

A Comparative study of enhanced photoluminescence properties of Gd_2O_3 ($Eu^{3+} = 1$ m%) by Co-doping Li^+ and Zn^{2+} via combustion and precipitation methods

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Abstract:

Gd_2O_3 is a useful host material because its crystallographic structure is similar to that of Y_2O_3 , a well-known host lattice for efficient phosphors. Detailed study on $Gd_{2-x-y}O_3Eu_xM_y$ ($x=1m\%$, $y=0, 0.1, 0.5, 1$ m% and $M=Li^+, Zn^{2+}$) have been carried out, preparing it by urea combustion method and precipitation method at $800^\circ C$. Photoluminescence properties, SEM, XRD, FTIR measurement have been carried out to characterize their structural, morphological and luminescent properties. Result shows that by incorporation of Li^+ and Zn^{2+} in $Gd_{2-x}O_3Eu_x$ ($x=1$ m%) would lead to remarkable increase of photoluminescence, by both methods and it is found that precipitation method is good method among both, for preparing in term of efficiency, morphology and quantity of final out put product. The enhance photoluminescence intensity assigned to the local distortion of crystal field surrounding the Eu^{3+} activator by Li^+ and Zn^{2+} ions co-doping having less ionic radii. Thus the prepared phosphor can be used as a good candidate in the field of light emitting phosphors, advance flat panel displays or color screen.

Keywords: Luminescence; SEM, XRD, FTIR, Rare earth ions; urea combustion method; precipitation method.

1. Introduction

Rare earth (RE) oxide compound such as Nd_2O_3 , Dy_2O_3 , Y_2O_3 etc widely used in high performance luminescent devices and other functional materials based on the electronic, optical and chemical characteristics arising from 4f electrons transitions [1,2]. Since oxide lattice are generally compatible with operation in Hg plasma and existing manufacturing, stability in high vacuum and absence of corrosive gas emission under electron bombardment. And in some embodiment, the nanocrystalline oxide based phosphors material provide reduced scattering. Among them Gd_2O_3 is recognized as a suitable host material owing to its adequate properties: low phonon energy (600 cm^{-1} , its ionic radius and charge approximately matches with other RE ions and its high chemical and thermal stability [2-5]. Especially its high thermal stability makes Gd_2O_3 one of the best matrixes for production of highly luminescent phosphors with excellent up/down conversion luminescent properties. Recent study shows that $Gd_2O_3:Eu^{3+}$ can be used in flat panel display and x-ray imaging system[5]. Due to its promising magnetic properties, it is used both as fluorescent marker for microscopy and as contrast enhancer for magnetic resonance imaging (MRI) [6]. Gd_2O_3 start crystallization at about $400^\circ C$ and crystalline size increases with annealing temperature[7], its phase transitions takes place from Cubic to monoclinic at temperature greater than $1500^\circ C$ [8] and it is found that cubic phase is more efficient for red emission under 254 nm excitations[9]. In recent decades nanoparticle size Gd_2O_3 with RE shows interesting character in the research of nanomaterials for biomedical applications [10], Magnetic anisotropy [11],and also used for high-performance positive magnetic resonance imaging contrast agents, X-ray computed tomography (CT) contrast agents, and gadolinium neutron capture therapy (GdNCT) agents in tumor targeting [12].Silica-coated $Gd_2O_3:Eu^{3+}$ are suitable for bio-imaging applications in fluorescence microscopy, specially for cancer imaging and therapy due to preparation of

composite nanorods with small, uniform shape and size distribution and excellent colloidal stability [13-14].

Today's, there is an obvious interest in developing environmentally friendly (i.e. non toxic) and stable inorganic rare earth based red phosphors for which oxide based phosphors are based candidates [15-16] as compare to sulfide-based or nitride based phosphors. Gadolinium oxide (Gd_2O_3) present good luminescent properties when doped with rare earth cations such as, Eu^{3+} , Tb^{3+} and use as phosphors for color television tube. It is an ideal system for energy transfer from Gd^{3+} to Eu^{3+} and its crystallographic structure is similar to that of Y_2O_3 , a well-known host lattice for efficient phosphors. $Gd_2O_3:Eu^{3+}$ phosphors have been extensively synthesized by different methods [17-25], among this sol-gel method, high temperature solid state method and hydrothermal method are generally used as commercial methods. Current literature serve shows that solution combustion method used to prepare $Gd_2O_3:Eu^{3+}$ co-doped with Li^+ enhances the luminescence intensity of $Gd_2O_3:Eu^{3+}$. In this investigation we observe that PL intensity again enhances by precipitation method as compare to urea combustion method of $Gd_2O_3:Eu^{3+}$ by co-doping with Li^+ and Zn^{2+} ions.

2. Experimental methods

In precipitation method, Gd_2O_3 (99.99%), Eu_2O_3 (99.99%), ZnO (99.99%) and $Li(NO_3)$ (99.99%) were used as starting material. First Gd_2O_3 , Eu_2O_3 and ZnO were dissolved in dilute HNO_3 (AR) to make nitrate solution with stoichiometric ratio of starting material. Solution of oxalic acid (dehydrated) was made in double distilled water and warming at 15-20minute, with continuous stir till transparent solution is obtained. The solution of oxalic acid was aided drop by drop in a mixture of rare earth nitrates i.e. yttrium nitrate, europium nitrate and zinc nitrate/lithium nitrate. Obtained precipitate was filtered out and washed with distilled water several times [26]. Then mixture dried on magnetic stirrer for $\frac{1}{2}$ hrs at $80^\circ C$, then obtain $Gd_{2-x-y}(OH)_3:Eu_xM_y$ was kept for heating at $800^\circ C$ for 4 hrs then we get $Gd_{2-x-y}O_3:Eu_xM_y$. Fig. 2 shows the flow chart for precipitation method of synthesis of $Gd_{2-x-y}O_3:Eu_xZn_y$ ($x=1m\%$) with Zn^{2+} co-doping.

For solution combustion method starting nitrate solutions with stoichiometric ratio of starting material was also made as above and stoichiometric amount of urea is used as reducing agent keeping urea to nitrate molar ratio as 2:1. Then the mixture was grinded until a uniform paste was achieved. Finally, paste was transferred to a crucible and heated at 450 to $550^\circ C$ in a furnace for 5-10 minute up to excess of free water evaporated and spontaneous ignition occurred. And then obtain fluffy white powder of $Gd_{2-x-y}O_3:Eu_xM_y$ phosphors were grind to obtain fine powder and then it was kept in furnace at $800^\circ C$ for 2h. The prepared phosphors were then used for PL excitation and emission measurements.

3. Results and discussion

Fig.1 shows the XRD pattern of $Gd_2O_3:Eu$ phosphor with Zn^{2+} and Li^+ co activators ions, it shows good agreement with standard JCPDS file no. 00-041-1105 belongs to cubic crystal structure. $Gd_2O_3:Eu$ phosphor composition is well known and lot of work had been done in the past few years. But here we mainly focused on the effect of codope on the luminescence properties and to observe the changes in the XRD pattern. Therefore from fig. 2, it observed that by co doping with Zn^{2+} and Li^+ co activators ions in the host lattice, there is no effect observes on the XRD pattern, only it affect the surface morphologies and luminescence properties, it is explain in the next section.

