



An investigation on the luminescence quenching mechanism of ZnGa₂O₄:Tb³⁺ phosphor

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ABSTRACT

Rod like green emitting ZnGa₂O₄:Tb³⁺ phosphor were synthesized and the effect of Tb³⁺ on the structural and optical properties of zinc gallate were analysed. Cubic spinel nature of ZnGa₂O₄:Tb³⁺ nano crystallite was verified from the x-ray diffraction. From the photoelectron spectroscopy analysis, chemical states of constituent elements were identified. Photoluminescence spectra reveal the green emission quenching and there are no reports about this mechanism from ZnGa₂O₄:Tb³⁺ phosphor synthesized via solid state reaction route. Quadrupole – quadrupole interaction leads to this quenching behaviour and the critical distance is 21 Å.

1. Introduction

The diversity in applications exhibited by zinc gallium oxide (zinc gallate-ZnGa₂O₄) such as in field emission displays, electroluminescent devices, photocatalyst, water splitting etc lead researchers to produce more stable and attractive forms of this inorganic oxide [1–3]. Also, the good optical transparency and conductivity features direct its applications in liquid crystal displays and in solar cells [4,5]. It is a cubic spinel with Zn²⁺ and Ga³⁺ ions possessing tetrahedral and octahedral coordination respectively, with a small inversion in site occupancy [6]. The wide bandgap of 4.4 eV helps this spinel oxide for better performance in various applications. Doping with Mn²⁺ or Tb³⁺ gives rise to green emission, whereas Cr³⁺ or Eu³⁺ doping leads to red emission [6–9].

Among the various methods of preparation, such as thermal evaporation [10], pulsed laser ablation [11], sol-gel [9], hydrothermal [12] etc, we employed the most common method for the synthesis of long lasting phosphor material, which is the solid state reaction method. Authors have already reported a comparative study of ZnO, Ga₂O₃ and ZnGa₂O₄ using this method [13]. The increased number of defects produced by the high sintering temperature leads to the after-glow shown by gallates, which is the advantage of using this method.

Rare earth doping in oxides have much interest in recent studies because of their enhanced optical properties emerged by the shielding effect produced by the outer orbit electrons. Here we report the synthesis of ZnGa₂O₄ doped with the lanthanide, terbium (Tb³⁺) ion by solid state reaction method. Effect of Tb³⁺ concentration on the properties of ZnGa₂O₄: Tb³⁺ phosphor is rarely reported. Also there are no

reports on the formation of ZnGa₂O₄:Tb³⁺ rods as obtained in this work. This phosphor is well known with its green emission resulting from ⁵D₄–⁷F₅ transition [7]. The f-f transitions responsible for this emission produce narrow, sharp photoluminescence emissions. There exists a quenching behaviour in PL spectra, due to the multipolar interaction, which induce energy transfer between the Tb³⁺ ions.

2. Experimental

The samples were synthesized by solid state reaction method, where the required metal oxides such as Zinc oxide [ZnO, 99%, MERCK] and Gallium oxide [Ga₂O₃, 99.99%, ALDRICH] were homogeneously mixed together with terbium nitrate [Tb(NO₃)₃, Sigma, 99.9%] using 2-propanol. After drying, the samples were annealed at a temperature of 1000 °C for 12 h. The detailed synthesis procedure is given in our previous report [13]. Samples were prepared for different doping concentrations of terbium. The final powder after sintering was ground using mortar and pestle and used for characterization.

