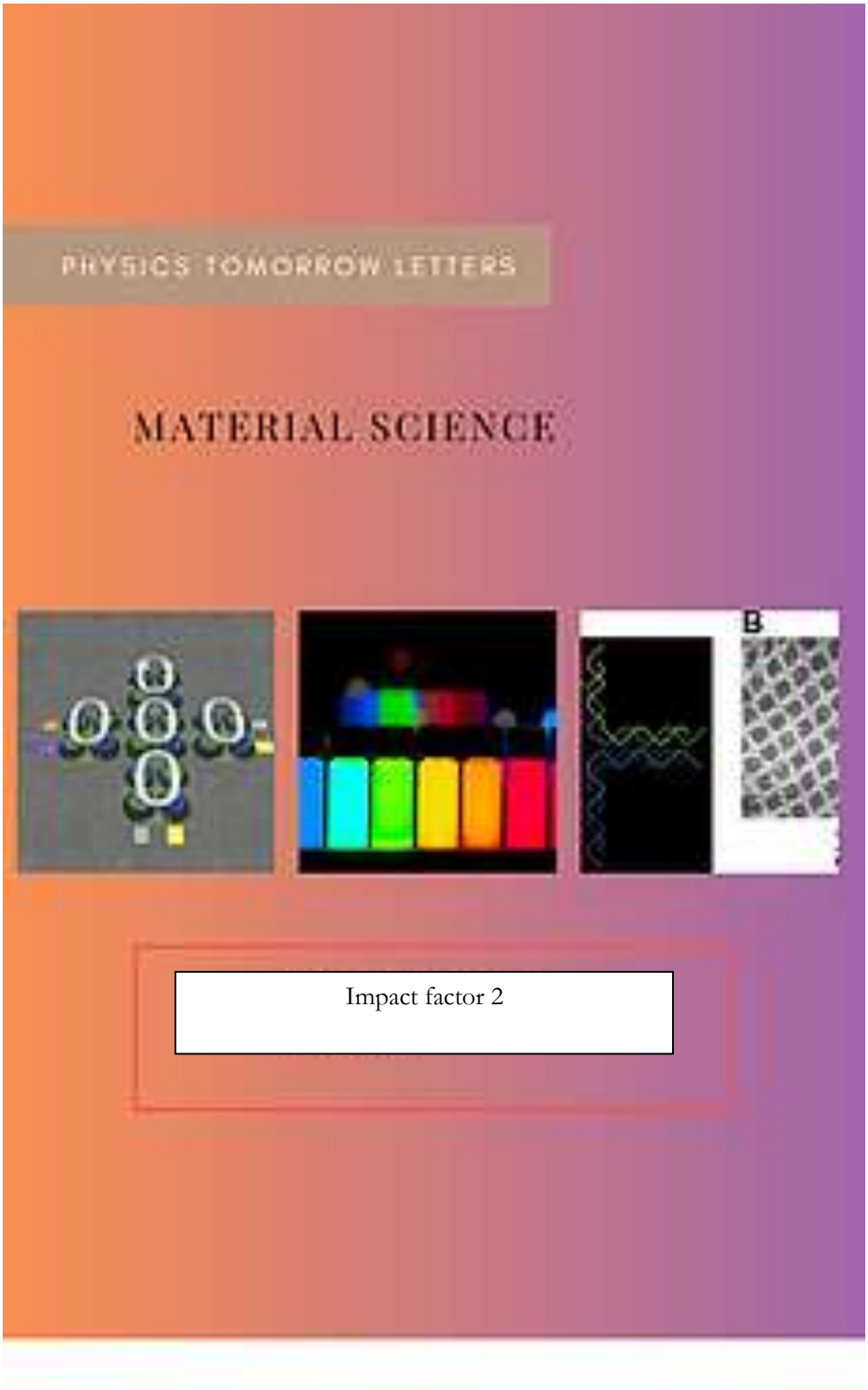
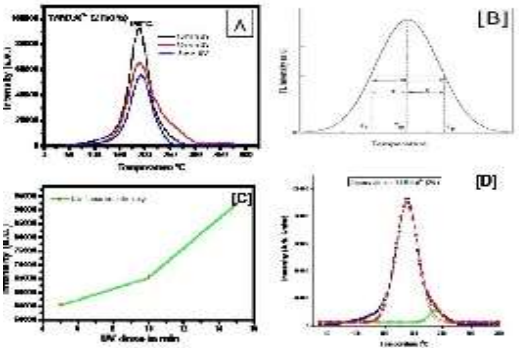
Material Science Letters **(IF 2)**
2021 ° 08(01) ° 02-08
https://www.wikipt.org/material-science-letters
DOI: 10.1490/ptl.dxdoi.com/5-65msci



Material Science Letters, 08(01): 02.-08.