The phase purity of the prepared phosphors by different methods are examined by powder X-ray diffractometer (XRD) using $Cu K\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) with a nickel filter to estimate crystallinity of the phases. From powder X-ray diffraction pattern of $Gd_2O_3:Eu^{3+}$ ($x = 1 m\%$) and co doping with Zn^{2+} and Li^+ co activators ions, Lattice constant were calculated using equation,

$$a = \frac{\lambda^2}{4\sin^2\theta} [h^2 + k^2 + l^2] \quad (1)$$

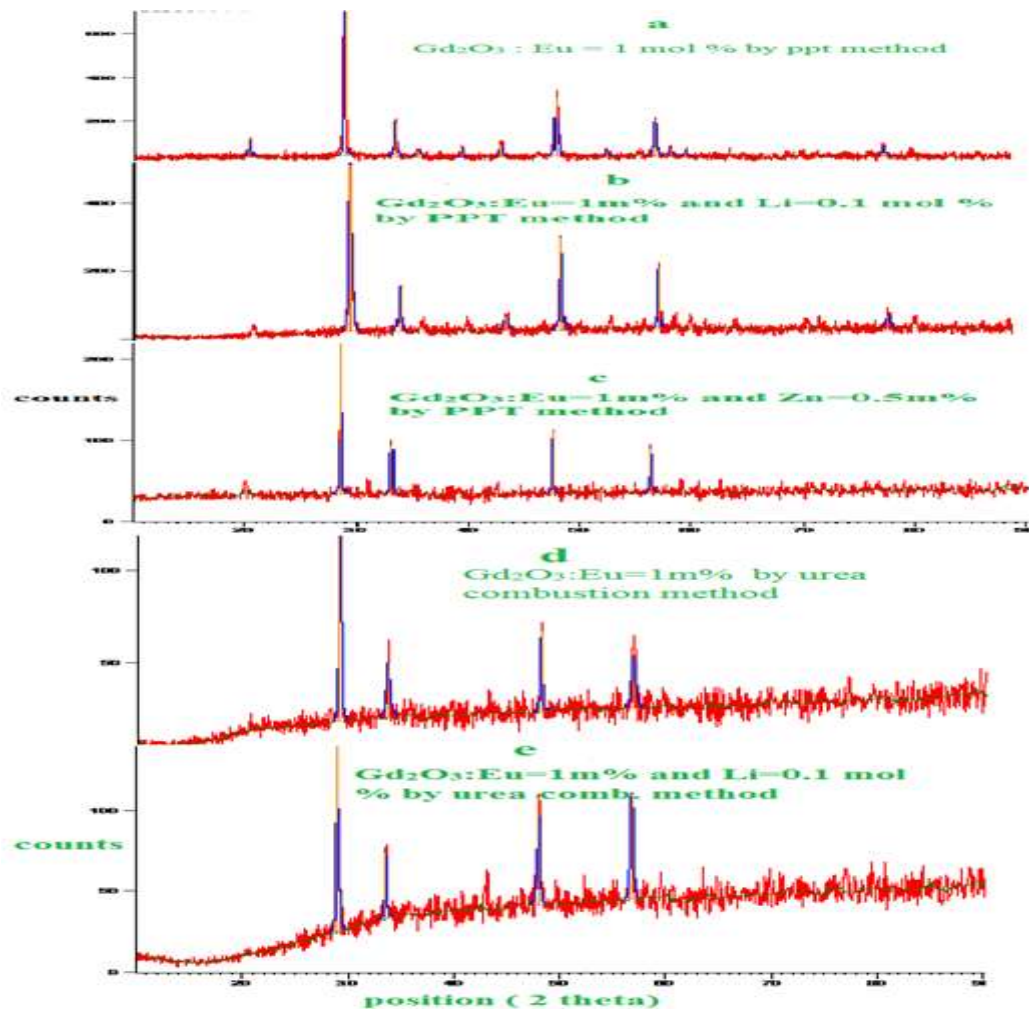


Fig. 1: XRD pattern of (a) $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+} = 1 \text{ m\%}$ by ppt method, (b) $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+} = 1 \text{ m\%}$ and $\text{Li}^+ = 0.1 \text{ m\%}$ by ppt method, (c) $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+} = 1 \text{ m\%}$ and $\text{Zn}^{2+} = 0.5 \text{ m\%}$ by ppt method, (d) $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+} = 1 \text{ m\%}$ urea comb. method, (e) $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+} = 1 \text{ m\%}$ and $\text{Li}^+ = 0.1 \text{ m\%}$ by urea combustion method.

In equation (1), a is lattice constant, λ is incident wavelength h, k, l are Millar indices and θ is Bragg's angle. The crystalline size was calculated from the broad XRD peaks using the Scherrer equation.

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

Where d is average grain size and β is the diffracted full width at half maximum and other quantities are maintained as above equation (1). Table (1) gives Lattice constant, crystalline size of $\text{Gd}_2\text{O}_3 : \text{Eu}$ phosphor co-doping with Zn^{2+} and Li^+ co-activator ions for (222) plane. From XRD result we see that position of (222) plane in $\text{Gd}_2\text{O}_3 : \text{Eu}$ shifted from 29.2° to 29.69° and 28.60° by Li and Zn doping respectively. This may be due to a small change in bond length and crystal field around Eu ions by Li and Zn doping in $\text{Gd}_2\text{O}_3 : \text{Eu}$.

Table (1): Lattice constant, crystalline size of $\text{Gd}_2\text{O}_3 : \text{Eu}$ phosphor and co-doping with Zn^{2+} and Li^+ co-activator ions

Sr.No.	Preparation method	Sample	FWHM (2θ)	Lattice constant (\AA)	Crystalline Size (nm)
1	urea combustion	$\text{Gd}_2\text{O}_3 : \text{Eu}$	0.2448	113.49	33.54

2	precipitation	Gd ₂ O ₃ :Eu,	0.1428	111.97	57.55
		Gd ₂ O ₃ :Eu, Li	0.1536	118.53	56.86
		Gd ₂ O ₃ :Eu, Zn	0.1836	116.77	44.26

N. Dhananjaya et al.[10,17] observed that PL emission intensity of Gd₂O₃:Eu increases as conc. of Eu³⁺ ions increase from 0.5 m% to 8 m% when prepared by combustion synthesis, also, E. Paritra et al [24] found that maximum conc. value of Eu³⁺ ions within Gd₂O₃:Eu³⁺ is 5 m%, when prepared by facile synthesis route, due to well incorporations of Eu³⁺ ions within the Gd₂O₃ structure. Thus for our Comparative study purpose we arbitrary fixed the Eu³⁺ =1 m% in this research paper, keeping in mind high price of RE europium. Fig. 2 shows excitation spectra of Gd₂O₃: Eu³⁺ (Eu=1m %) keeping emission at 612 nm by urea combustion method and precipitation method. This broad excitation spectra of Gd₂O₃:Eu³⁺ (Eu=1 m %) assigned to charge transfer band (CTB) ligand dependant (extending from 220 to 280 nm) of Eu³⁺ - O²⁻ band. Here we observe that intensity of excitation spectra of Gd₂O₃: Eu³⁺ (Eu=1 m %) prepared by precipitation method is greater as compare to same sample prepare by urea combustion method.

In the present investigation, we have successfully synthesized Gd₂O₃: Eu³⁺ (Eu=1m%) with Li⁺ and Zn²⁺ co-doping phosphors by urea combustion method and precipitation method, both methods are simple, time saving and economical methods at cooperatively lower temperature (800°C), that shows nearly same characteristics curves. PL emission spectra of all samples were recorded using excitation wavelength of 254 nm for comparative study in the range from 570 nm to 650 nm only. Gd₂O₃: Eu³⁺ (Eu=1 m%) prepared by urea combustion method and precipitation method and their PL emission spectra are as shown in Fig. 3, here we observe that Gd₂O₃: Eu³⁺ (Eu=1 m%) prepared by precipitation method shows maximum PL intensity.