Bruker AXS D8 advance x-ray diffractometer was used for the analysis of phase and structural parameters, by x-ray diffraction (XRD) technique. Scanning electron microscopy (SEM) was employed for morphological study using TESCAN VEGA 3 SBH. Thermo Scientific K-ALPHA X-ray photoelectron spectroscopy (XPS) was employed for the analysis of elemental composition and chemical states of the synthesized sample. The diffuse reflection for the bandgap determination was recorded using Varian, Cary 5000 UV–VIS–NIR Spectrophotometer. Horiba Fluoromax-4C Spectrofluorometer was used for the determination of various defects and the emission behaviour in the synthesized

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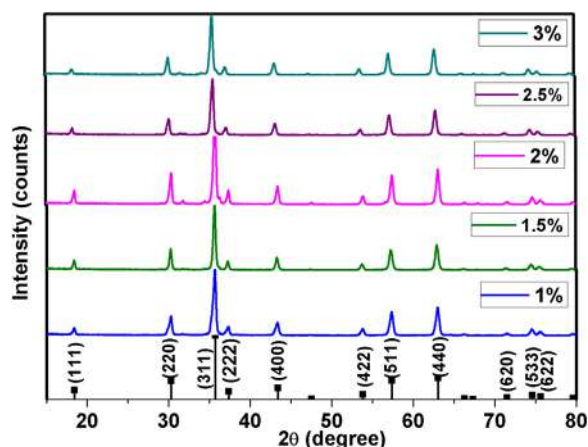


Fig. 1. X-ray diffraction pattern of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ for different molar concentrations of Tb^{3+} .

Table 1

Variation in lattice constants with molar concentration of Tb^{3+} ion.

Tb^{3+} molar concentration (%)	Lattice parameter (Å^3)	Grain size (nm)
Bulk	8.336	–
1	8.342	20
1.5	8.345	25
2	8.359	24
2.5	8.377	28
3	8.38	20

sample using photoluminescence (PL) study.

3. Results and discussions

The x-ray diffractogram showing the major reflections of Tb^{3+} doped zinc gallate is represented in Fig. 1. Although there is a broadening due to the size effect, XRD exhibits the well crystalline and pure nature of synthesized zinc gallium oxide. All the diffraction peaks agree with the same JCPDS, having file no. 86–0415 keeping spinel cubic structure with $\text{Fd}3\text{m}$ spacegroup. With the incorporation of Tb^{3+} ion, there is a shift to the lower angle side compared to the JCPDS. The peak shift increases with the activator concentration and it is noticeable for 2.5 and 3 mol%. This shift is due to the high ionic radius of the dopant Tb^{3+} ion (92 pm) compared to the host Ga^{3+} ion (76 pm), which causes an increase in lattice parameter values (Table 1).

The crystallite size of the samples were calculated using the Scherrer formula (relation 1), which connects grain size (D) with x-ray wavelength (λ), full width at half maximum (β) and glancing angle (θ) and the obtained values are in the range 20–30 nm.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

There is an expression relating interplanar distance (d_{hkl}) with lattice parameter (a) and miller indices $[hkl]$, which can be utilized for the determination of lattice constants (Eq. (2)).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

The calculated crystallite size and lattice parameter values with molar concentration of Tb^{3+} is arranged in Table 1.

Fig. 2 represents the SEM and TEM micrographs of the sample with 2.5 mol% of Tb^{3+} . SEM reveals the one dimensional growth of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor (Fig. 2a). From the TEM image also (inset of Fig. 2b) we can confirm this rod like nature of the phosphor. The HRTEM image of the micro rod which exhibits the crystal lattice planes is shown in Fig. 2b. These 1D structures have improved optoelectronic applications [14]. The SAED pattern showing the electron diffraction from a selected area, with lattice planes (111) and (220) is represented in Fig. 2c. This type of spot pattern is a peculiarity of rod like structures.

SEM images of Tb^{3+} doped zinc gallate for varying doping concentrations is portrayed in Fig. 3. There is no observable change in the micrographs with varying Tb^{3+} concentration. All exhibit clustered rod like behaviour having micro length.

