

Luminescence studies on lanthanide ions (Gd^{3+} , Tb^{3+}) doped YAG:Ce phosphors by combustion synthesis

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Abstract : YAG:Ce,RE (RE: Gd^{3+} , Tb^{3+}) phosphors have been synthesized by combustion synthesis employing glycine-urea fuels at 500°C. Crystal structures, luminescent properties of the phosphors are analyzed. XRD study of polycrystalline powder shows the formation of YAG phase at low temperature. The emission spectra of phosphors shows gradual shift towards longer wavelength with the increase of doping concentration of Gd^{3+}/Tb^{3+} ion. However co-doping results in significant decrease in the emission intensity.

Keywords: w-LED, YAG:Ce, codoping, red shift

I. Introduction

White light-emitting diodes (w-LEDs) have attracted more attention and interest due to its promising features, such as low cost, energy efficient, mercury-free, long lifetimes, and compactness. They are replacing conventional light sources in a broad range, including visual signals, lighting and illumination, and non-visual applications[1]. A white light can be produced by simply mixing red, green, and blue LED (multiple LED) but produces a poor white. Apart from that it becomes impractical due to variation of LED color properties because of manufacturing tolerances and different light output degradation rates.

Another very convenient way for production of white LEDs is based on a combination of a blue LED (InGaN chip) with a blue to yellow down conversion phosphor. White light is generated by the combination of non-absorbed blue emission from blue LED and broad yellow emission from Ce^{3+} activated yttrium aluminum garnet ($Y_3Al_5O_{12}:Ce^{3+}/YAG:Ce^{3+}$) phosphor as per Blasse and Brill [2]. Presently commercial white LEDs available in market use coating of YAG:Ce phosphor on a blue LED chip. To be used as an illumination source, white LEDs should have good colour-rendering property. Conversely, blue LED pumped white LEDs with YAG:Ce phosphor have low colour-rendering index due to deficiency in red spectral region[3]. To meet the needs for white LEDs, there is a need to obtain a phosphor with ideal optical properties that has a broad emission band covering the green and red regions in the blue-light excitation. One promising way for the shift towards longer wavelength i.e. red shift of the emission wavelength is to modify the composition of the host lattice through a solid solution with similar crystal structure and another way is to utilize the energy transfer between the co-doped activators. Yellow light emission from YAG:Ce phosphor arises due to 5d-4f transition of Ce^{3+} . This transition is very sensitive to presence of other lanthanide ions in the host and conditions employed for their synthesis[4-7]. Therefore, blending other red-emitting phosphors into the YAG:Ce phosphor or doping other rare earth ions with a different radius to expand the YAG:Ce emission band to induce a red shift of the YAG:Ce luminescence have been proposed as solutions to this problem[8-11]. Co-doping red emitting ions as co-activators into YAG: Ce^{3+} was extensively studied[12].

Substituting Y^{3+} with Tb^{3+} , Gd^{3+} can shifts the emission band of YAG:Ce³⁺ to the long wavelength side, which can improve the color-rendering properties of the w-LEDs due to the enhanced emission intensity in red spectral region. Pan et al. already reported on the effect of Gd^{3+} co-doping[13] and Lin et al. reported Tb^{3+} codoping[6] in YAG:Ce synthesized by solid state reaction techniques.

YAG phosphor has been synthesized using various novel methods to achieve a fine and pure nonagglomerated powder, high emission efficiency, narrow particle size distribution, and high crystallinity. Some novel methods of preparation are precipitation[14,15] flame spray pyrolysis[16], sol-gel[17], sol-gel combustion[18], glycolthermal[19], combustion synthesis using urea [13,20] by molten salt synthesis or carbohydrazide fuels[21], by burning a mixture of yttrium aluminum hydroxyl nitrates, urea, and acetic acid[22], by pulsed laser ablation[23] etc. YAG phosphors doped with activators are mainly synthesized by solid state reaction techniques that require high sintering temperatures (above 1800°C) to eliminate intermediate phases[24]. Though several soft chemical routes have been explored for synthesis of YAG doped phosphors, most of these methods are complex and high cost for the industrialization. The methods like sol-gel process and hydrothermal synthesis require expensive chemicals or equipment and involve procedural complexity. Moreover, phase pure materials are not obtained in one step and prolonged annealing at temperatures around 1400°C is necessary. Combustion synthesis is a low temperature technique which offers an exclusive synthesis

route via a highly exothermic redox reaction between metal nitrates and organic fuel/s for the production of multi-element oxides. The reaction itself supplies the energy for the component oxides and produces a homogenous product in very short time at low temperature. The as-synthesized product is high in purity, usually single phase, and chemically homogenous. The activators in such phosphor are expected to be uniformly distributed throughout the host material due to the atomic mixing of the reactants in the initial solution.