Effect of Gd3+ ion concentration on photoluminescence and thermoluminescence studies of Y4Al2O9 phosphor

The current paper reports the synthesis of Gadolinium (Gd) doped $Y_4Al_2O_9$ phosphor by solid state reaction method. Powder X-beam diffraction (PXRD) tools are very much coordinated with the standard monoclinic system with space group P21/c. XRD investigation reveals that particles size was found in the range ~60-70 nm. The optical (PL) and thermoluminescence (TL) behavior of Gd doped $Y_4Al_2O_9$ phosphor were investigated. From the TL data of $Y_4Al_2O_9:Gd^{3+}$ nanophosphor with UV irradiation, it is observed that considerable amount of re-trapping is taking place in all the TL second order peaks. Photoluminescent spectroscopy (PL) was used to analyse luminescence properties of the prepared phosphor. The emission spectra have peaks centered at 473 nm in blue region. The process of emission mechanism is also discussed.



[A] TL Glow curve of YAM:Gd³⁺ [B] Representative diagram of different parameters used in the glow – curve shape method [C] UV Dose Vs Intensity plot of YAM:Gd³⁺ [D] Deconvoluted curve of YAM:Gd³⁺

RESEARCH PAPER.

Keys: *Phosphor; Photoluminescence (PL); Thermoluminescence (TL); Solid state reaction method (SSR).*

Submitted	18/09/20
Revised	19/10/20
Accepted	01/11/20

Vikas Dubey et. al. "Effect of Gd3+ ion concentration on photoluminescence and thermoluminescence studies of Y4Al2O9 phosphor" Material Science Letters, vol. 2, no. 6.

DOI - 10.1490/ptl.dxdoi.com/5-65msci

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1. Introduction

Y4Al2O9 (YAM) Al-oxide or alumina is a technologically important material for many optical, electronic, mechanical and nuclear applications. Because, it offers excellent mechanical properties, good chemical stability, high temperature (2020 °C), denseness (4.44 g/cm3), low high-temperature thermal physical phenomenon and low permeability to rare earth impurity. High Injury tolerant ability, that endure it as a prospective material for thermal and/or environmental barrier coating applications [1-4]. Therefore, it is a promising host material for rare earth ions to produce efficient luminescent media, previous theoretical and experimental investigations have incontestable applications, it's necessary to systematically investigate the structural, optical, thermal, and mechanical properties of YAM. In addition, significant energy transferring from the host material to the RE element is an efficient solution to circumvent the suppressed absorptions of RE ions with the 4f–4f transitions. As a matter of fact, a large range of wavelengths can be emitted from these phosphors because remarkable luminescence quantum yields can be achieved for the f-f transitions [2,5].

The TL properties of $Y_4Al_2O_9$ (YAM) samples of different dopant materials, which can enhance TL properties, have been studied by several researchers for several decades [5, 6]. Moreover, modification of alumina with transitions and semiconductor elements such as chromium and silicon oxides is expected to increase the number of defects in alumina structure and improve its absorption ability [5-8].

In this work, the role of Gd as dopant introduced in YAM phosphor a nanostructure, prepared by the solid state reaction method, will be explored in details. Various investigations of such newly prepared samples have been carried out leading to great benefit of having an enhanced radiation-dosimetry system through TL studies and optical studies such as PL. The prepared phosphor sample was characterized using XRD for structural characterization.