This emission spectra of Gd₂O₃: Eu³⁺ for Eu³⁺=1 m% prepared by different methods contain a series of sharp lines in the region 580 to 650 nm. The lines belongs to transitions between ⁵D₀→⁷F_J (J=0, 1, 2, 3). The strongest sharp peak at 612 nm (red region) is due to ⁵D₀→⁷F₂ (electric dipole transition) called as hypersensitive and other peak arises due to magnetic dipole transitions. The peaks of Eu³⁺ are strongly influence by crystal field surrounding it. In the emission spectra the peaks around 588 nm and 612 nm are assigned to ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ transitions of Eu³⁺ ions, respectively. The intensity distribution of the ⁵D₀→⁷F_J (J=0, 1, 2, 3) levels depends on the symmetry of the local environments around Eu³⁺ ions and can be described in term of Judd-Ofelt theory [27, 28]. When Eu³⁺ is located at a lower symmetry local site (without an inversion centre), then ⁵D₀→⁷F_J (J=0, 1, 2, 3) emission transition is often dominated in there emission spectra. Therefore, the Eu³⁺ ions occupy non

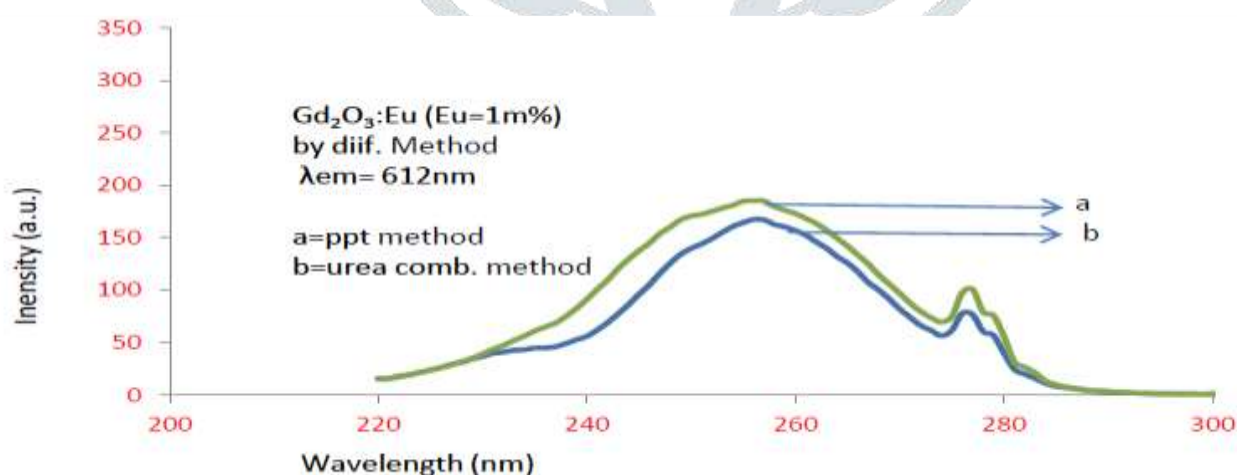


Fig. 2: Excitation spectra of Gd₂O₃: Eu³⁺=1 m% at 612 nm prepared by different method.

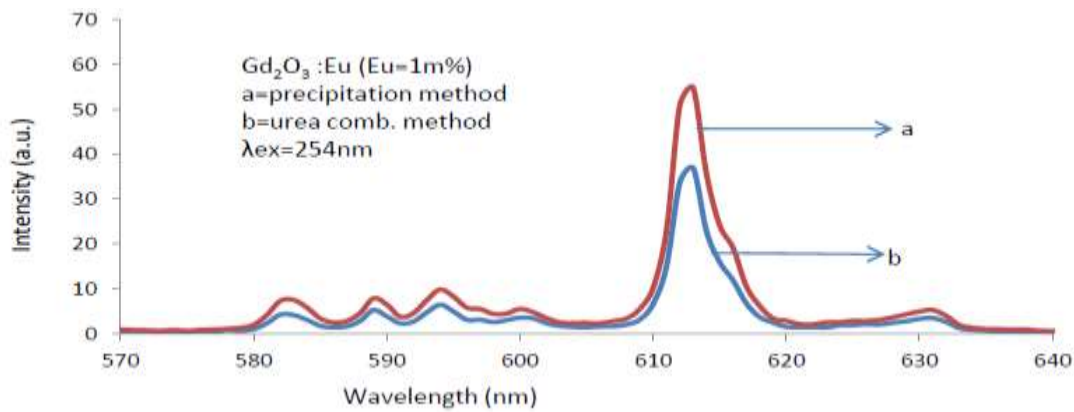


Fig. 3: Emission spectra of $Gd_2O_3: Eu^{3+}$ ($Eu^{3+}=1m\%$) for different method.

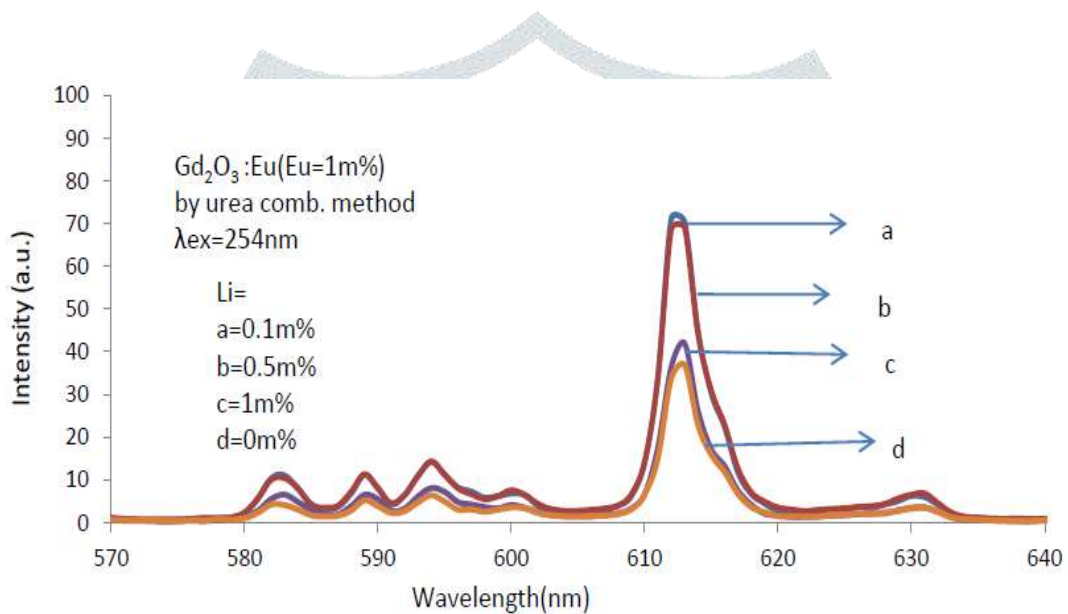


Fig. 4: Emission spectra of $Gd_2O_3: Eu^{3+}$ ($Eu^{3+}= 1 m\%$) for different concentration of lithium at 254 nm prepared by urea combustion method.

