

Research Article

Bright white light up-conversion luminescence from Yb³⁺/Er³⁺/Tm³⁺ tridoped gadolinium gallium garnet nano-crystals for multicolor and white light-emitting diodes

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ABSTRACT

Gadolinium Gallium Garnet nanophosphors with Yb³⁺/Er³⁺/Tm³⁺ triply-doped ions were synthesized via the Sol-gel Pechini method and annealed at different temperatures ranging from 800 to 1200 °C. The approximate average crystallite sizes were determined within the range of 26–56 nm by using X-ray diffraction analysis. Color-tunable up-conversion emission was explored in nanomaterials by varying excitation power under 975 nm excitation wavelength by varying excitation power and Tm³⁺ concentration for white light emission. Bright white light up-conversion luminescence from Yb³⁺/Er³⁺/Tm³⁺ tridoped Gd₃Ga₅O₁₂ was recorded. The color quality coordinates for Gd₃Ga₅O₁₂:2%Yb³⁺/1%Er³⁺/1.5%Tm³⁺ nanophosphors annealed at 1000 °C were found to be x = 0.3244, y = 0.3297 at room temperature under 975 nm infrared excitation, which falls within the white zone of the 1931 International Commission on Illumination diagram. Nanophosphors show extreme near-infrared radiation at 800 nm, which is also beneficial to deeper tissue penetration and promotes plants' growth.

1. Introduction

Rare earth (RE) activated up-conversion nanophosphors (UCNPs), which generates visible light under near-infrared excitation, have attracted considerable interest since they find potential applications in fluorescent biological imaging, solid-state lighting, displays, the back-light of LCD screens, optical thermometric materials, and white light-emitting diodes (WLEDs) [1–3]. Particularly, phosphor-converted WLEDs (pc-WLEDs) use a diode that pumps a single or combination of phosphors. The performance and quality of the WLEDs are affected by the luminescence properties of the phosphors.

There is growing demand for new and efficient RGB-based (red, green, blue) white-light emission nanophosphors, which can serve as lighting sources over the conventional incandescent and fluorescent lamps for solid-state lighting and indoor plant growing [4–6]. Therefore, more and more attention has been paid to the development of single-component white light-emitting nanophosphors with single, co-doped, or tridoped rare-earth ions to improve the color properties of the WLED devices.

Rare-earth ions activated garnets are promising hosts for white light generation studies owing to physical, chemical, and optical properties such as hardness, high thermal stability, optical isotropy, thermal conductivity and possess some advantages due to two or more RE⁺ centers for the generation of multicolor emission [7–12]. Gadolinium gallium garnet (Gd₃Ga₅O₁₂, GGG) nanocrystals are a promising host material for up-conversion (UC) emission with a higher melting point (~1740 °C), higher refractive index (~2), and lower phonon energy (~650 cm⁻¹) [13,14].

Up to now, there have been several reports on up-conversion luminescence from single-doped (Er³⁺, Nd³⁺, Eu³⁺) [15–20] and co-doped (Eu³⁺-Yb³⁺, Nd³⁺-Yb³⁺, Ho³⁺-Yb³⁺, Er³⁺-Yb³⁺, Pr³⁺-Yb³⁺, Tm³⁺-Yb³⁺) [2,19–24] nano-crystalline gadolinium gallium garnets.

Our group has recently reported for the first time the fabrication of Yb³⁺/Er³⁺ co-doped GGG nanophosphors that display bright white, and green up-conversion luminescence preliminarily explored a possibility for optical thermometry [24].

However, to the best of our knowledge, little research has reported on the UC-photoluminescence properties of tridoped (Yb³⁺/Tm³⁺/