The chemical state identification of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor was done by XPS technique and the corresponding spectra is as shown in Fig. 4. The survey spectra of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ consist of binding energy peaks corresponding to Zn 2p, Ga 2p, Ga 3d, O 1s and Tb 3d elemental states as shown in Fig. 4.1. A binding energy peak representing C 1s (~ 284.6 eV) element is observable from the spectra, which is meant for the charge correction while taking XPS [15]. The fine spectra for each constituent elements, which indicate their chemical states are portrayed in Fig. 4(2)–4(6). The variation in peak energy values with molar concentration of dopant ion, for individual elemental species of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ is recorded in Table 2. The formation of zinc gallate spinel is established from energy separation (ΔE) between Zn $2p_{3/2}$ and Ga $2p_{3/2}$ values which is ~ 96 eV [16]. The energy peak at 530 eV confirms the presence of O^{2-} ion in zinc gallate [17]. The energy difference between Zn $2p_{3/2-1/2}$ and Ga $2p_{3/2-1/2}$ for $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ are given in Table 2, which are comparable with the standard values of 22.97 and 26.84 eV respectively which confirms the bonding of Zn^{2+} and Ga^{3+} with O^{2-} [15,18,19]. The 3d state of Ga^{3+} is responsible for the peak around 20 eV [20]. The fine spectra of Tb^{3+} in $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ is shown in Fig. 4(6), and the peak corresponds to the 3d chemical state with a total angular momentum value of $3/2$ [21].

$\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ exhibits almost 90% diffuse reflectance over the visible region of the DRS spectra, and it is almost identical for all activator concentrations (Fig. 5a). Also, there exists an absorption band in the UV region around 370 nm which arise from the intra- $4f^8$ transitions ie $4f^8$ to $4f^75d$ transition of Tb^{3+} ion [22].

From the reflectance (R) values, band gap values can be estimated by making use of Kubelka-Munk relation (Eq. (3)), which connects R with absorption (k) and scattering (s) coefficients [23,24]. Fig. 5b represents the Tauc plot of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor for different activator concentrations. The calculated bandgap values are recorded in

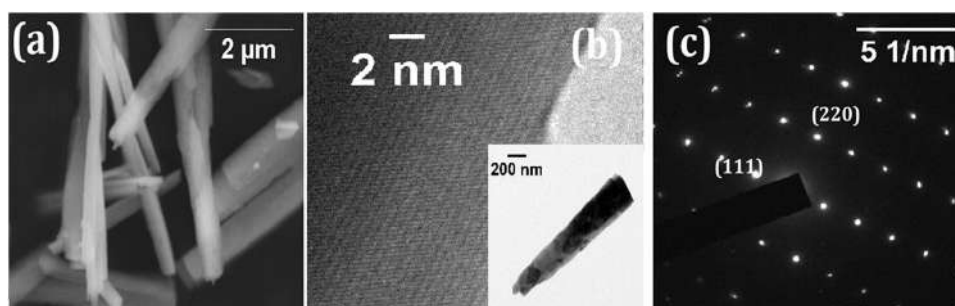


Fig. 2. (a) SEM, (b) HRTEM and TEM [inset] images and (c) SAED pattern of $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor for 2.5 mol% Tb^{3+} concentration.