2. Experimental parts

2.1. Preparation method

To prepare $Y_4Al_2O_9:Gd^{3+}$ with various concentrations of gadolinium (0.1 -2.5 moL%) was prepared via high temperature modified SSRM. fired in air at 1000°C for 1 hour in a muffle furnace followed by intermediate grinding using agate mortar and pestle. for nearly 45 minutes., Al_2O_3 Gd_2O_3, and H_3BO_3 used as raw material in stoichiometric molar ratio (0.1% to 2.5% of Gd) for preparation. After being ground thoroughly by using an agate mortar by dry grinding up to 45 minute, powder was transferred to alumina crucible and then heated in a muffle furnace at 1300°C for 4 hours [9]. The phosphor materials were cooled to room temperature naturally. Solid state reaction methods have several advantage over the other methods.

2.2. *Samples characterization*

The XRD analysis were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector).

3. Results and discussion

3.1 XRD

The average crystallite sizes of the both samples were calculated according to the modified Scherrer equation as follows:

$$\mathrm{Ln}(\beta) = \mathrm{Ln}\left(\frac{k\lambda}{L}\right) + \mathrm{Ln}\left(\frac{1}{\cos(\theta)}\right)$$

Where β is the width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians, λ is the X-ray wavelength in nanometer (nm), θ is the diffraction angle, L is the crystalline size and K is a constant related to crystalline shape and normally taken as 0.9. The crystallite sizes, L, were found to be 62.13 and 73.55 nm for the Gd^{3+} ion doped $Y_4Al_2O_9$ phosphor The average crystallite sizes confirm the successful synthetic method in preparing the present nanophosphors. The $Y_4Al_2O_9$ phase crystallizes in monoclinic system with space group P21/c. [2,16]. By using this method uniform particle diameter were achieved so we adopted solid state reaction method.

3.2 TL-response study

Figure 2[A] illustrates the TL-glow curve of Gd^{3+} ion doped $Y_4Al_2O_9$ phosphor nanophosphor sample that previously subjected to 5-15 min UV exposure time.

Determination of Kinetic Parameters: The TL-glow curve is characteristic of the different trap levels that lie in the band gap of the material. We calculate kinetic parameters such that trap depth (Ɛ), order of kinetics (β) and frequency factor (Ṡ) are reliable dosimetric study parameters for thermoluminescent materials. The study shows when sample was irradiated by UV 254 nm source.

The values of τ, δ and ω were calculated,

where 'τ' is the low temperature(temp) half width of the glow curve i.e. $\tau = T_m - T_1$,

'δ' is the high temp half width of the glow curve i.e $\delta = T_2 - T_m$

'ω' is the full width of the glow peak at its half height i.e. $\omega = T_2 - T_1$ (Figure 3[b].

μ_g =(shape factor = δ/ω) it is clear that the glow peaks obey the second order kinetics. The trap depth also known as the activation energy of the luminescence centers is calculated using Chen's equation.

The sample was read out for different exposure time at a heating rate of 6.7^{O}C/sec using TLD reader. The main resulted glow peak of the sample was located at about 191^{O}C. The trap depth also known as the activation energy of the luminescence centers is calculated using Chen's equation YAM:Gd^{3+} phosphors show second order kinetics, (Table 1) [10-15].

Table 1: Shape factor (μ), activation energy (E) and frequency factor (s) of UV irradiated YAM:Gd^{3+} (1mol %)

UV minutes	T_1 (K)	T_m (K)	T_2 (K)	μ	δ	ω	$\mu = \delta/\omega$	*Activation energy (E) eV*	*Frequency factor (s) s^{-1}*
15 min	439	464	484	25	20	45	0.44444	1.10587	1.73×10^{13}

Table 2: Shape factor (μ), activation energy (E) and frequency factor (s) of UV irradiated De-convoluted YAM:Gd3+ (1mol %)

UV minutes	T_1 (K)	T_m (K)	T_2 (K)	μ	δ	ω	$\mu = \delta/\omega$	*Activation energy (E) eV*	*Frequency factor (s) s^{-1}*
Peak 1	439	464	484	25	20	45	0.44444	1.10587	1.73×10^{13}
Peak 2	491	512	530	21	18	39	0.46154	1.61239	1.49×10^{17}

3.3 PL Spectroscopic study

Figure 3[A] show the excitation and Figure 3[B] show emission spectra of $Y_4Al_2O_9$:Gd^{3+} phosphor. The excitation spectra of $Y_4Al_2O_9$:Gd^{3+} phosphor mainly consist of the charge transfer and (CTB) of Gd^{3+} located in 220–400 nm. The observed excitation and emission depends on the transition between the energy levels of Gd^{3+} ion. Stronger chemical bond between Gd–O bond and Al^{3+} ions forms for the crystalline phosphor [16].