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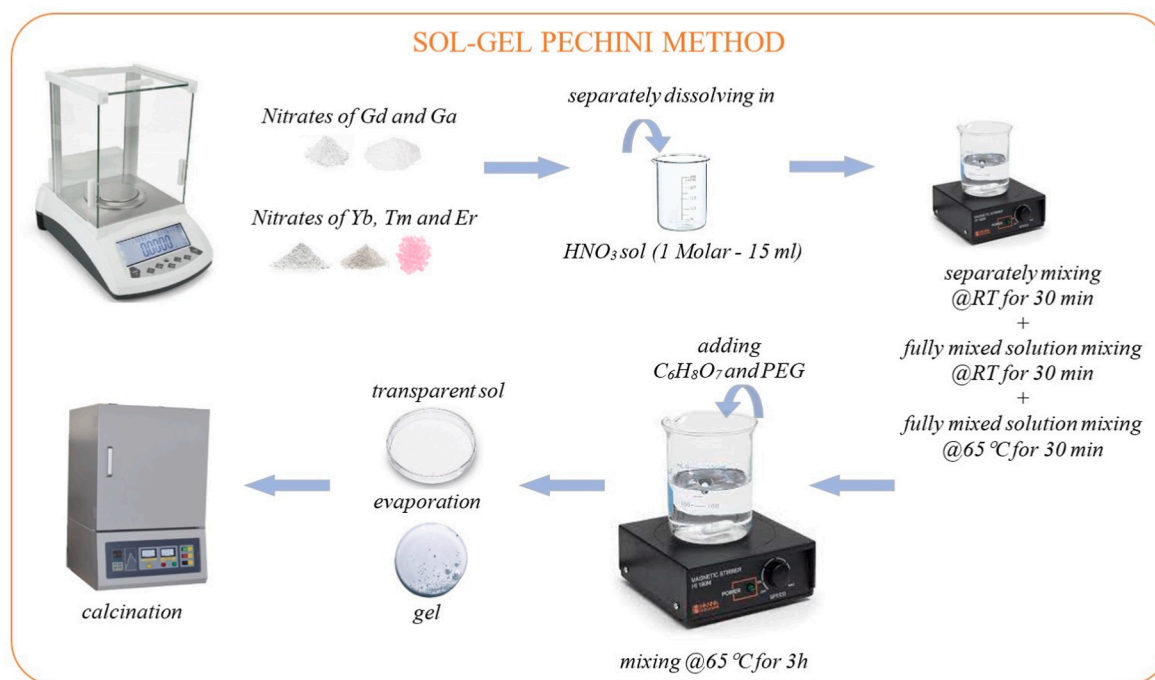


Fig. 1. Synthesis Procedure of the $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$: GGG Nanophosphors.

Ho^{3+} , $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Yb}^{3+}$, $\text{Yb}^{3+}/\text{Bi}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$) $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ phosphors [25–29]. Two studies have been carried out in the literature on $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$ triply doped GGG-based white light studies. Firstly, Mahalingam et al. studied the up-conversion emission properties of Yb^{3+} (10 mol%)/ Er^{3+} (1 mol%)/ Tm^{3+} (1 mol%): $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ prepared via Pechini method [29]. The nanocrystalline GGG sample did not produce white light and hardly any light was observed.

Secondly, Sun et al. investigated the up-conversion emission properties of Yb^{3+} (x mol%)/ Er^{3+} (1 mol%)/ Tm^{3+} (1 mol%): $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (x mol % = 1, 3, 5, 10) prepared via a simple citric acid propellant combustion method [28]. As a result, their XRD patterns of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ indicate the cubic $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, Ga_2O_3 , and Gd_2O_3 phases. A white UC emission was achieved for Yb^{3+} (10 mol%)/ Er^{3+} (1 mol%)/ Tm^{3+} (1 mol%): $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ nanocrystals under 974.5 nm laser excitation. It is shown that multicolor rare-earth-doped UC-emission depends on phosphor synthesis methods, the concentration of the doping ions, activators/sensitizers, size symmetry, and excitation laser power.

In this work, to obtain multicolor and white emission in visible region $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$ tridoped GGG phosphors with various dopant ratios were prepared via Solgel Pechini method by using polyethylene glycol as a cross-linking agent and citric and nitric acid as a chelating agent. Their optical behaviors are studied by the 975 nm excitation power of the laser diode as the excitation source.