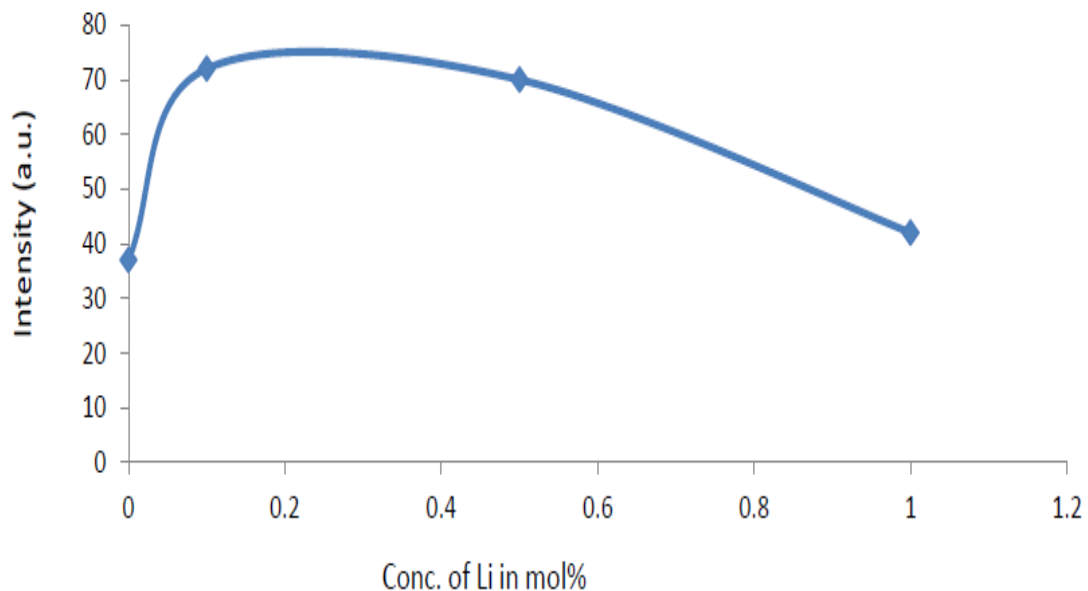


Fig. 5: Variation in PL intensity with concentration of Li^+ prepared by urea combustion method.

inversion symmetric Gd^{3+} sites. This means that when the Eu^{3+} ion is located at a low symmetry local site without inversion centre. Thus the strongest ${}^5D_0 \rightarrow {}^7F_2$ transitions (612 nm) are due to the Eu^{3+} ions in proposed host.

The PL intensity of asymmetry ratio (${}^7F_2/{}^7F_1 = 612/588$) transitions, gives a measure of the degree of distribution from the inversion symmetry of the local environment of Eu^{3+} ion in the matrix, found to be same for both method of preparation. Although the transition ${}^5D_0 \rightarrow {}^7F_1$ is electric dipole forbidden and derives its intensity due to magnetic dipole operator and here we see that m_j splitting of 7F_1 takes place into four sublevels due to crystal field and we get four peaks at 583 nm, 589 nm, 594 nm and 600 nm, that conform the asymmetrical octahedral environment around rare earth ion [28-30]. One small peaks observed at 630 nm due to ${}^5D_0 \rightarrow {}^7F_4$ magnetic dipole operator.

PL emission spectra of $Gd_2O_3:Eu^{3+}(Eu=1m\%)$ for different concentration of lithium at 254nm by urea combustion method is as shown in Fig. 4, which gives maximum intensity of 72 for $Li=0.1 m \%$ which is 1.94 times more as compare to $Li=0 m \%$ in $Gd_2O_3: Eu^{3+} (Eu=1 m \%)$, and Fig. 5 shows the variation of PL intensity of $Gd_2O_3: Eu^{3+} (Eu^{3+}=1m \%)$ with conc. of Li by urea combustion method, which shows that PL intensity increases up to 0.1mol % of lithium beyond that concentration quenching takes place. When we prepared same sample by precipitation method, we see that maximum intensity is 139 for $Li=0.1m\%$ which is 2.52 time more as compare to reflect that best doping value of lithium ion given sample is 0.1m% beyond that concentration quenching takes place. These all results of Li coping $Gd_2O_3: Eu^{3+} (Eu=1 m \%)$ are summarized at Table (2).

Table 2: Comparison of intensity of $Gd_2O_3: Eu^{3+} (Eu=1 m\%)$ prepared by different method with Li^+ co-doping.

Method	Intensity of $Gd_2O_3:Eu^{3+}(Eu=1m\%)$	Max. intensity of $Gd_2O_3:Eu^{3+}(Eu=1m\%)$ with Li	Max. conc. of Li in $Gd_2O_3:Eu^{3+}(Eu=1m\%)$ in mol %
Urea combustion	37	72	0.1
Precipitation	55	139	0.1

Thus, we see that by co-doping Li, intensity of $Gd_2O_3:Eu^{3+} (Eu=1 m \%)$ increases by some factor in all three methods but it is more in precipitation method compare to urea combustion method. Since in precipitation method obtain quantity of output product is also more. Thus by comparing these two methods, we can conclude that precipitation method of preparation of $Gd_2O_3:Eu^{3+} (Eu=1 m\%)$ with Li co-doping is very good for view in term of cost, intensity and quantity of powder production at the end of process. Fig.8 shows the emission spectra of $Gd_2O_3:Eu^{3+} (Eu=1 m \%)$ for different concentration of zinc at 254 nm by urea combustion method, where we see that maximum intensity is 69 for $Zn=0.1 m\%$ which is 1.86 time more as compare to $Zn=0m\%$ in $Gd_2O_3:Eu^{3+} (Eu=1 m \%)$ by urea combustion method and Fig. 9 shows the variation of PL intensity of $Gd_2O_3:Eu^{3+} (Eu=1m\%)$ with conc. of Zn^{2+} by urea combustion method, this graphs shows that PL intensity increases up to 0.1m% and then intensity decreases exponentially with conc. of Zn^{2+} . Fig.10 shows the emission spectra of $Gd_2O_3:Eu^{3+} (Eu=1 m\%)$ for different concentration of zinc at 254 nm by precipitation method. From Fig. 10 we see that maximum intensity is 108 for $Zn^{2+}=0.5 m\%$ which is approximately 1.96 time more as compare to $Zn^{2+} = 0 m\%$ in $Gd_2O_3:Eu^{3+} (Eu=1 m \%)$ by precipitation method. Fig. 11 shows the variation of PL intensity of $Gd_2O_3:Eu^{3+} (Eu=1 m \%)$ with conc. of Zn^{2+} by precipitation method. Thus it is noted that in later methods PL intensity is found to increase up to 0.5 m% of Zn^{2+} beyond that conc. quenching takes place.