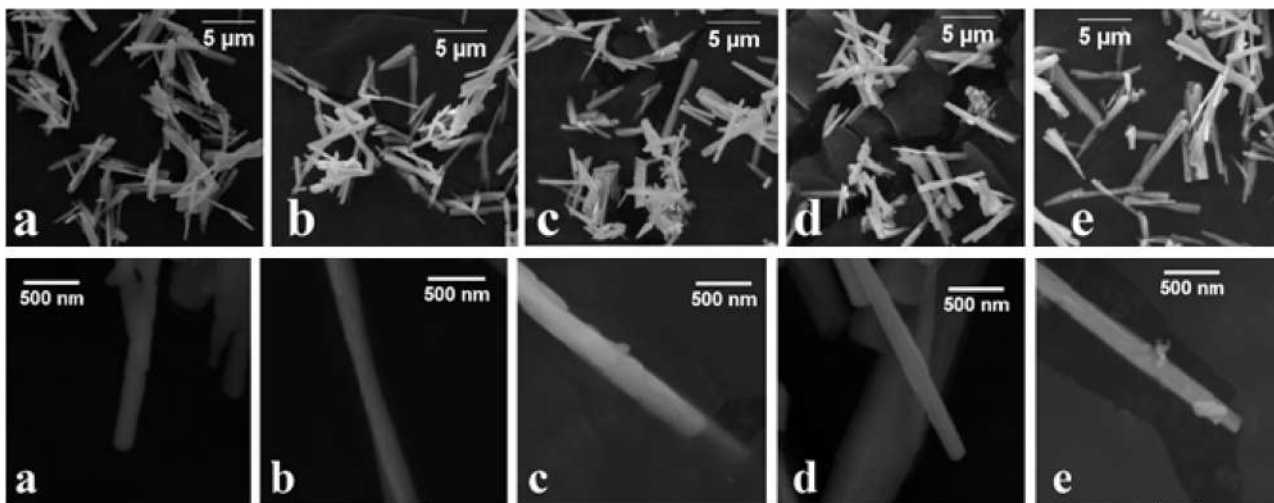


Fig. 3. (a) SEM images of ZnGa₂O₄:Tb³⁺ phosphor with varying molar concentrations of Tb³⁺ [a, b, c, d and e denotes 1, 1.5, 2, 2.5 and 3 mol% doped samples respectively].