In the present work, the advantages of YAG:Ce has been enhanced using addition of co-dopant Gd³⁺ and Tb³⁺ separately by single step combustion synthesis[25], carried out at 500°C furnace temperature without taking recourse to any post combustion thermal treatment. The concentration of Ce was varied to optimise the dopant amount that produces maximum yellow luminescence in YAG. In optimised YAG:Ce, co-dopant Gd /Tb was introduced in varied concentration to achieve maximum red component in the phosphor. Synthesis of such phosphor with enhanced red emission can be possible at low temperature.

II. Experimental

YAG:Ce; YAG:Ce, Gd and YAG:Ce, Tb were prepared by controlled one step autocombustion process by mixed fuels. All the precursor components were taken in stoichiometric proportions from nitrate salts of the precursor elements. To achieve this, all the oxide /carbonate precursors including the rare earth component were changed into their nitrate salt by suitable reaction with nitric acid. For synthesis of YAG:Ce, the starting materials used for preparation of the phosphor were Y₂O₃ (99.90%), Al(NO₃)₃.9H₂O (99.99%), Ce₂(CO₃)₃ (99.99%), HNO₃ (69% GR), NH₂CONH₂ (99.99%) and C₂H₅NO₂ (99.99%). The redox reaction was carried out between nitrates and organic fuels. The oxidizing element is oxygen from the metal nitrates while the reducing elements are C, H and Y. Nitrogen is neither an oxidiser nor a reducer in combustion reactions. For synthesis of YAG:Ce,Gd; in addition to the above starting materials Gd₂O₃(99.99%) was reacted with nitric acid and used in the nitrate form. For synthesis of YAG:Ce, Tb; Tb₂O₃ (99.99%) was used in the nitrate form. Atomic mixing of the elements can be maximizes by mixing of nitrates and organic fuels urea and glycine together in aqueous solution. The nitrate to fuel ratios were calculated by the method described earlier[21,26]. Yttrium nitrate does not have exothermic reaction with urea. Hence mixed (glycine + urea) fuel was used for synthesis since glycine has exothermic reaction with yttrium nitrate and urea with aluminum nitrate. Due to the presence of large water of crystallization in aluminium nitrate, a thick paste was formed. A china dish containing the paste was inserted in a preheated furnace at 500°C. Since the process is exothermic, in few minutes the paste foamed and a flame was produced and lasted for several seconds. The process continued heating and the solution bubbled and expanded and at a certain instance, autocombustion of urea and glycine took place with fire ignited within the dish. The reaction completed in few minutes and resultants in fluffy voluminous bright yellow mass of YAG:Ce. The dish was immediately removed from the furnace and fluffy mass was crushed by agate mortar to acquire as-synthesized phosphor. YAG:Ce,Gd and YAG:Ce,Tb phosphors were also prepared in a similar manner with various concentrations. Concentration of Ce was varied from 0.5 to 1.5 mole%, Gd /Tb from 10 to 30 mole%. Since YAG:Ce (1mol%) was found to produce the highest PL intensity, different percentages of Gd and Tb was co-doped in YAG:Ce (1 mol%). The structure of the phosphor powders were characterized by X-ray diffraction patterns recorded on Philips PANalyticalX'pert Pro diffractometer. PL characteristics were studied using a Hitachi F-4000 spectrofluorimeter at room temperature using 1.5 nm spectral slit widths in the range of 200–700 nm.

III. Results And Discussion

Fig.(1) shows the XRD pattern of Gd³⁺ codoped YAG:Ce samples obtained after combustion reaction at 500°C. X-Ray diffraction shows that the synthesized YAG:Ce, Gd phosphors exhibit identical XRD patterns corresponding to Y₃Al₅O₁₂ matching perfectly with the ICDD file 88 – 2048. In the present XRD spectra lines corresponding to YAP (2θ = 34.236), YAM (2θ = 29.289) or YAH (2θ =32.832) could not be seen confirms the formation of single phase of YAG at low temperature. Ionic radii of dopant Ce³⁺ and codopant Gd³⁺/Tb³⁺ are 0.115 and 0.106 / 0.104 nm respectively, and hence can go in substitutional position of Y³⁺ which has ionic radius of 0.102 nm.