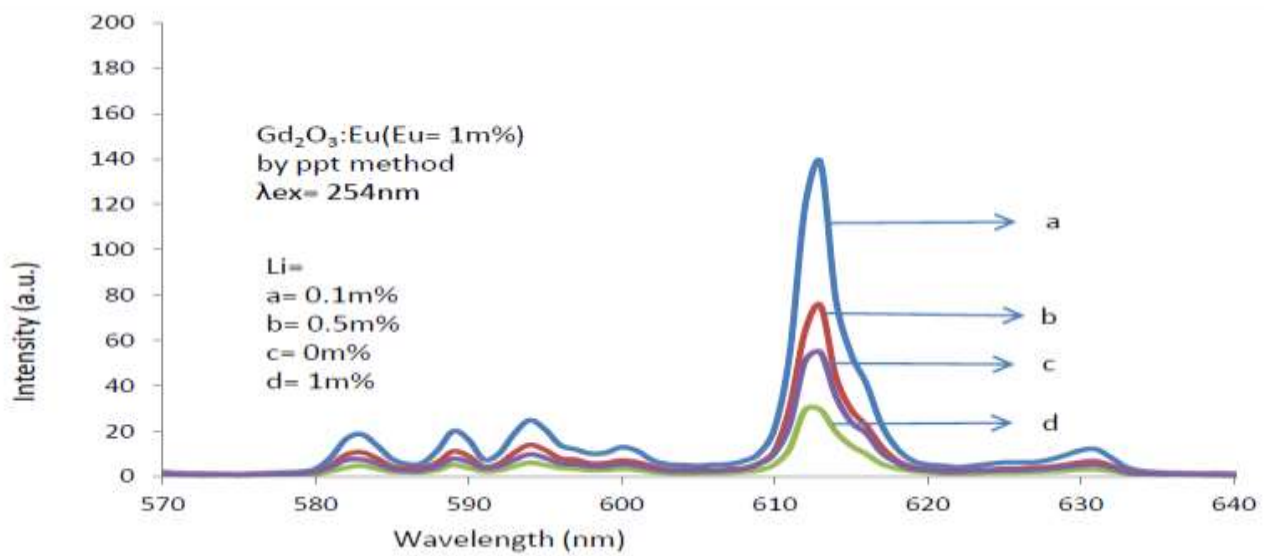


Fig. 6: Emission spectra of Gd₂O₃: Eu = 1 m% for different concentration of lithium at 254 nm prepared by ppt method.

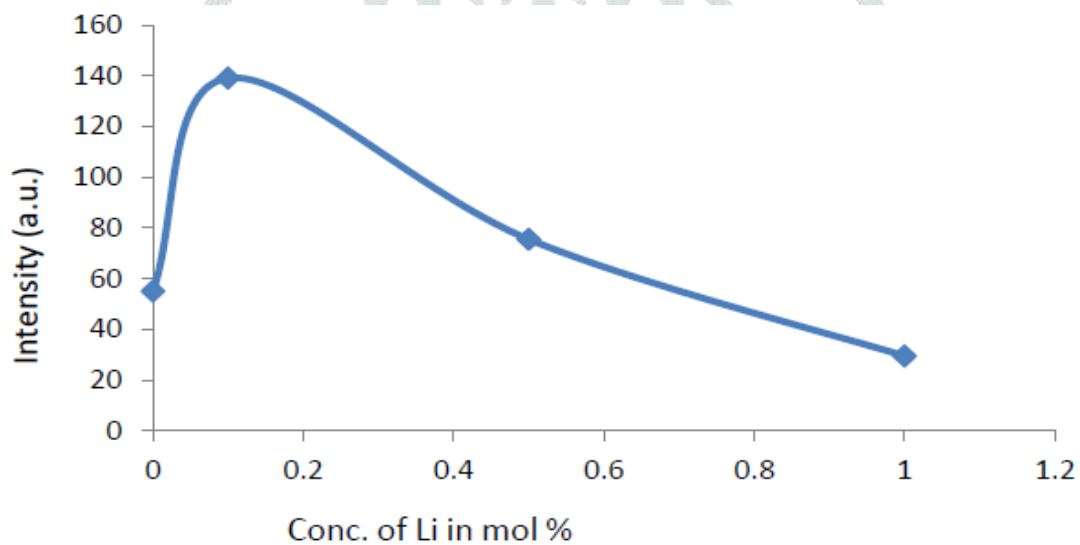


Fig. 7: Variation in PL intensity with concentration of Li⁺ prepared by ppt method.

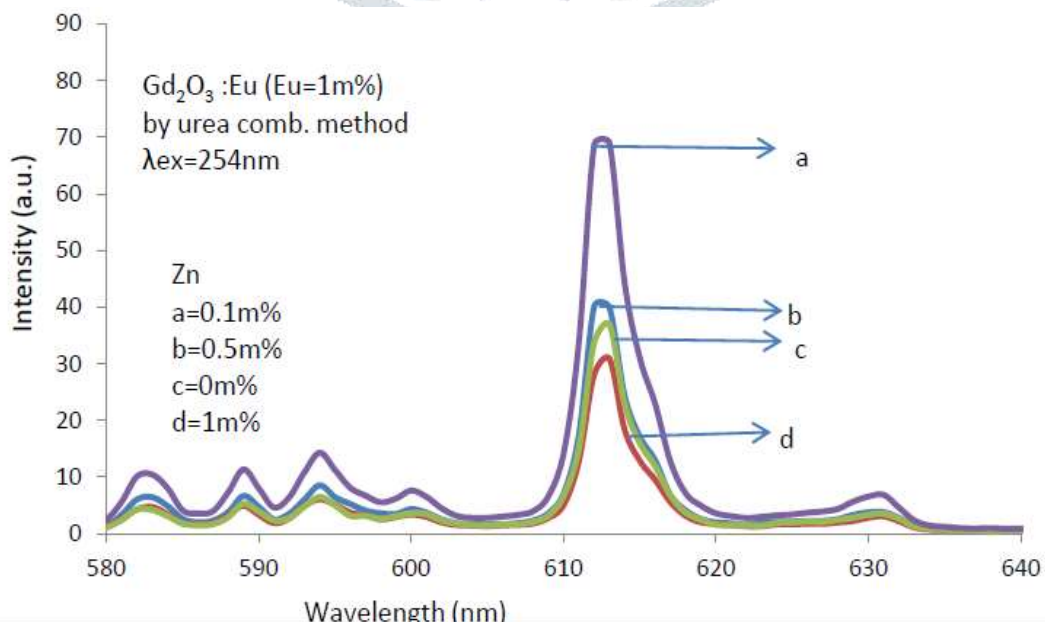


Fig. 8: Emission spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+} = 1 \text{ m\%}$ for different concentration of Zn^{2+} at 254 nm prepared by urea combustion method.

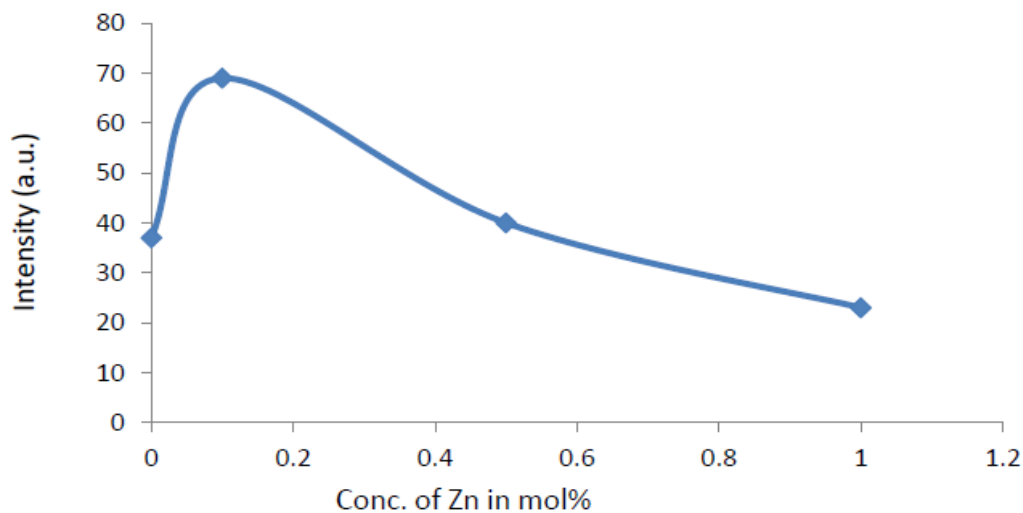


Fig. 9: Variation in PL intensity with conc. of Zn^{2+} by urea combustion method.

