the  $\text{Tm}^{3+}$  ion, while the green and the red components from the  $\text{Er}^{3+}$  ions. Moreover, the  $\text{Yb}^{3+}$  ions are used as sensitizers in the upconversion process and do not contribute to the overall visible luminescence. The  $\text{Yb}^{3+}$  ion has only one excited electronic energy state (although this state will split into three Stark levels when doped in solid matrices) at approximately 980 nm ( $^2\text{F}_{5/2}$ ) with a very high absorption cross-section and undergoes efficient energy transfer to other suitable dopant ions making it an ideal sensitizer for the UC process.

## 2. Experimental Details

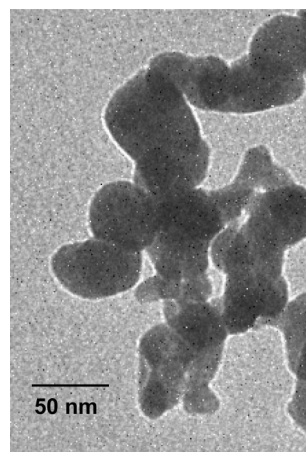
**Materials.**  $\text{Tm}(\text{NO}_3)_3$ ,  $\text{Er}(\text{NO}_3)_3$ ,  $\text{Yb}(\text{NO}_3)_3$ ,  $\text{Lu}(\text{NO}_3)_3$ ,  $\text{Gd}(\text{NO}_3)_3$ ,  $\text{Ga}(\text{NO}_3)_3$ , citric acid, and polyethylene glycol were all ultrahigh purity reagents purchased from Aldrich and used without further purification. Aqueous  $\text{NH}_4\text{OH}$  (28–30%) from Anachemia was used as received. Milli-Q water with a resistance of 18 M $\Omega$  was used in all experiments.

**Synthesis of  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -Doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  Nanocrystals.** The nanocrystals of composition  $\text{Lu}_{2.64}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$  were prepared via the Pechini sol-gel method. Stoichiometric amounts of  $\text{Tm}(\text{NO}_3)_3$ ,  $\text{Er}(\text{NO}_3)_3$ ,  $\text{Yb}(\text{NO}_3)_3$ ,  $\text{Lu}(\text{NO}_3)_3$ , and  $\text{Ga}(\text{NO}_3)_3$  ultrahigh purity reagents were dissolved in 25 mL of an 1 M aqueous solution of  $\text{HNO}_3$ . Citric acid (2 times the metal ion concentration) was added and the mixture was heated to 90 °C under stirring. A total of 4.0 g of polyethylene glycol (PEG) was added and the mixture was maintained at 90 °C for 30 min under stirring. The solution was kept in an oven at the same temperature for 24 h. During this time the solvent slowly evaporates leading to a gel formation, which was then calcined at 900 °C for 16 h in a furnace. A similar procedure was used for the synthesis of  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  and  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  control samples as well as the  $\text{Lu}_{2.64}\text{Y}_{0.06}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$  reference sample. For the preparation of microcrystalline  $\text{Lu}_{2.64}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ , the coprecipitation method was used. Aqueous  $\text{NH}_4\text{OH}$  (28–30%) was added dropwise to the aqueous mixture containing the corresponding lanthanide nitrates. The resulting white precipitate was dried under vacuum for 24 h before it was heated to 1000 °C for 16 h.

**Techniques.** The XRD patterns of the samples under study were measured with a Thermo ARL X'TRA powder diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å, Bragg-Brentano geometry, Peltier Si(Li) cooled solid state detector). The TEM measurement was performed with a JEOL JEM-2000 FX microscope operating at 80 kV equipped with a CCD camera (Gaten). Roughly, 1 mg of the sample was dispersed in 5 mL of ethanol and sonicated for 2 h. One drop of the resulting suspension was evaporated on a carbon film supported on a 300 mesh copper grid. EDX measurements were performed with the ECON EDS unit attached to the Philips CM200 TEM instrument. The sample preparation for the EDX is similar to that of the TEM. For the luminescence measurements, the nanocrystalline sample was packed in a 1 mm diameter capillary tube and excited using a Coherent fiber-coupled F6 series 980 nm laser diode (maximum power of 800 mW), coupled to a 100  $\mu\text{m}$  (core) fiber. The upconverted visible emissions were collected at right angle with respect to the incident beam and then dispersed by a 1 m Jarrell-Ash Czerny-Turner double



**Figure 1.** Experimental (scattered) and calculated (solid line) X-ray diffraction pattern for the  $\text{Tm}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystalline powders. The (hkl) crystallographic planes are shown. The bottom trace is the difference pattern.