2. Experimental methods

2.1. Material synthesis

A series of $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$ tridoped $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ powder phosphors were prepared using the Solgel Pechini method with nitrates of Ga, Gd, Yb, Er, Tm and then annealed at 800, 1000, and 1200 °C for 2 h. Gd (NO_3)₃·6H₂O (99.99%), Ga(NO_3)₃·H₂O (99.99%), Yb(NO_3)₃·5H₂O (99.9%), Er(NO_3)₃·5H₂O (99.99%), and Tm(NO_3)₃·5H₂O (99.99%) were used as starting materials. All materials were purchased from Sigma-Aldrich company. The rare-earth ions dopant ratios for the GGG powders are 2.0 mol% Yb^{3+} , 1.0 mol% Er^{3+} and x mol% Tm^{3+} (x = 0.5, 1.0, 1.5 and labeled as GGG:YET1, GGG:YET2, and GGG:YET3, respectively). The further synthesis procedure of the nanophosphors is summarized in

Ref. [24]. Briefly, all starting materials were weighted at stoichiometric ratios (Gd/Ga = 0.56) based on (1 M) was added to the solution under fixed stirring to dissolve the materials. Citric acid as a chelate ligand and polyethylene glycol (PEG) as a cross-linking agent were added under constant stirring at 65 °C for 3 h to obtain the highly transparent gel (Fig. 1). After the transparent sols were obtained, they aged for ten days at room temperature. Then the samples precursors were annealed in the muffle furnace at 800, 1000, and 1200 °C at a 7 °C/min⁻¹ heating rate for 2 h.

2.2. Characterization

The crystal structures of the tridoped gadolinium gallium garnet phosphors were examined using the X-ray diffraction (XRD) technique. The XRD spectra were taken using Rigaku–XRD diffractometer (2200 D/MAX, Japan), operating at 40 kV source voltage and 30 mA between 10° and 70° (2θ) under Cu-Kα radiation ($\lambda = 0.15418$ nm). Crystalline phases were identified by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) database.

Diffusive reflectance spectra were taken to identify the absorption lines of RE^{3+} ions in GGG nanophosphors. A PerkinElmer Model Lambda 35 UV–Vis spectrometer was used to record the diffusive reflectance spectra in the range of 400–1000 nm at room temperature.

The up-conversion emission spectra of the nanopowders were obtained in the range of 400–850 nm during the excitation of a 975 nm laser diode (CNI MDL-H-975 Model). The emission from the nanophosphors was focused on a monochromator (Princeton Inst.-SP2500i) and detected by an Acton series-SI440 silicon detector. A short pass filter was placed in front of the monochromator slit (Edmund optics, 950 nm) to block the scattered excitation light. The laser pump power was determined using a power meter (Coherent Field Max II-TOP Model).

AsenseTek-Lighting Passport Model Illuminance Meter was used to determine the color quality parameters such as the color chromaticity coordinates (CIE-1931), the color rendering index (CRI), and the correlated color temperature (CCT). All the measurements were recorded at room temperature.

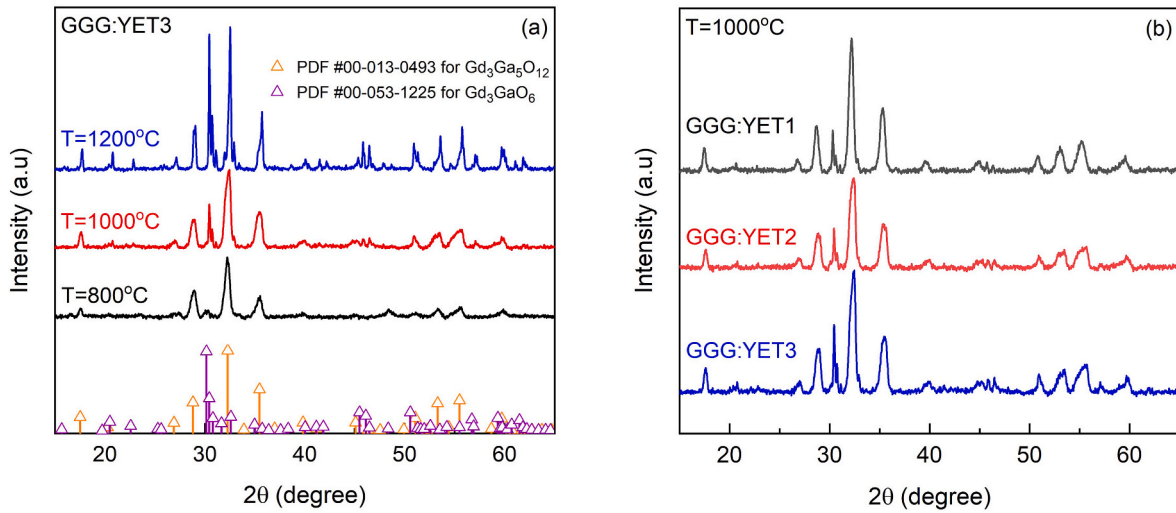


Fig. 2. XRD patterns of the GGG:YET3 nanophosphors annealed at different temperatures (a), and GGG nanophosphors with different Yb/Er/Tm doping concentrations (b).