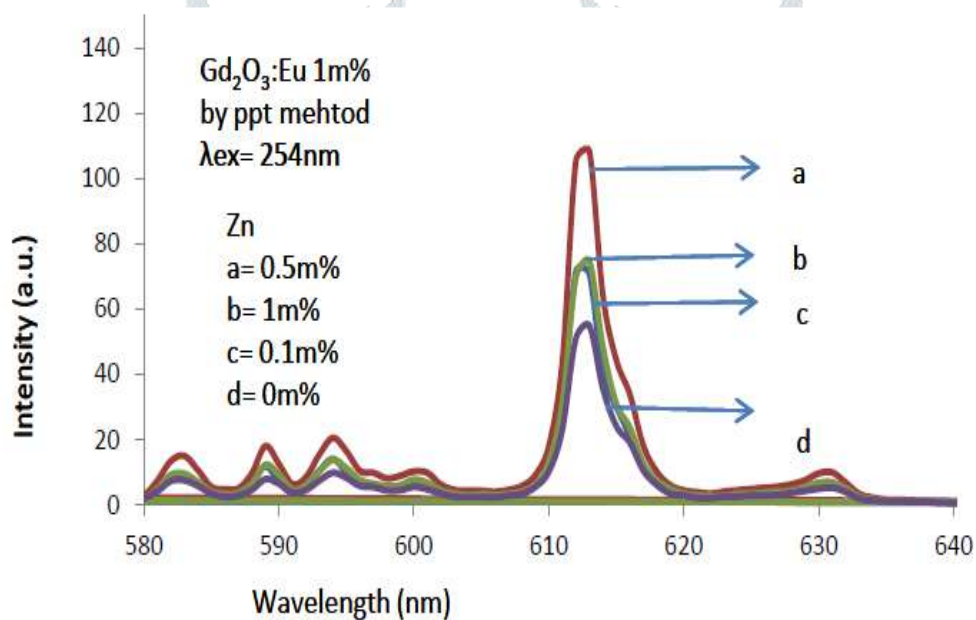


Fig. 10: Emission spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+} = 1 \text{ m\%}$ for different concentration of Zn^{2+} at 254 nm by ppt method.

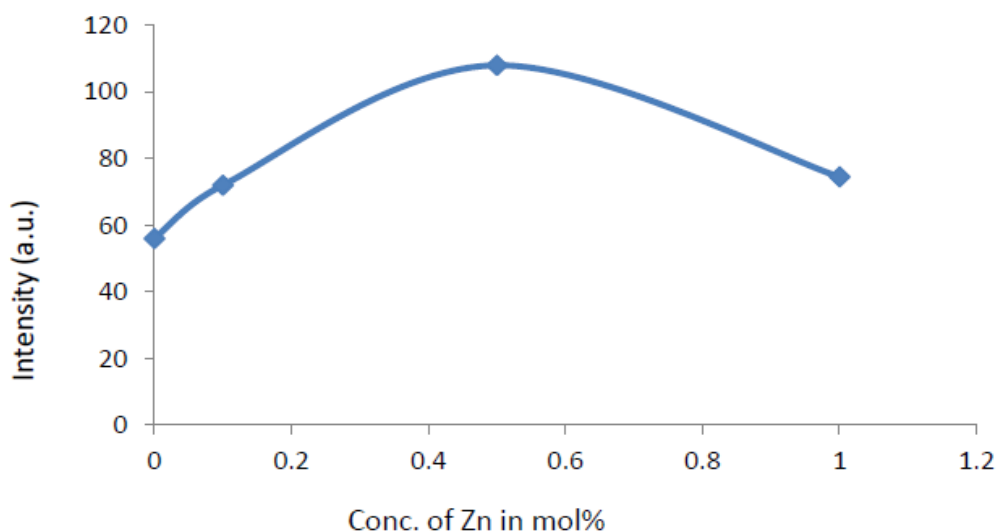


Fig. 11: Variation in PL intensity with conc. of Zn²⁺ prepared by ppt method.

Thus, we see that by co-doping Zn in Gd₂O₃:Eu³⁺ (Eu=1 m%) intensity increases by some factor in these methods, and out of these two methods precipitation method is good process for preparation of Gd₂O₃:Eu³⁺ (Eu=1 m%) with Zn²⁺ co-doping, in view of cost and intensity and quantity of output product. These all results of Zn²⁺ co-doping in Gd₂O₃:Eu³⁺ (Eu=1 m%) are summarized at Table (3).

Table 3: Comparison of intensity of Gd₂O₃:Eu³⁺ (Eu=1 m%) prepared by different method with Zn²⁺ co-doping.

Method	Intensity of Gd ₂ O ₃ :Eu ³⁺ (Eu=1m%)	Max. intensity of Gd ₂ O ₃ :Eu ³⁺ (Eu=1m%) with Zn ²⁺	Max. conc. of Zn in Gd ₂ O ₃ :Eu ³⁺ (Eu=1m%) in mol %
Urea combustion	37	69	0.1
Precipitation	55	108	0.5

The PL measurements indicated no significance change in the shape and position of emission spectra, except PL intensity. This fact indicates that the charge transfer from the O²⁻ to Eu³⁺ is enhance and more efficient with incorporation of Li⁺ and Zn²⁺ ions and these ions act as an intermediation for transfer of excitation energy from the host lattice to the activator which lead to enhancement of PL intensity. The improvement of PL intensity with Li⁺ and Zn²⁺ ions may be attributed to the improved crystallinity (i.e., adding Li⁺ and Zn²⁺ impurities may influence the morphology of Gd₂O₃:Eu³⁺ by participating in the nucleation and growth, in which many overall factors integrate to dominate the process) which lead to higher oscillator strength for the optical transition as well as enlarged grain sizes inducing lower scattering loss [29, 31]. Further substitution of Li⁺ and Zn²⁺ ions into Gd³⁺ sites would eventually a substantial number of oxygen vacancies might act as sensitizer for the energy transfer from host to Eu³⁺ ion due to strong mixing of charge transfer states which enhances the luminescence intensity [11,14].

The PL intensity enhancement may be due to that particular conc. of Li⁺/Zn²⁺, and Eu³⁺ ions might have gone to particles boundaries. This is possible due to sudden onset of thermodynamical process which extract europium from symmetrical octahedral sites of Gd₂O₃ lattice and place them at particle boundary and shows simultaneous emission from site due to different crystal field splitting [32, 33]. The requirement of the charge compensation by the substitution dopant ion in gadolinium would required different number of dopant ions and related to vacancy states [11], since atomic radii of europium, gadolinium, lithium and zinc are 2.0 Å, 1.79 Å, 1.55 Å and 1.33 Å respectively and it is observed that by adding impurities ion of smaller size in the host, host try to shrinks and this factor favor or inhibit the formation of structural defects,

which are able to control the degree of structural order and disorder in the material and consequently, number of intermediate energy levels within the band gap of host lattice [34]. Which alter the crystal field surrounding the Eu^{3+} ions, thus sites offered for Eu^{3+} ion will have more reduced symmetry which is able to lift the parity selection rule and increase transition probability of electron, and then result in an increase of PL intensity. And it is also proposed that the occupation of Gd^{3+} sites by smaller Li^+ ions could create a number of oxygen vacancies, which may act as sensitizer for effective energy transfer [35]. Again we can enhance the obtain intensity of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) with Li^+ and Zn^{2+} co-doping by finding proper concentration of Eu^{3+} ion and calcinations temperature when prepared by precipitation method that can be strengthened by ion-doping induced higher energy phonons. These all results of Li^+ and Zn^{2+} co-doping in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) are summarized at Table 4. Fig. 12 gives the SEM micrograph images, prepared by precipitation method of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Zn}=0.5 \text{ m} \%$, (c) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Li}^+=0.1 \text{ m} \%$. These images were observed as homogeneous and irregular size fine crystals in nanometer range without agglomerations. Fig. 13 shows SEM images prepared by urea comb. method of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$), with $\text{Li} = 0.1 \text{ m} \%$ (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$), with $\text{Zn}=0.1 \text{ m} \%$. Images are fluffy and porous in nature. Agglomerations are generally obtain in combustion methods are also observed in these image also, to minimize their surface free energy. The pores and voids presents on the surface of samples are due to the huge amount of gases released during synthesis process.