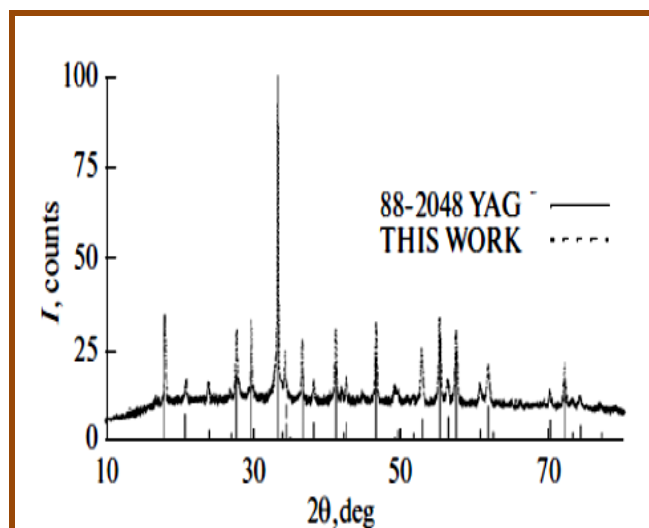


Figure 1: XRD results for YAG:Ce,Gd compared with the ICDD data file

YAG has a bcc structure; space group $Ia\bar{3}d$ with 160 atoms in the cubic cell. The Y ions occupy the $24(c)$ sites and each are dodecahedrally coordinated to eight O. The O atoms occupy the $96(h)$ sites. There are two different sites for Al, Al_{oct} occupy the $16(a)$ site with an octahedral point symmetry and Al_{tet} atoms occupy the $24(d)$ sites with a tetrahedral point symmetry. The garnet structure can be viewed as inter connected octahedraons, tetrahedrons, and dodecahedrons with shared O atoms at the corners[27]. Thus the solid-state structure of $Y_3Al_5O_{12}$ consists of a network of four- and six-fold coordinated aluminium atoms. The yttrium atoms reside in the dodecahedral interstices formed by the corner-sharing arrangement of the AlO_4 and AlO_6 polyhedra. The particles of oxides do not exhibit a lattice expansion with incorporation of certain amount of dopant in YAG ceramics. Consequently, the unit cell volume remains nearly constant as well.

In view of the improvement of luminescence properties of YAG singly doped phosphors, the way of double activation in the host lattice could be successfully used. The co-activators change the symmetry and vibrational modes around the luminescent centers and influences the Stark splitting of the 4f levels in the rare earth which results in change in crystal field around it[28]. The co-activators may act as a sensitizer for the energy transfer to the rare earth ion[29] or a charge compensator or as a preventer of nonradiative energy transfer via defects[30]. Usually, the luminescence spectrum modifies when there is double incorporation of different lanthanide ions into host crystalline lattice due to the formation of new emission centers.

The emission of Ce^{3+} is very sensitive to crystallographic environment, which results in red or blue shift of Ce^{3+} emission. Ce^{3+} has a single electron in the 4f shell with $4f^1$ configuration and its excited state is $4f^05d^1$. In YAG, Ce occurs in trivalent state by losing its two 6s electrons and one of the 4f electrons. Due to shielding effect by outer shell electrons, the f-orbital remain nonbonding whereas the low lying d orbitals are sensitive to the host crystal coordinative environment.

The emission from 4f-5d levels in Ce^{3+} is broad in character as the crystal field splitting of the 2-D level ion is large in the garnet structure. For Ce^{3+} , the lowest excited state splits into $^2D_{3/2}$ and $^2D_{5/2}$ state due to the spin-orbit coupling. The Ce^{3+} emission is involved with the ground $4f^1$ and the excited $4f^05d^1$ state, each of which is split into $^2F_{7/2}$, $^2F_{5/2}$ and $^2D_{3/2}$, $^2D_{5/2}$ states respectively. The Ce^{3+} emission results from the electron transition from the lowest 5d band to $^2F_{7/2}$, $^2F_{5/2}$ states of the Ce^{3+} ion. Fig. (2) shows excitation spectra for Ce^{3+} doped YAG. The PL excitation spectrum of YAG:Ce, sample consists of two excitation bands, one at 340 nm in the UV and the other at 460nm in the blue region at RT.

Fig.(3) shows the emission intensity and its variation with different Ce^{3+} concentration. The maximum intensity was achieved for about 1 mol% Ce^{3+} concentration at wavelength 528 nm. When Ce^{3+} amount was increased beyond this limit concentration quenching effect was observed. Thus the optimal concentration for Ce has been chosen as 1 mole %. The inset curve shows the relation between the relative intensity for various Ce^{3+} doped concentration.