Table 1

Average crystallite sizes of GGG: YET nanophosphors.

Samples ID	T = 800 °C	T = 1000 °C	T = 1200 °C
GGG: YET1	26	29	51
GGG: YET2	28	31	50
GGG: YET3	28	30	56

3. Results and discussion

3.1. Structural properties

The X-ray diffraction spectra of the GGG:Yb³⁺/Er³⁺/Tm³⁺ nanocrystals were investigated to confirm the phase purity of the nanophosphors (Fig. 2). The crystalline single-phase structure of cubic Gd₃Ga₅O₁₂ (garnet) phase (JCPDS card no 53–1225) is identified for powders heat-treated at 800 °C. A small amount of secondary orthorhombic Gd₃GaO₆ (gallate) phase (JCPDS card no 13–0493) slowly grows as annealing temperature increases. Gd₃Ga₅O₁₂ (garnet) phase has been stayed dominant for all samples annealed at different temperatures. In addition, the proportions of areas under the most intense peak corresponding to the two phases, can provide a relative evaluation for all nanocrystals. It is observed in Fig. 2, as the concentration

increases, the content ratio corresponding to the relative area ratios in favor of the garnet phase increases. The ionic radius of the Yb³⁺ and Tm³⁺ ion [30] is smaller than the ionic radius of the Er³⁺ ion. It has been suggested that the gallate phase will not occur for rare earth elements with an ionic radius greater than Nd³⁺ and less than Er³⁺ ion [31]. Therefore, we can say that Yb³⁺ and Tm³⁺ ions mostly prefer to replace Gd³⁺ ions in the garnet phase compared to the gallate phase.

XRD spectra of the samples labeled as GGG:YET3 with different annealing temperatures are given in Fig. 2(a) as an example. The diffraction peaks indicate that the crystal lattice structure of the host is not affected by the RE³⁺ dopant ions. The XRD patterns of GGG nanophosphors with different Yb³⁺/Er³⁺/Tm³⁺ doping concentrations are shown in Fig. 2(b). The main peaks (2θ = 32.3°) gently shifted to the larger angles with the rise of RE³⁺ ion concentration, caused by the discrepant ionic radii between the Gd³⁺ (1.053 Å; the coordinate number is 8) and RE³⁺ (Yb³⁺: 0.99 Å, Tm³⁺: 0.99 Å, and Er³⁺: 1.00 Å for the eight coordinate numbers) ions [30,31].

The average crystallite size (D) was calculated by the Scherrer equation [32], $D = K\lambda/\beta\cos\theta$, where K is the dimensionless shape factor, has a value of about 0.9, λ is the X-ray wavelength (0.15418 nm), β is the full-width at half maximum (FWHM) of the peak, and θ is the diffraction angle. The most substantial peak at 2θ = 32.29° was chosen to analyze the crystallite sizes of the powder samples. The particle size of the