To study the effect of Gd^{3+} concentration emission spectra was recorded for different concentration of Gd^{3+} ion from 0.5 - 2.5 mol%. The peak position remains unaffected from Gd^{3+} concentration it only affects the intensity of emission peaks. Intensity of emission peaks increases up to 1.5 mol % Gd^{3+} ion after this concentration a decrease in intensity is observed due to quenching [16-22]. The band gap of the material were already calculated in previous papers [23-25].

The CIE coordinates were calculated by PL data using the spectral energy distribution of the YAM:Gd^{3+} sample (Figure 3c). The colour-coordinates (x = 0.18 y = 0.28) are obtain for the Gd doped emit blue light. So the prepare phosphor was capable for blue LED.

4. Conclusion

Sample was successfully synthesized YAM:Gd^{3+} doped phosphor by the solid state reaction method. XRD pattern confirms that synthesized sample shows monoclinic structure. The particle size was found to be in the 65-72nm range. The prepared phosphor also examined by TL technique. For recording TL glow curve every time .5 mg phosphor was irradiated by ultraviolet (UV) 254nm source and fixed the heating rate at $10^0C\ s^{-1}$. Sample shows well resolved peak at 190^0C for 2mol% of Gd^{3+}. The activation energy 0.768 eV was found as well as sample shows the second order of kinetic. The rate of escaped electron per second was calculated by frequency factor and its value is $2.72 \times 10^{09} s^{-1}$. The PL emission peak of $Y_4Al_2O_9$:Gd^{3+} phosphor is centered at 472 nm shows blue emission confirmed by CIE.

Conflict of Interest Statement

Authors declare there is no conflict of interest.

Acknowledgement

Authors are very thankful to TEQIP-III CSVTU Bhilai for funding through Collaborative Research Project CSVTU Project Ref. No. CSVTU/CRP/TEQIPIII/16 date 17/08/2019. Also very thankful to Department of Physics Govt. V.Y.T.PG. Auto. College Durg for support of lab experiments.