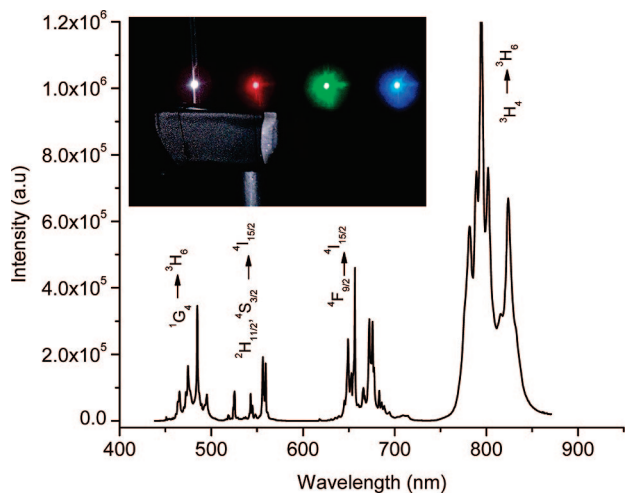


**Figure 2.** TEM image of the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals prepared by Pechini method.

monochromator with an optical resolution of  $\sim 0.15$  nm. The visible emissions were detected by a thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube. A preamplifier model SR440 Standard Research Systems, processed the photomultiplier signals and a gated photon counter model SR400 Standard Research Systems data acquisition system was used as an interface between the computer and the spectroscopic hardware. The signal was recorded under computer control using the Standard Research Systems SR465 software data acquisition/analyzer system.

## 3. Results and Discussion

Figures 1 and 2 show the X-ray diffraction (XRD) pattern and TEM image, respectively, of the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystalline material prepared via the Pechini sol-gel method. The XRD pattern of the obtained powders confirms the formation of well-crystallized single-phase of lutetium gallium garnet (space group Ia-3d) and the calculated pattern matches well with the experimental one. A lattice parameter of 12.19693 Å was obtained, which is close to that reported for the lutetium gallium garnet single crystal (12.188 Å).<sup>20</sup> The calculated crystallite size from the XRD data is  $73 \pm 1$  nm which is slightly larger than the average size of ca. 50 nm measured from the TEM analysis. EDX analysis was performed in order to obtain the concentration of lanthanide

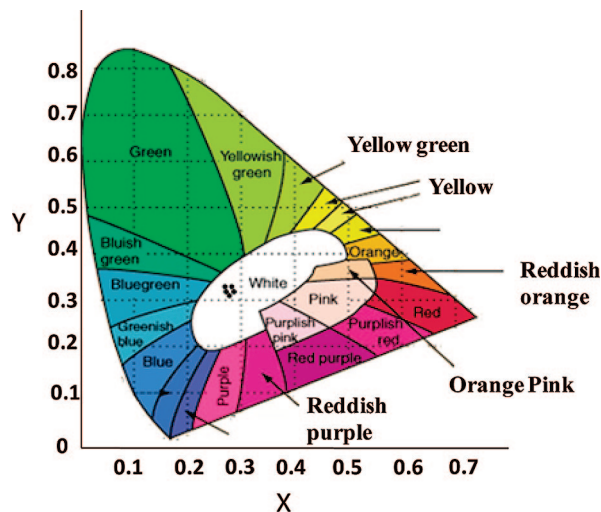


**Figure 3.** Room temperature upconversion luminescence spectrum of  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystalline garnets following 980 nm excitation. Inset displays a digital photograph of the white light from the  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  sample and the red, green and blue emissions obtained from the same sample by placing appropriate color filters.

ions present in the sample (Figure S1). The result yielded a Ga/Lu ratio of 1.48 for the  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  garnet and is in good agreement with the expected ratio of 1.67. The calculated ratio of lanthanide ions was determined to be 0.8:8.5:0.8 for  $\text{Tm}^{3+}:\text{Yb}^{3+}:\text{Er}^{3+}$ , which is slightly lower than the theoretical 1:10:1 ratio. We believe this loss is due to the evaporation of the metal ions during the heat treatment. To confirm the results, measurements were done on three different samples of the same concentration. All three samples exhibited similar results suggesting that the loss due to evaporation is reproducible.