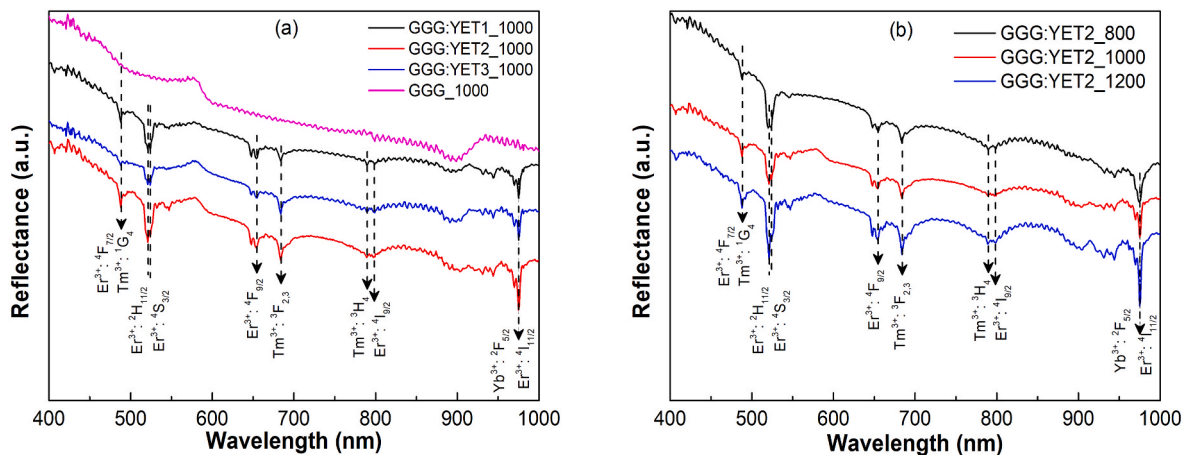


Fig. 3. Reflectance spectra of GGG:Yb³⁺/Er³⁺/Tm³⁺ nanocrystals and undoped GGG samples with 1000 °C annealing temperature (a), GGG:YET2 nanopowder with different annealing temperatures (b).

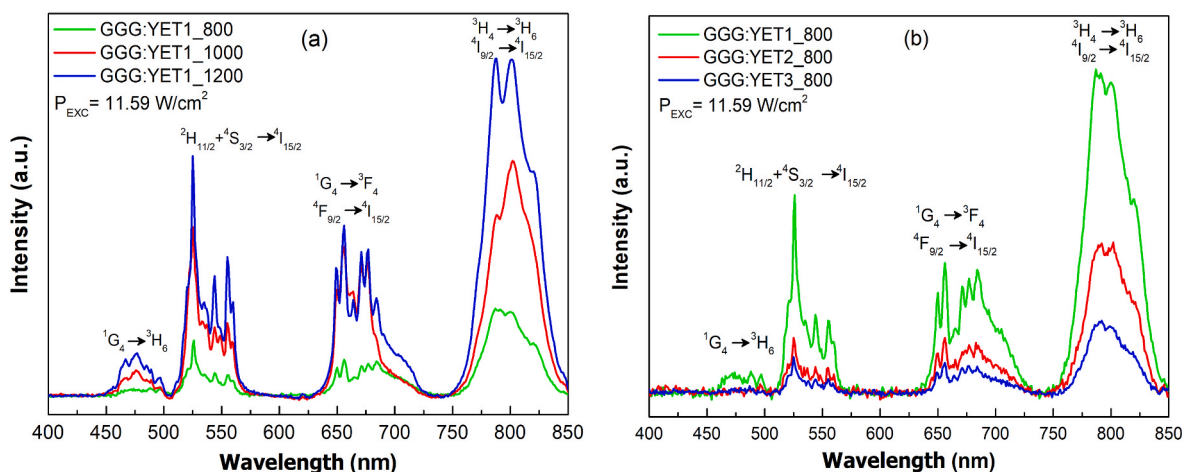


Fig. 4. Annealing temperature effect on the UC-emission spectra of the GGG: YET1 nanopowders (a). UC-emission spectra of GGG:2.0%Yb³⁺/1.0%Er³⁺/x%Tm³⁺ (x = 0.5, 1, 1.5) annealed at 800 °C (b).