Supplimentary documents

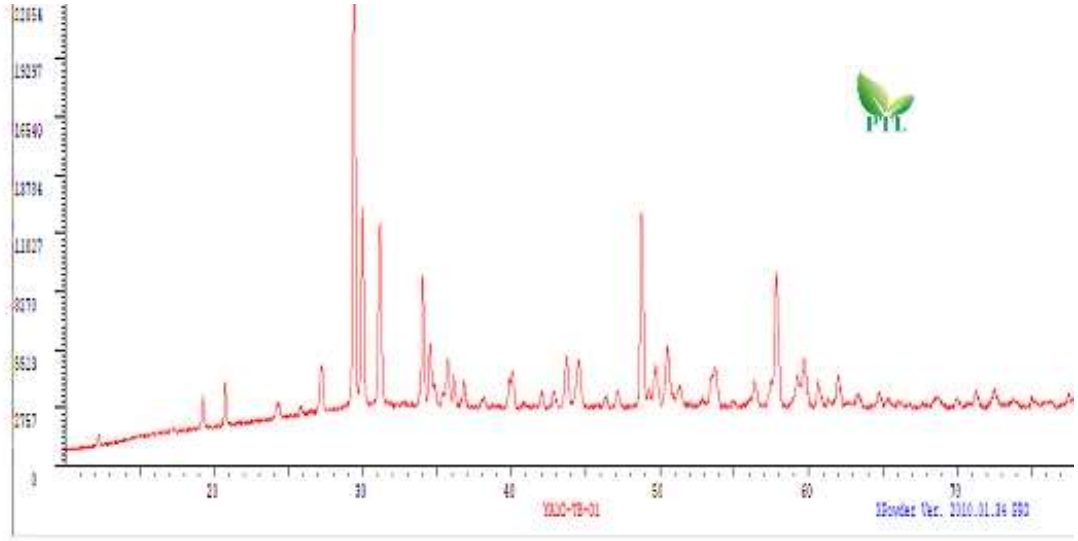

Figure 1 | XRD patterns of the of Gd^{3+} ion doped $Y_4Al_2O_9$ phosphor

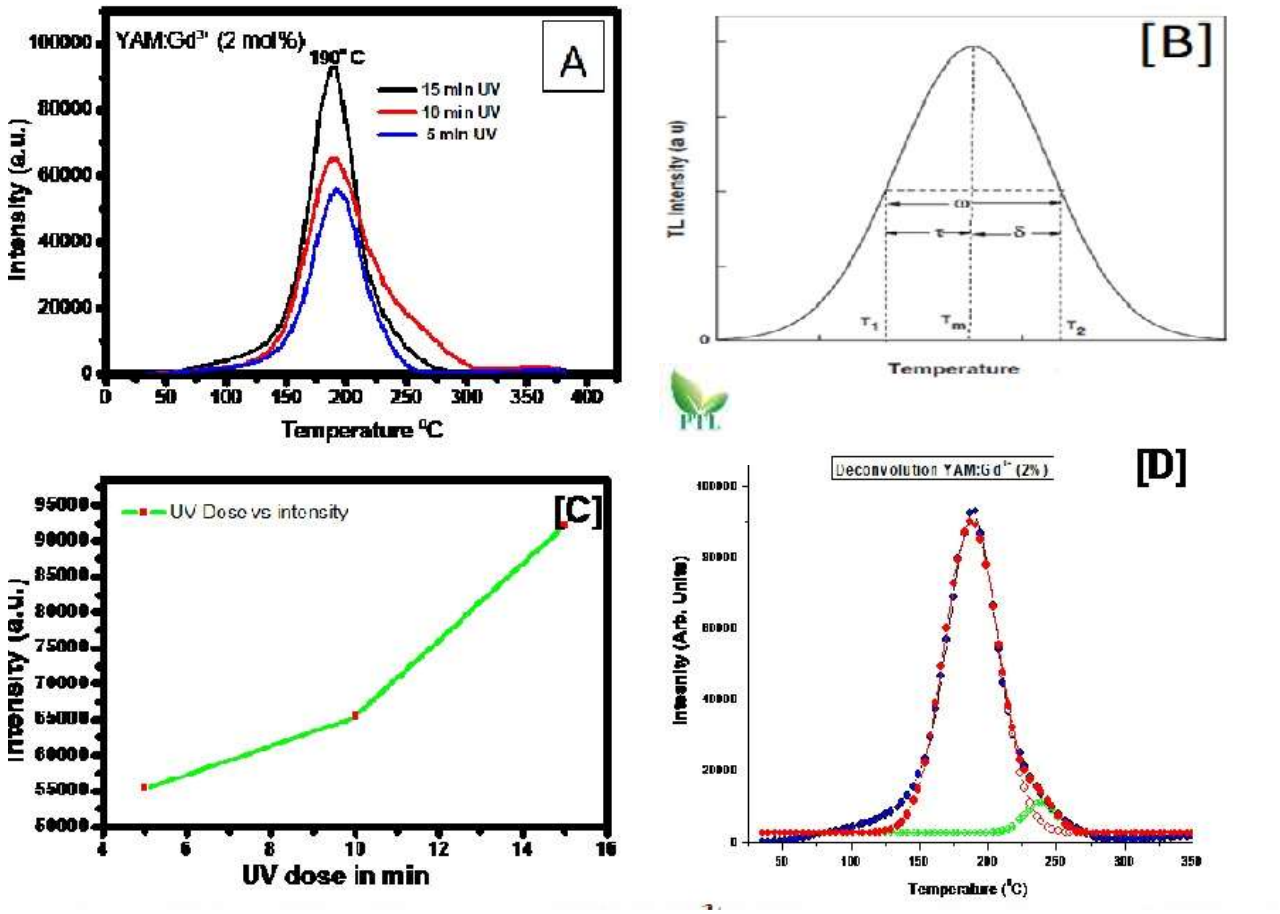

Figure 2(A-D) | [A] TL Glow curve of YAM:Gd^{3+} [B] Representative diagram of different parameters used in the glow – curve shape method [C] UV Dose Vs Intensity plot of YAM:Gd^{3+} [D] Deconvoluted curve of YAM:Gd^{3+}