Figure 3 shows the upconverted emission spectrum in the range 450–900 nm obtained using an excitation wavelength of 980 nm with a laser power of 500 mW ( $55.5 \text{ W/cm}^2$ ). The sharp blue emissions and NIR emission peaks centered at 475 and 800 nm are attributed to the transitions  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  and  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transitions, respectively, of the  $\text{Tm}^{3+}$  ion. The emission peaks observed around 550 nm are assigned to the ( $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$ )  $\rightarrow$   $^4\text{I}_{15/2}$  transitions of the  $\text{Er}^{3+}$  ions, while the observed red emission peaks centered at 670 nm are attributed to the  $\text{Er}^{3+}$   $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  transition. Although a very weak contribution to the red 670 nm emission peak due to the  $^1\text{G}_4 \rightarrow ^3\text{F}_4$  transition of  $\text{Tm}^{3+}$  is likely, it is over shadowed by the strong red emission from  $\text{Er}^{3+}$  ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ) transition (see Figure 3).<sup>12</sup> The inset in Figure 3 displays a digital photograph of the upconverted white light from the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  garnet nanocrystals as well as the individual red, green and blue emissions from the same sample obtained by placing appropriate color filters. The sample shows a strong white light emission and is clearly visible to the naked eye at a pump power as low as 30 mW ( $3.4 \text{ W/cm}^2$ ) demonstrating the high efficiency of the upconversion process.

To show that cooperative upconversion from  $\text{Yb}^{3+}$  pairs (i.e., two  $\text{Yb}^{3+}$  ions are excited to the  $^2\text{F}_{5/2}$  state and interact with each other to reach a virtual state at 490 nm) did not lead to the blue emission near 475 nm,  $\text{Y}^{3+}/\text{Yb}^{3+}$  codoped lutetium gallium garnet of composition  $\text{Lu}_{2.64}\text{Y}_{0.06}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$  was prepared as reference sample, since trivalent yttrium is optically silent. The upconverted emission spectrum of the reference sample showed no characteristic cooperative blue emission upon excitation with 980 nm laser (the very weak features are due to the presence of lanthanide impurities present in the lutetium, yttrium and ytterbium nitrates) and thereby confirming that the observed

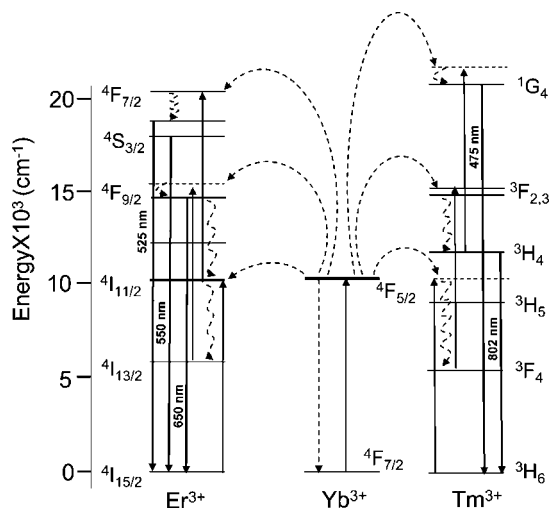


**Figure 4.** CIE diagram indicating the color coordinates calculated from the upconverted emission spectra of  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$ , fall within the white region for different laser power densities. The pump powers densities and the corresponding x, y coordinates are  $68 \text{ W/cm}^2$  (0.261, 0.324),  $64 \text{ W/cm}^2$  (0.263, 0.325),  $60 \text{ W/cm}^2$  (0.267, 0.33),  $55.5 \text{ W/cm}^2$  (0.272, 0.335), and  $50 \text{ W/cm}^2$  (0.27, 0.338).

strong blue emission at 475 nm in the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  sample originates from the  $\text{Tm}^{3+}$  ions (see Figures S2 and S3).