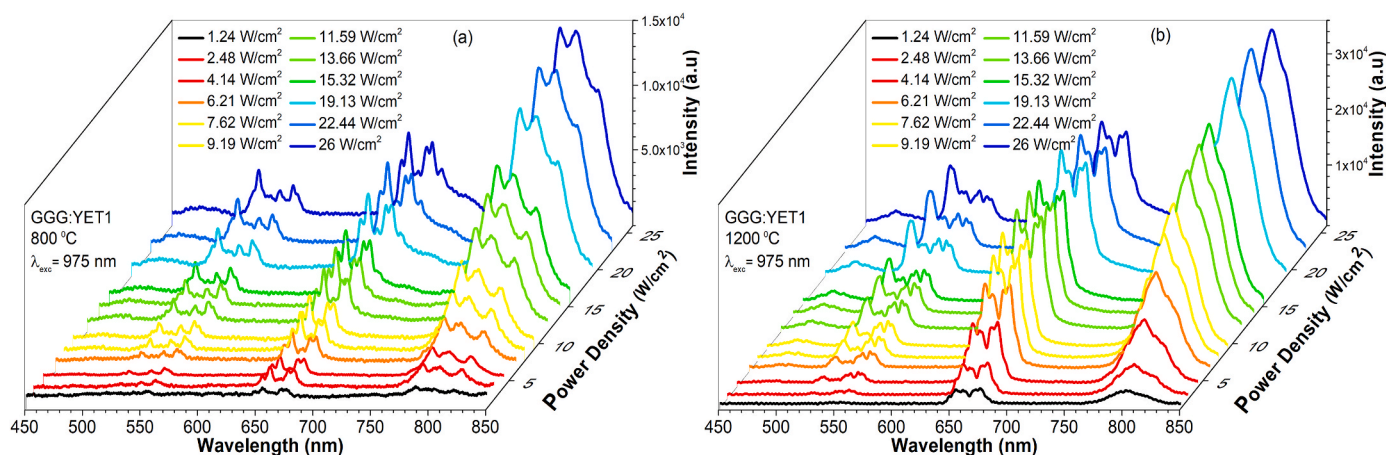


Fig. 5. Effect of the laser excitation power on the photoluminescence spectra of the GGG: YET1 nanopowders annealed at (a) 800 °C and (b) 1200 °C.

nanopowders is listed in Table 1. The results indicate that the particle size increases with increasing annealing temperature.

3.2. Diffuse reflectance measurements

Fig. 3 gives the diffusive reflectance spectra of GGG:Yb³⁺/Er³⁺/Tm³⁺ nanopowders and undoped GGG nanocrystal samples. To compare the effect of both the dopant concentration and the heat treatment on the profile and the peak positions of the transitions, reflectance spectra of GGG:Yb³⁺/Er³⁺/Tm³⁺ nanocrystals, undoped GGG samples with 1000 °C annealing temperature and GGG:YET2 nanopowder with different annealing temperatures were given in Fig. 3 (a) and (b), respectively. The profile and the peak position of each transition remain almost same with changing dopant concentration and heat treatment suggesting that there is no appreciable change in the structure of the nanopowders for the local environment of the dopant.

3.3. Up-conversion emission properties

Fig. 4 illustrates the UC-emission spectra of Yb³⁺/Er³⁺/Tm³⁺ triply doped GGG in the 400–850 nm wavelength region under 975 nm excitation with the diode laser. The influence of annealing temperature and Tm³⁺ doping content on the RGB emission intensity were given in Fig. 4 (a) and (b), respectively. Each spectrum consists of four bands

corresponding to blue, green, red, and near-infrared (NIR) emissions. The blue emission corresponding to the ¹G₄ → ³H₆ transition of Tm³⁺ ion is approximately 476 nm. The ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} transitions of Er³⁺ ions are centered at about 525 and 547 nm and correspond to the green emissions. The red emissions around 673 and 655 nm correspond to the ⁴F_{9/2} → ⁴I_{15/2} and ¹G₄ → ³F₄ transitions of Er³⁺ and Tm³⁺ ions, respectively. The NIR emissions correspond to the ⁴I_{9/2} → ⁴I_{15/2} and ³H₄ → ³H₆ transitions of Er³⁺ and Tm³⁺ ions, respectively.

The annealing temperature dependency of the emission intensity for GGG:YET1 is depicted in Fig. 4(a). UC-emission intensities increase with the increasing annealing temperatures. Fig. 4(b) indicates that as the Tm³⁺ concentration increases, UC-emission intensities decrease. The number of irradiated nanoparticles per unit volume increases with the increasing content of Tm³⁺ ions, the average distance between Tm³⁺ ions decreases, the energy transfer possibility increases and leads to the decrease in up-conversion luminescence intensity [33,34].

The UC-photoluminescence spectra of nanocrystal phosphors were also measured in the range of 400–850 nm under 975 nm excitation with the diode laser by varying the excitation power between 1.24 W/cm² and 26 W/cm². Fig. 5 shows the UC spectra of GGG: YET1 nanopowders at lower and higher annealing temperatures. The emission peaks of the Yb³⁺/Er³⁺/Tm³⁺ tridoped powders have blue, green, red, and NIR emissions, as shown in Fig. 5. The up-conversion emission of nanopowders increases with the increasing excitation power and shows a decrease after saturation reaching.