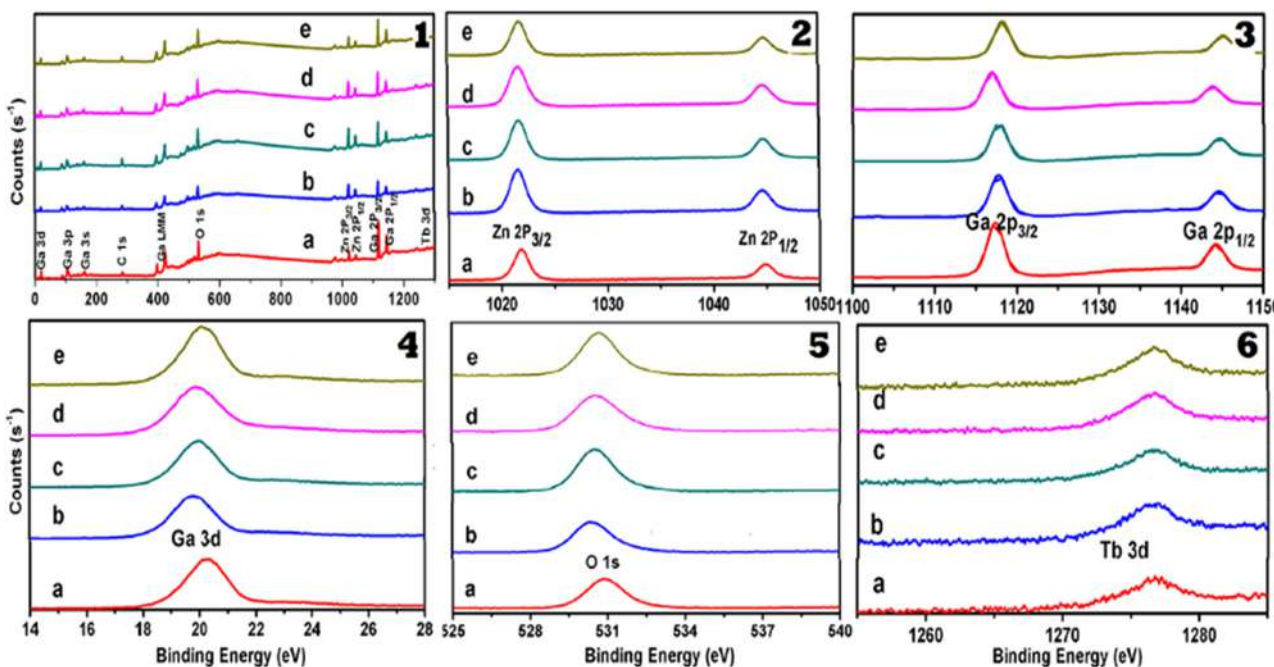


Fig. 4. (1) XPS survey spectra and fine spectra of (2) Zn 2p, (3) Ga 2p, (4) Ga 3d, (5) O 1s & (6) Tb 3d of ZnGa₂O₄:Tb³⁺ for different doping concentrations [a, b, c, d and e denotes 1, 1.5, 2, 2.5 and 3 mol% respectively].

Table 2
Effect of Tb³⁺ incorporation on binding energy of ZnGa₂O₄:Tb³⁺ phosphor.

Chemical state	Binding energy (eV)				
	1%	1.5%	2%	2.5%	3%
Zn 2p _{3/2}	1021.78	1021.46	1021.62	1021.68	1021.73
Zn 2p _{1/2}	1044.87	1044.61	1044.77	1044.63	1044.82
Ga 2p _{3/2}	1117.39	1117.71	1117.80	1116.86	1118.24
Ga 2p _{1/2}	1144.56	1144.63	1143.83	1144.88	1145.04
Ga 3d	20.29	19.80	20.01	19.92	20.11
O 1s	530.93	530.34	530.53	530.54	530.69
Tb 3d	1276.66	1276.55	1276.58	1276.68	1276.75
Energy separation, ΔE (eV)					
Zn 2p _(3/2-1/2)	23.09	23.15	23.15	22.95	23.09
Ga 2p _(3/2-1/2)	27.17	26.92	26.03	28.02	26.8

Table 2.

$$\frac{k}{s} = \frac{(1 - R)^2}{2R} \tag{3}$$

The grain size as well as band gap are varying with doping concentration but not in a specific order. Fig. 5c represents the crystallite size and band gap variations with molar concentrations of Tb³⁺. Defects in the samples produce band tails which reduces the band gap whereas higher carrier concentration will increase the band gap (B M shift) [25,26]. These two factors, band tails and BM shift may be causing the small fluctuations in band gap.

The photoluminescence behaviour of ZnGa₂O₄:Tb³⁺ phosphor is depicted in Fig. 6a. On exciting with a wavelength of 290 nm, intense emissions with peaks at 490 and 547 nm were observed. They are attributed to the characteristic emission lines of activator Tb³⁺ ion. The first peak around 490 nm is due to ⁵D₄ → ⁷F₆ transition and the one at

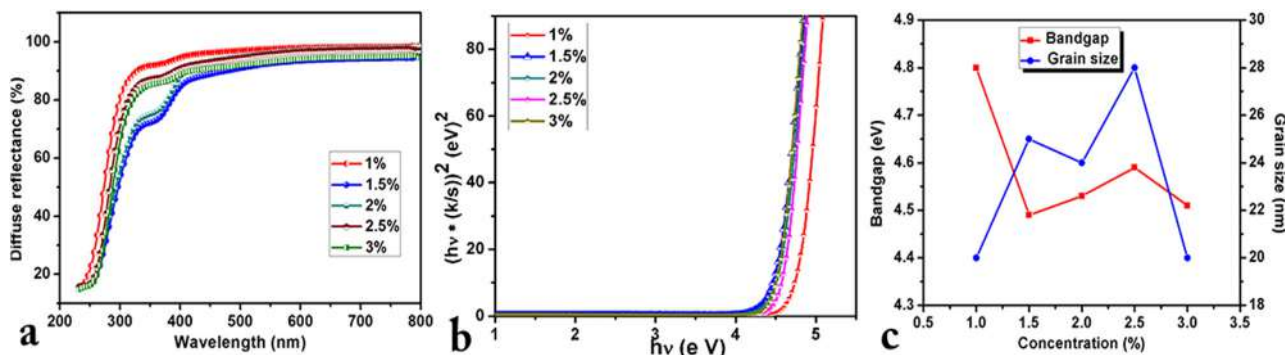


Fig. 5. (a) Diffuse reflectance spectra, (b) Tauc plot and (c) variation of band gap and crystallite size of ZnGa₂O₄:Tb³⁺ phosphor with mol% Tb³⁺.