Table 4: Comparison of intensity of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) prepared by different method with Li^+ and Zn^{2+} co-doping.

Method	Intensity of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$)	Max. intensity of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) with Li	Max. intensity of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) with Zn
Urea combustion	37	72	69
Precipitation	55	139	108

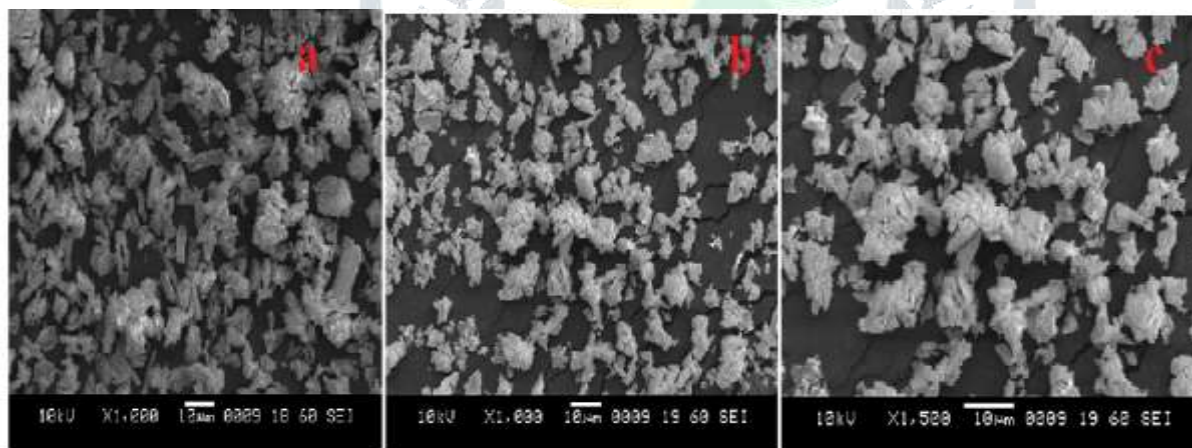


Fig.12: SEM images of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$), (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) with $\text{Zn}^{2+}=0.5 \text{ m} \%$ by ppt, (c) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}=1 \text{ m} \%$) with $\text{Li}^+=0.1 \text{ m} \%$ by ppt.

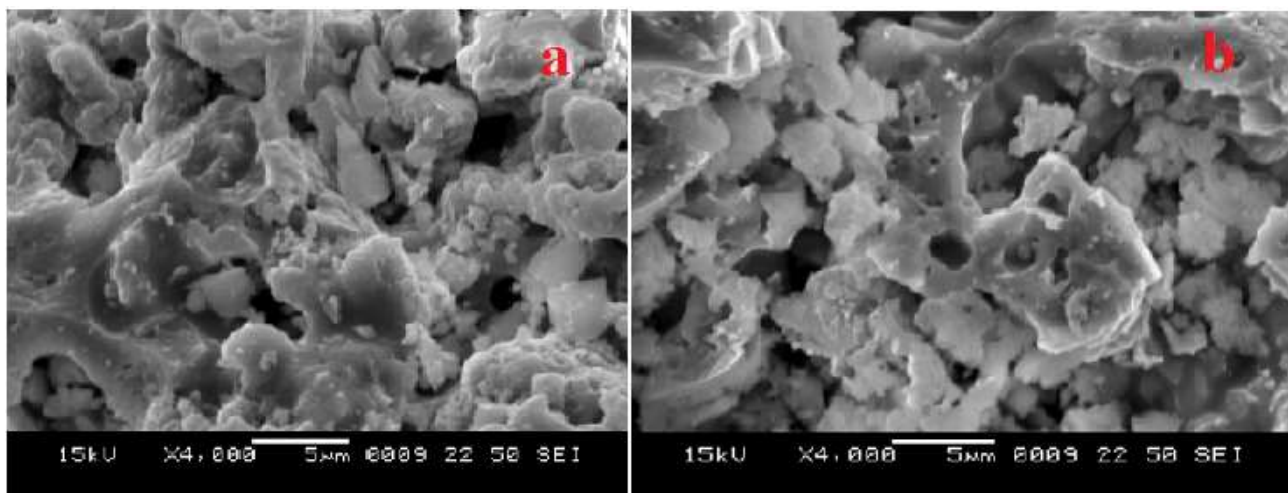


Fig.13: SEM images of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (Eu=1 m%), with $\text{Li}^+=0.1$ m% (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (Eu=1 m%), with $\text{Zn}^{2+}=0.1$ m% prepared by urea comb. methods.