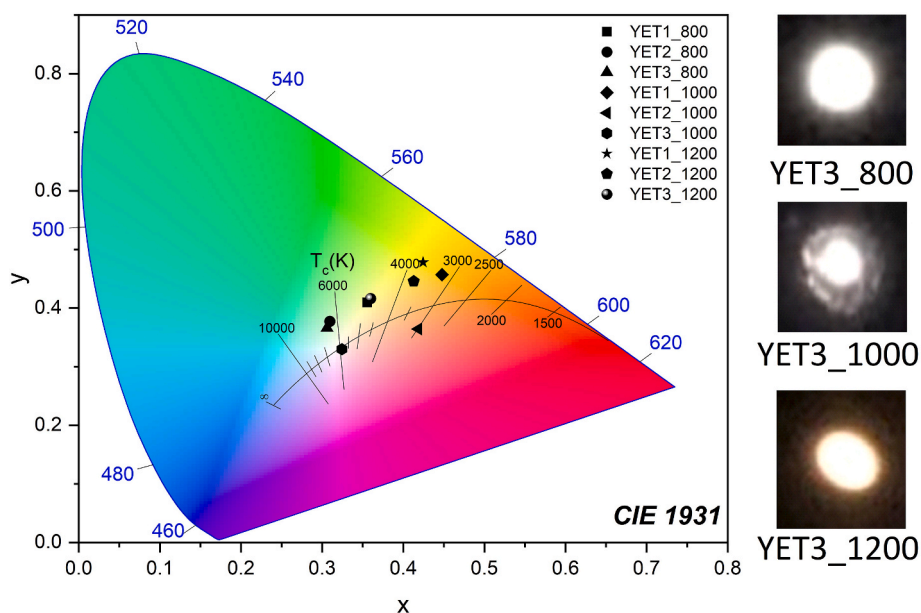


Fig. 8. CIE-1931 coordinates and emission photographs of YET:GGG nanophosphors with respect to different Tm³⁺ doping content and annealing temperature.

Table 3

Summary of Yb³⁺/Er³⁺/Tm³⁺ doped up-conversion nanophosphors (UCNPs) for single-component white light-emitting phosphors.

Phosphors	λ_{exc} (nm)	Power density P(W/cm ²) or Power (W)	Chromaticity coordinates (x, y)	Method	UC Band region	Ref
Gd ₃ Ga ₅ O ₁₂	975 nm	4.14 W/cm ² 0.5 W	(0.3244, 0.3297)	Solgel Pechini method	Blue-Green-Red-NIR	This work
Gd ₃ Ga ₅ O ₁₂	974.5 nm	16.3 W/cm ² 30.5 W/cm ²	(0.37, 0.42) (0.35, 0.41)	Propellant combustion Synthesis method	Blue-Green-Red	[28]
Y ₂ O ₃	980 nm	34.87 W/cm ²	(0.32, 0.34)	Combustion method	Violet- Blue-Green-Red	[35]
GdPO ₄	980 nm	3 W	(0.33, 0.38)	Solvothermal method	Blue-Green-Red	[36]
Lu ₃ Ga ₅ O ₁₂	980 nm	3.4 W/cm ²	(0.27, 0.33)	Solgel method	Blue-Green-Red-NIR	[29]
CaF ₂	980 nm	20 W/cm ² 32 W/cm ²	(0.337, 0.352) (0.310, 0.340)	Hydrothermal method	Violet-Blue-Green-Red	[37]
Gd ₂ O ₃	980 nm	20 W/cm ²	(0.335, 0.336)	Wet-chemical method	Blue-Green-Red	[38]
KY ₃ F ₁₀	980 nm	10.5 W/cm ²	(0.306, 0.363)	Hydrothermal method	Blue-Green-Red-NIR	[39]
Gd ₄ O ₃ F ₆	980 nm	300 W/cm ²	(0.33, 0.34)	Coprecipitation method	Blue-Green-Red-NIR	[40]
α -TeO ₂	980 nm	36.4 W/cm ²	(0.34, 0.33)	Hydrothermal method	Blue-Green-Red	[41]
β -TeO ₂			(0.32, 0.33)			
CaTiO ₃	976 nm	20 W/cm ²	(0.341, 0.335)	Solgel method	Blue-Green-Red	[42]
LaOF	980 nm	10 W/cm ²	(0.331, 0.368)	Modified Solgel Pechini method	Blue-Green-Red	[43]
Y ₂ O ₃	975 nm	830 W/cm ²	(0.2910, 0.3831)	Thermal Decomposition method	Blue-Green-Red	[44]
SrF ₂	974 nm	4 × 10 ⁵ W	(0.308, 0.332)	Co-precipitation method	Blue-Green-Red	[45]
Y ₂ SiO ₅	950 nm	1.5 W	(0.334, 0.332)	Sol-gel method	Blue-Green-Red	[46]
NaYF ₄	980 nm	7 W	(~0.33, ~0.30)	Thermal Decomposition method	Blue-Green-Red	[47]
TiO ₂	980 nm	2 × 10 ³ W	(0.3175, 0.3382)	Sol-gel method	Blue-Green-Red	[34]
Y ₂ Si ₂ O ₇	975 nm	352 W/cm ²	(0.3370, 0.3303) (0.3063, 0.3172)	Sol-gel method	Blue-Green-Red-NIR	[4]