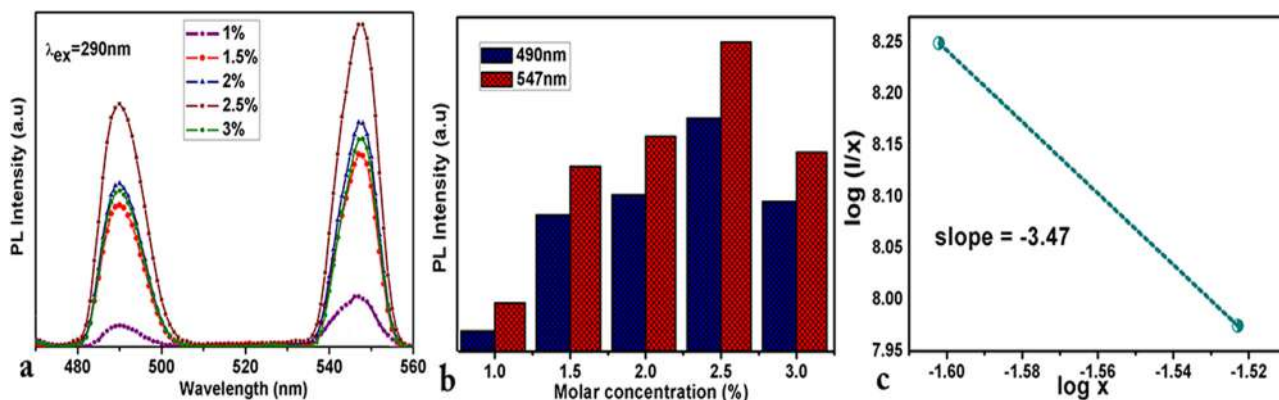


Fig. 6. (a) Photoluminescence spectra, (b) peak intensity variation and (c) log(x) vs log(I/x) graph of ZnGa₂O₄:Tb³⁺ phosphor with different concentrations of Tb³⁺.

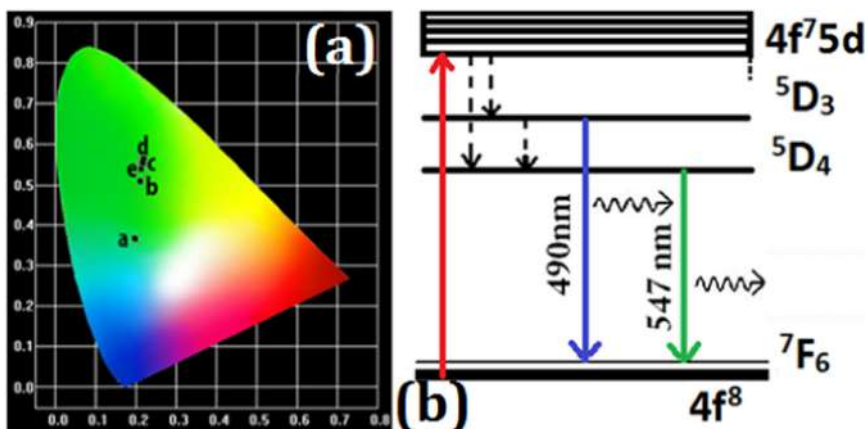


Fig. 7. (a) CIE chromaticity diagram and (b) energy band diagram for ZnGa₂O₄:Tb³⁺ phosphor [a to e represents 1–3 M concentration of Tb³⁺ and - - represents the nonradiative emissions].

Table 3
Variation in optical parameters with molar concentration of Tb³⁺ ion.