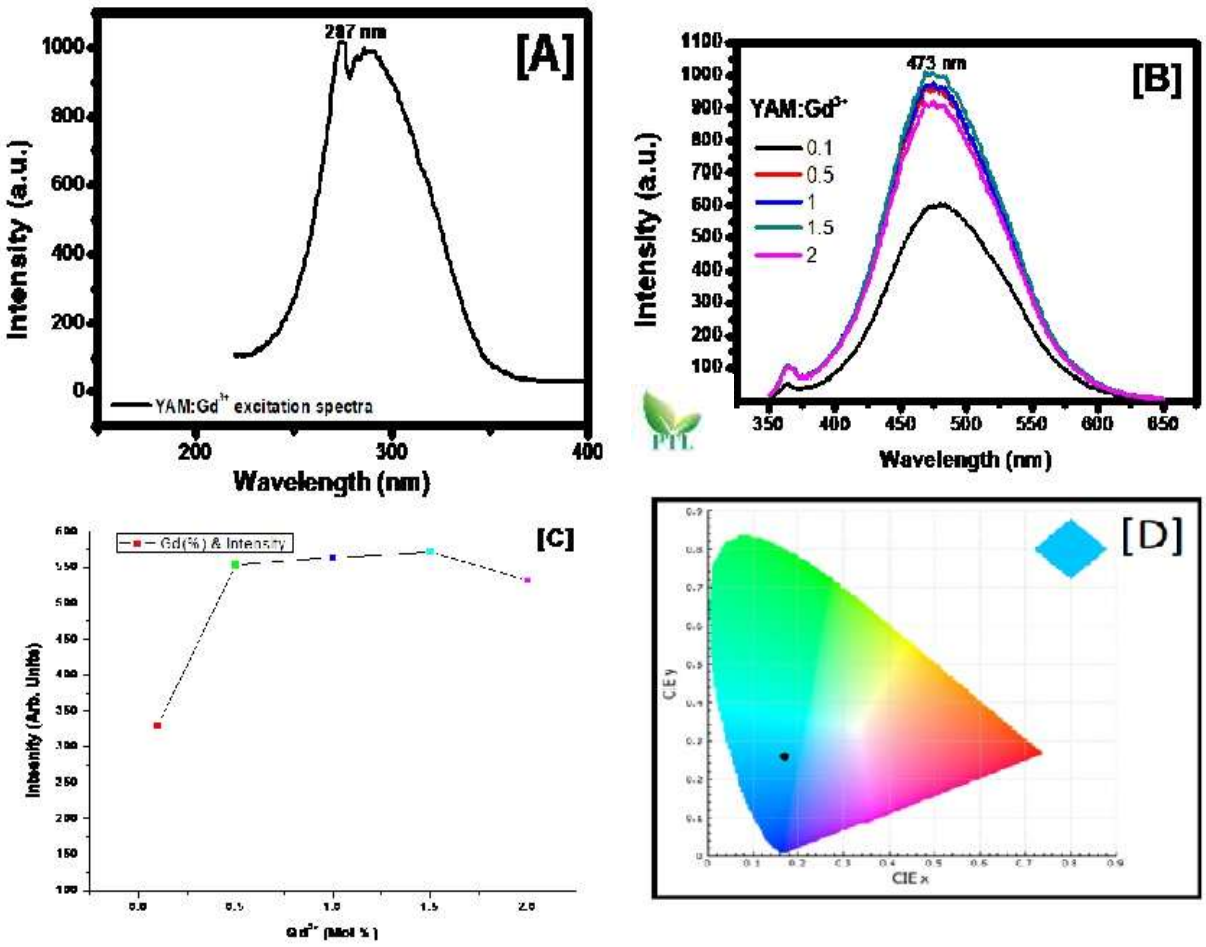

Figure 3(A) | Excitation spectra of YAM:Gd^{3+} (B) Emission spectra of YAM:Gd^{3+} (C) Effect of Gd^{3+} concentration (D) CIE Coordinates

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