so-called quasi-level (QL). Next, a cooperative sensitization process can populate the ¹G₄ energy level of neighboring Tm³⁺ ions. Then the red (656 nm) and blue emissions (476 nm) occur by the relaxation of Tm³⁺ ions from the ¹G₄ level to the ³F₄ and ³H₆ levels, respectively. In addition, the ³F_{2,3} excited level is populated by two subsequent energy transfer processes from Yb³⁺ to Tm³⁺: In the first, ³H₅ energy level is populated by the energy transfer (ET): ³H₆ (Tm³⁺) + ²F_{5/2} (Yb³⁺) → ³H₅ (Tm³⁺) + ²F_{7/2} (Yb³⁺). Then the population of ³H₅ decreases by the nonradiative energy transfer from the ³H₅ level to the ³F₄ level. In the second, The energy transfer from (ET): ³F₄ (Tm³⁺) + ²F_{5/2} (Yb³⁺) → ³F_{2,3} (Tm³⁺) + ²F_{7/2} (Yb³⁺) increases the population of the ³F_{2,3} excited level to generate the red emission (656 nm). Then the ³F_{2,3} level decays nonradiatively to the ³H₄ excited level to generate the infrared emission

at 787 nm.

3.5. Color chromaticity properties

The CIE-1931 (x; y) coordinates, color temperature (CCT), and color rendering index (CRI) values of the nanopowders under 4.14 W/cm² excitation power density are shown in Table 2 and drawn in Fig. 8 for comparison. Changing the Tm³⁺ ion concentration affects the quality of the color coordinates, and as the Tm³⁺ concentration increases, the CCT and CRI values of its emissions increase. The CCT and CRI values of the nanopowders annealed at 800 °C vary between 4856 K and 6571 K and 67–89, respectively. The CIE-1931 color quality coordinates of Gd₃Ga₅O₁₂:2%Yb³⁺/1%Er³⁺/1.5%Tm³⁺ nanopowders annealed at

1000 °C fall well within the white zone ($x = 0.3244$, $y = 0.3297$). These results indicate that the single-component GGG nanophosphors can be suitable for solid-state lighting. We have also summarized $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$ tridoped up-conversion nanophosphors (UCNPs) for single-component white-emitting phosphors in literature (Table 3).

4. Conclusion

Triply doped gadolinium gallium garnet nanocrystals were synthesized using the Solgel Pechini method with different heat-treated and various $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$ dopant ratios. The bright white up-conversion emission was obtained under the 975 nm laser excitation. Color chromaticity coordinates were shifted regularly with the pumping densities, the annealing temperatures, and the Tm^{3+} concentrations. Upon the 4.14 W/cm² laser excitation power density, bright white light is achieved in the $\text{Gd}_3\text{Ga}_5\text{O}_{12}:2\%\text{Yb}^{3+}/1\%\text{Er}^{3+}/1.5\%\text{Tm}^{3+}$ nanocrystals, and the calculated CIE color coordinates of (0.3244, 0.3297) fall well within the white zone. GGG could be considered an efficient host material under infrared excitation. GGG-based white upconverting phosphors may have potential applications in lighting technology, multicolor fluorescent labels, and plant cultivation.

CRedit authorship contribution statement

Hümeyra Örüciü: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Sevcen Tabanlı:** Investigation, Visualization. **Murat Erdem:** Investigation, Visualization, Writing – review & editing. **Yavuz Öztürk:** Resources, Investigation. **Gönül Eryürek:** Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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