Molar concentrations of Tb ³⁺ (%)	Band gap (eV)	CIE coordinates	
		x	y
1	4.8	0.20	0.37
1.5	4.49	0.21	0.51
2	4.53	0.22	0.55
2.5	4.59	0.22	0.56
3	4.51	0.21	0.54

547 nm is assigned to ⁵D₄ → ⁷F₅ electronic transition [7,22,27]. Spectroscopic studies shows that the type of transitions ⁵D₄ → ⁷F₅ and ⁵D₄ → ⁷F₆ is electric-dipole and magnetic-dipole respectively. The ratio of

intensities of ⁵D₄ → ⁷F₅ to ⁵D₄ → ⁷F₆ also known as green to blue luminescence ratio is a good parameter to find out the extent of distortion in the crystal lattice. Thus the PL analysis can be used for the determination of asymmetry in local environment around Tb³⁺ ion as reported in the case of Eu³⁺ and Dy³⁺ ions [27–30].

With increase in Tb³⁺ concentration, the PL intensity of its characteristic emissions also increases upto 2.5% and then decreases (Fig. 6b). At higher concentrations, the reduction in spacing between the dopant ions and its pairing leads to the probability of cross relaxation, hence quenching of emission intensity. The given excitation energy is transferred between the dopant ions (Tb³⁺) and promote quenching of green emission. The critical distance (R_c), which is the shortest distance between dopant ions to bring about the concentration quenching can be calculated using the expression [31]:

$$R_c \approx 2 \left[\frac{3V}{4X_c \pi Z} \right]^{\frac{1}{3}} \quad (4)$$

where V = volume of unit cell = 582.18 \AA^3 , $Z = 5$, number of cations per unit cell, X_c = critical concentration after which quenching begins = 0.025. So the critical distance for Tb^{3+} ions in $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ is evaluated to be 21 \AA .

The restricted distance for exchange interaction is about 4 \AA , hence no exchange interaction is possible and the energy transfer is achieved by multipolar interaction. Since the Dexter and Van Uitert formulated a relation for finding out the type of multipolar interaction among the activator ions which stimulate the energy transfer [32,33]. It connects the activator concentration (x) with intensity of emission (I) by the relation;

$$\frac{I}{x} = k \left[1 + \beta [x]^{\frac{Q}{3}} \right]^{-1} \quad (5)$$

where k and β denotes constants of host lattice and Q represents the type of interaction. $Q = 6, 8, 10$ respectively for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. It can be estimated from the slope of the $\log(x)$ vs $\log(I/x)$ graph [Fig. 6.c]. In our case, slope of the graph = $-3.46 = -Q/3$ ie $Q \sim 10$, which implies that the multipolar interaction in $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor which induce the energy transfer is quadrupole-quadrupole interaction.

Commission Internationale de l'Elclairage (CIE) chromaticity diagram, which is the quantization of PL emission is represented in Fig. 7a. The diagram visually represents the change in color from bluish green to green with the molar concentration of Tb^{3+} ion. The corresponding CIE coordinates are arranged in Table 3.

The various electronic transitions from the Tb^{3+} ion, which are responsible for the characteristic emissions in the PL spectra is also depicted in Fig. 7.b. On exciting with 290 nm, electrons are transferred from $4f^8$, ground state to the $4f^75d$ excited state. From there, electrons are shifted to the 5D_4 and 5D_3 levels by a non-radiative transition (through phonon interaction) as displayed. From the excited 5D levels, de-excitation to 7F_6 level occurs together with emissions at 490 nm and 547 nm.

4. Conclusions

Green emitting $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$ phosphor for different activator concentrations were prepared and their structural and optical properties were analysed with respect to Tb^{3+} molar concentrations. The rod like zinc gallate exhibit concentration quenching behaviour due to quadrupole-quadrupole interaction among the activator ions. The emission color gets shifted from bluish green to green on increasing the terbium concentration. This intense green emission can be made use of in display devices and for imaging purpose in biomedical field.

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