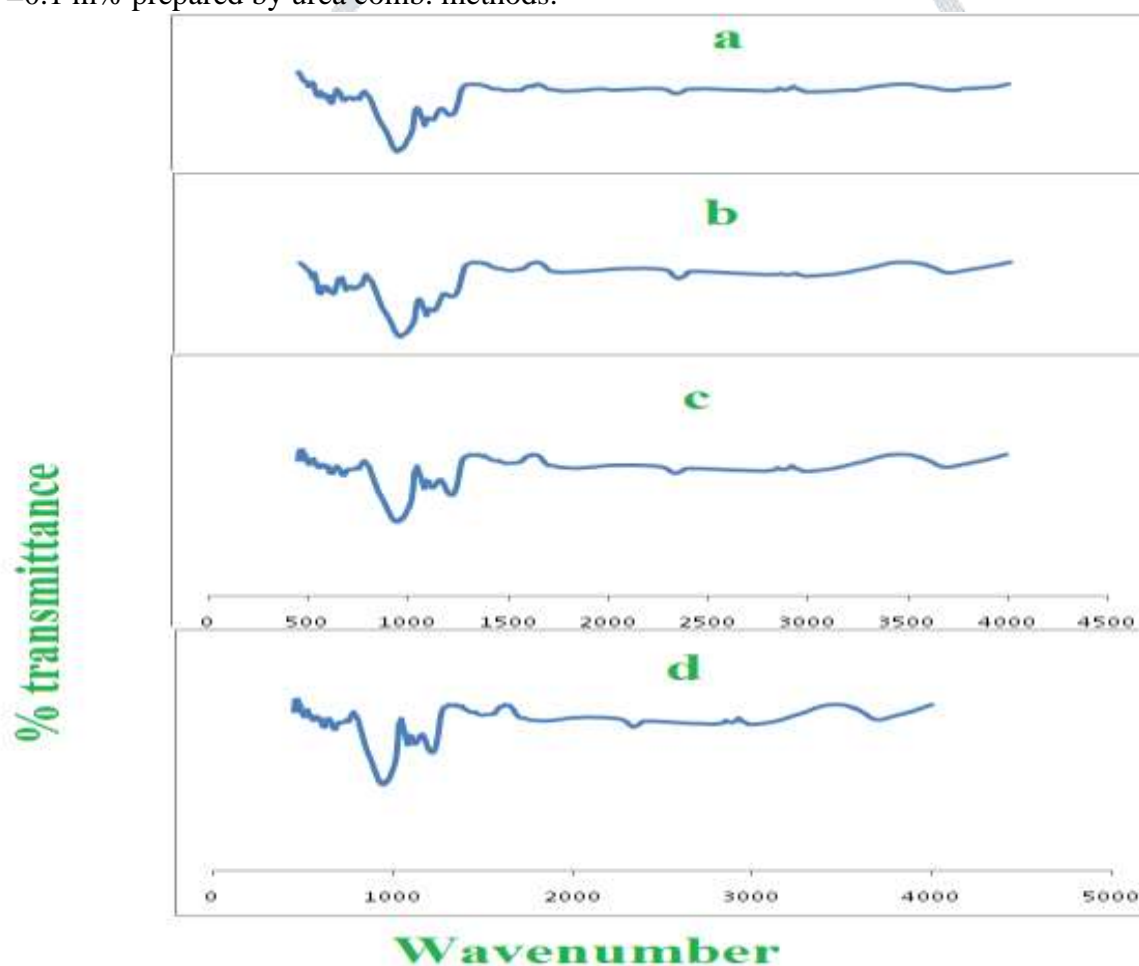


Fig. 14: FTIR Results of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (Eu=1 m%) by ppt method, (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Zn}^{2+}=0.5$ m% by ppt, (c) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Li}^+=0.1$ m% by ppt method, (d) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, with $\text{Li}^+ = 0.1$ m% by urea comb. method.

Fig. 14 shows the FTIR spectra of (a) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ by ppt method, (b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Zn}^{2+}=0.5$ m% by ppt method, (c) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Li}^+=0.1$ m% by ppt method, (d) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with $\text{Li}^+ = 0.1$ m% by urea comb. method. The spectrum shows a broad peak at around 980 cm^{-1} is assigned to the C-O vibration, the bands toward lower wavenumber side from 500 cm^{-1} to 800 cm^{-1} are associated with the vibrations of Gd-

O bond. The two small peaks round 1190 cm⁻¹ and 1240 cm⁻¹ are attributed to stretching, symmetric and asymmetric vibrations of nitrate complex.

4. Effect of impurity ions on luminescence of Gd₂O₃:Eu³⁺ phosphors

From the PL excitation and emission spectra, it observed that maximum concentration of Li⁺ and Zn²⁺ in Gd₂O₃:Eu³⁺ gives maximum intensity under the different synthesis routes, this may be due to that particular concentration of Li⁺/Zn²⁺. By cooping impurity ions Zn²⁺ and Li⁺ in Gd₂O₃:Eu³⁺ to study their influence on the luminescence of Eu³⁺ ions, we observed that the position of emission wavelengths of Gd₂O₃:Eu³⁺ is not affected by the addition of these impurity ions. But, the emission intensity is influenced by the addition of the Li⁺ and Zn²⁺ impurity ions. This indicates that environment around Eu³⁺ is not influenced by the addition of impurity ions. But addition of small concentration of monovalent and divalent impurity (Li⁺ and Zn²⁺) enhances the emission intensity due to change in symmetry around Eu³⁺ ions that is from C₂ symmetry to S₆ symmetry [36]. The enhanced emission intensity of Eu³⁺ by the addition Li⁺ and Zn²⁺ may be attributed to reduction of interstitial oxygen. The oxygen vacancy generated by Li⁺ and Zn²⁺ ion incorporation in the lattices. The oxygen vacancy in the lattice promotes the energy transfer from the excited carrier in lattices to the Eu³⁺ activator ion, leading to an increase in the luminescence efficiency. Second possible reason is the energy transfer process i.e. co-operative energy transfer between Eu³⁺ ions and Zn²⁺/Li⁺ ions. The decrease in emission intensity may be attributed to the formation of non luminescent zinc oxide and lithium oxide in the host. Since ionic radii of gadolinium, lithium and zinc are 105.8 pm, 90 pm and 74 pm [37,38] respectively and it is observed that by adding impurities ion of smaller size in the host, host try to shrinks and this factor favour or inhibit the formation of structural defects, which are able to control the degree of structural order and disorder in the material and consequently, number of intermediate energy levels within the band gap of host lattice [39]. Adding Li⁺ and Zn²⁺ impurities may influence the morphology of Gd₂O₃:Eu³⁺ by participating in the nucleation and growth, in which many overall factors integrate to dominate the process.

From Photoluminescence result we see that intensity of Gd₂O₃:Eu³⁺ with Li⁺ / Zn²⁺ ion, prepared by precipitation method is found to be more as compare to prepare it by urea combustion methods. That can be sudden onset of thermodynamical process in urea combustion method which extract europium from symmetrical octahedral sites of Gd₂O₃ lattice and place them at particle boundary and shows simultaneous emission from site from different crystal field splitting [41-42]. Morphological image shows the second reason that is in urea combustion method fig.13 shows formation of agglomerated porous nature of powder sample and fig.13 shows formation of fine grany morphology of powder sample when prepared by precipitation method. Thus well crystalline sample is important for good PL. Again we observe that maximum concentration of Li⁺ and Zn²⁺ impurities is different in different preparation method that is due to the requirement of the charge compensation by the substitution dopant ion in gadolinium ions and related to vacancy states [40,43].

PL measurement of all samples indicates no significant change in the emission shape or position except PL intensity and that are strictly depends on method of preparation and conc. of co-dopant Li⁺ and Zn²⁺ ions like that in Y₂O₃:Eu³⁺ sample[39]. Since Y₂O₃:Eu³⁺ phosphor is one of the commercial component of tri-color lamp phosphor thus prepared Gd₂O₃:Eu³⁺ phosphor with co-doping by Li⁺ and Zn²⁺ can be used as an important material in lamp industry in place of Y₂O₃:Eu³⁺.

5. Conclusions

Gd₂O₃:Eu³⁺ (Eu=1 m%) co-doped with Li⁺ and Zn²⁺ has been synthesized by simple, time saving and economical methods at cooperatively lower temperature (800^oC). Increase in photoluminescence intensity of Gd₂O₃:Eu³⁺ (Eu=1 m%) co-doped with Li⁺ and Zn²⁺ may be assigned to co doping of smaller size impurity as compare to Gd³⁺ and Eu³⁺ which reduces stress between the host matrix and altered the crystal field surrounding Eu³⁺, eventually substantial number of oxygen vacancy on the surface of phosphor. Gd₂O₃:Eu³⁺ (Eu=1 m%) with Li⁺ and Zn²⁺ co doping prepared by precipitation method shows enhance PL intensity as compare to urea with dominant red emission, which can be used as high performance display material. PL measurement of all samples indicates that PL intensity strictly depends on method of

preparation and conc. of co-dopant Li^+ and Zn^{2+} in sample $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$. Morphological study shows that the phosphor prepared by precipitation method is more homogeneous and irregular size fine crystals in nanometer range. $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (Eu=1 m%) prepared by precipitation method shows maximum PL intensity as compare to combustion synthesis method, on same scale reading, at particular excitation and as compare to use Zn^{2+} as co-doping, it is convenience to use Li^+ as co-doping for good luminescence intensity. Since red phosphor is one of the commercial components of tri-color lamp phosphor thus prepared $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphor with co-doping by with Li^+ and Zn^{2+} can be used as an important material in lamp industry.

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