To measure the color of the visible emission that the human eye perceives, the Commission internationale de l'éclairage (CIE) coordinates were calculated. The CIE is the standard reference for defining colors and is obtained by considering the sensitivity of the human eye to different colors (wavelengths).<sup>21</sup> The calculated color coordinates for the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  garnets (0.27, 0.33) fall well within the white region of the CIE diagram (Figure 4). Even more interesting is the fact that the color coordinates changed only slightly when the incident laser densities were varied between 50 and  $70 \text{ W/cm}^2$  and is indicated in Figure 4.

To verify that the ratios of the optically active  $\text{Ln}^{3+}$  ions (i.e., 1:10:1,  $\text{Tm}^{3+}:\text{Yb}^{3+}:\text{Er}^{3+}$ ) used to produce white light in the  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals was optimized, we performed several control experiments (see Figures S4–S7). We synthesized  $\text{Lu}_3\text{Ga}_5\text{O}_{12}:\text{Tm}$ ,  $\text{Yb}$ ,  $\text{Er}$  nanocrystals with an identical ratio but with different concentrations (1.5:15:1.5,  $\text{Tm}^{3+}:\text{Yb}^{3+}:\text{Er}^{3+}$ ). The sample exhibited strong white light emission and is confirmed by the CIE coordinates, which fall within the white region (0.28, 0.30). This clearly indicates that keeping the ratio constant, albeit with different overall dopant concentrations, does not change the optical properties of the material. Furthermore, a microcrystalline  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$  (1:10:1) doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  sample was synthesized via the coprecipitation method. Aside from the overall increase in intensity, which is typical in bulk materials, upconverted white light was also obtained with similar CIE coordinates (0.26, 0.32). Moreover, a  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$  (1:10:1) doped  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nanocrystalline sample, synthesized using the Pechini method, did not produce upconverted white light. The calculated CIE color coordinates (0.25, 0.36) did fall close to the edge of the white region; however, to bring them into the white region (0.26, 0.32), the  $\text{Yb}^{3+}$  ion (sensitizer) concentration was increased from 0.037 to 0.046 mmol. These control experiments indicated that ratios of dopant ion concentration were optimized and, could be extended to other garnet hosts without too much difficulty. To get an idea on the relative intensity of the emission between the  $\text{Ln}^{3+}$ -doped  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$



**Figure 5.** Schematic representation of the upconversion mechanisms responsible for the generation of white light from  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals.

and  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  white light samples, we excited the samples with a 980 nm pen-diode laser (<20 mW). The light output from the  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  sample was visible to the naked eyes whereas hardly any light was observed from the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  sample.

To further understand the effect of the concentration of the dopant ions on the optical properties of the material, we prepared  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  samples with different ratios of  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Er}^{3+}$  ions (1:10:0.5, 0.5:10:1, 0.8:10:1, 1:10:0.8, 1:12:1, and 1:15:1). The resulting CIE color coordinates calculated from the corresponding upconverted emission spectrum are shown in Figure S8 (for clarity results from only four samples are shown). It is clear from the results that changing the ratio of the three lanthanide ions in sol-gel derived  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals, the CIE coordinates, except for the ratio (0.5:10:1) fall within the white region. These experiments prove that even for a slight change in the ratios of the lanthanide ions in  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$ , white light could still be achieved.

To better understand the mechanisms by which the  $^1\text{G}_4$  ( $\text{Tm}^{3+}$ ),  $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$ , and  $^4\text{F}_{9/2}$  ( $\text{Er}^{3+}$ ) states are populated, the upconverted luminescence intensity  $I$  of the blue ( $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ), the green ( $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ), and the red ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ) transitions was measured as a function of the pump power  $P$ . The slope of the curve  $\ln(I)$  versus  $\ln(P)$  was determined to be 2.16, 1.92, and 1.65 for the blue, green, and red emissions, respectively, allowing us to therefore propose that two photons partake in the green and red upconversion processes. A three photon process ( $n = 3$ ) was expected for the upconverted blue  $\text{Tm}^{3+}$  emission from the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transition and the observed lower value of  $n$  (2.16) could be explained by saturation of the upconversion process, as also observed for  $\text{Tm}^{3+}$ -doped gadolinium gallium garnet nanocrystalline powders.<sup>7</sup>

The dominant upconversion mechanisms responsible for the emission of white light are presented in Figure 5. Although, cross-relaxation between Er–Er ions can occur,<sup>22,23</sup> we believe these mechanisms are minimized due to the relatively low concentration of  $\text{Er}^{3+}$  ions and high concentration of  $\text{Yb}^{3+}$  ions present resulting in the  $\text{Er}^{3+}$  ions being well-separated from each other (the same is also true for Tm–Tm interactions). The results shown in Figure 5 differ from those reported by Chen et al. for  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$ -doped  $\text{Y}_2\text{O}_3$  nanocrystals.<sup>13</sup> The authors reported an additional cross-relaxation process between  $\text{Tm}^{3+}$  ( $^3\text{H}_4 \rightarrow ^3\text{H}_6$ ) and  $\text{Er}^{3+}$  ( $^4\text{I}_{13/2} \rightarrow ^4\text{S}_{3/2}$ ) responsible for the population of

the  $^4\text{S}_{3/2}$  and  $^2\text{H}_{11/2}$  states of  $\text{Er}^{3+}$ . However, it is clear from the strong emission peak observed at 802 nm ( $^3\text{H}_4 \rightarrow ^3\text{H}_6$ ) that in the  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  nanocrystals made via the sol-gel method, the only possible mechanism for populating the  $\text{Er}^{3+}$  emitting states ( $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) is via energy transfer from the excited  $\text{Yb}^{3+}$  sensitizer. This is a clear indication that the activator ions,  $\text{Tm}^{3+}$  and  $\text{Er}^{3+}$ , are spatially well separated and no significant energy transfer occurs between these two ions. Thus, the energy transfer occurs mainly from the  $\text{Yb}^{3+}$  sensitizer. The average Er–Tm ion distance  $d$  in the present material can be estimated using the equation<sup>24</sup>

$$d = \left( \frac{3}{4\pi N} \right)^{1/3} \quad (1)$$

where  $N$  is the total  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ion density. From crystallographic data,<sup>25</sup> the average Er–Tm distance was determined to be 9.7 Å. It is therefore plausible that the energy transfer processes between the  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions are not very efficient as the average Er–Tm distance is at the upper limit of the range of the reported critical distances for an efficient energy transfer between lanthanide ions (below 9–10 Å).<sup>26–28</sup>

We postulated that the  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions are well separated (9.7 Å) resulting in inefficient cross-relaxation between the two ions. As a result, this causes the color coordinates in the CIE diagram to change only slightly with the pump power. The small change in the CIE coordinates with the incident pump power suggests that the material would be ideal for getting controllable color temperature. The color temperature of a light source is the temperature (in K) at which the heated blackbody matches the color of the light source and is a unique feature to solid state lighting devices in the development of white light-based LEDs.

#### 4. Conclusions

To conclude, we have demonstrated for the first time, the generation of strong white upconversion emission from  $\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ -doped lutetium garnet nanocrystals. The white light was observed by the naked eye at laser powers as low as 30 mW (3.4 W/cm<sup>2</sup>). The calculated CIE color coordinates fall well within the white region and excitingly change only very little with the incident pump power. These two significant characteristics in combination with the thermal stability of the lutetium garnets make this material an ideal candidate for the development of white light based lasers and LEDs. Moreover, several control samples indicated that the ratio utilized for the optically active dopant ions were optimized and could be extended to other garnets without much variation. In addition, even for a slight change in the ratios of the dopant ions, white light was still achieved. Finally, the sol-gel method employed in the preparation of the material is amenable for the growth of large-area devices by simple dip or spin coating of the precursor materials.

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**Supporting Information Available:** EDX spectrum of  $\text{Lu}_{2.64}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ , TEM images of  $\text{Lu}_{2.64}\text{Y}_{0.06}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$  and microcrystalline  $\text{Lu}_{2.64}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ , XRD results of  $\text{Lu}_{2.64}\text{Y}_{0.06}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ , and up-

converted emission spectra of microcrystalline  $\text{Lu}_{2.64}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ ,  $\text{Lu}_{2.64}\text{Y}_{0.06}\text{Yb}_{0.3}\text{Ga}_5\text{O}_{12}$ , and  $\text{Gd}_{2.58}\text{Er}_{0.03}\text{Tm}_{0.03}\text{Yb}_{0.36}\text{Ga}_5\text{O}_{12}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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