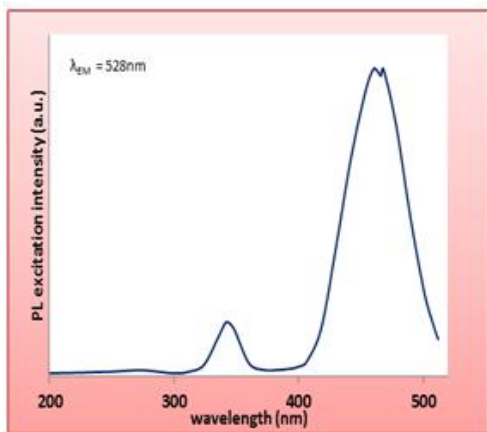


Figure 2: PL excitation spectra for Ce^{3+} ($\lambda_{em} = 528 \text{ nm}$)

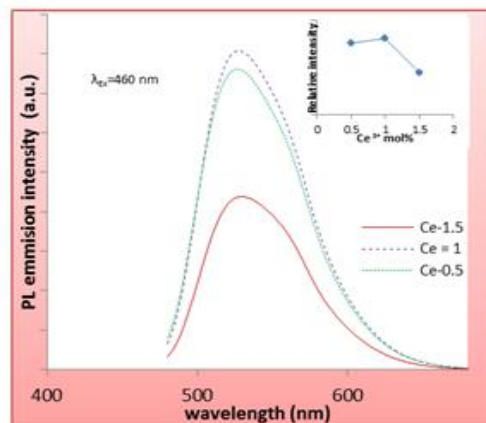


Figure 3 :PL emission spectra of YAG:Ce phosphors with varying amount of Ce^{3+}

Due to the relative flexibility of the aluminate garnets to replace Y^{3+}/RE^{3+} ions in dodecahedral sites and Al^{3+} in tetrahedral/octahedral sites, it is possible to modify the $Y_3Al_5O_{12}$ composition to alter the Ce^{3+} emission band to meet potential spectral requirements. The crystal field around the rare earth is affected by the co-activation. By co-activating YAG:Ce by Gd /Tb there has been a change of symmetry

The PL excitation spectrum for YAG:Ce, Gd is same as that of YAG:Ce (Fig. 2) and the content of Gd ($x=10$ to 30 mol %) is increased in $Y_{2.97-x}Gd_xAl_5O_{12}:Ce_{0.03}$ phosphors. The emission character changes with the concentration of Gd^{3+} in the phosphor system. The increase in concentration of Gd^{3+} , shifts the emission band towards longer wavelength as in the Fig.(4). As the concentration of Gd increases, the emission wavelength shifts from 528 nm to 543 nm with the expense of intensity as shown in the inset.

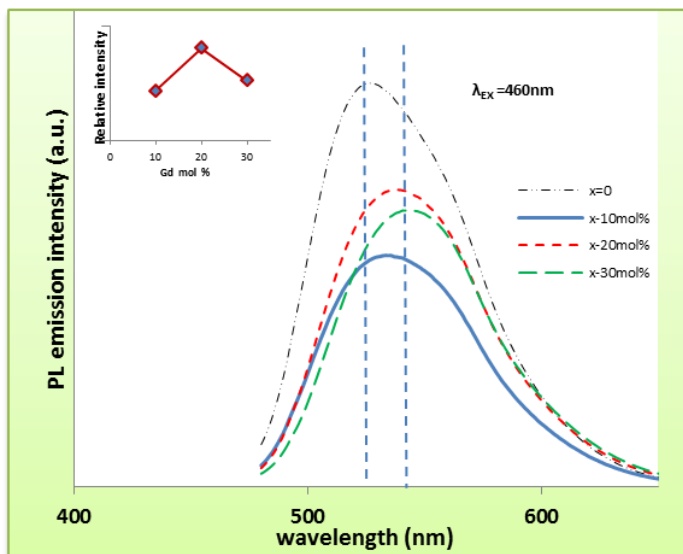


Figure 4: PL emission spectra of $Y_{2.97-x}Gd_xAl_5O_{12}:Ce_{0.03}$ phosphors with various x values.

Codoping YAG:Ce with Tb ions also results in longer wavelength shift of Ce^{3+} . Excitation spectrum corresponding to YAG:Ce,Tb shows in Fig.(5), consists of peaks at 229 nm, 275 nm, 340nm and 460nm. Broad peaks centered around 460 and 340 nm are characteristic of transitions of Ce^{3+} and a relatively sharp peak around 275nm and 229 nm is seen only for Tb doped sample arising due to 4f-5d transition of Tb.

PL emission spectra of $Y_{2.97-x}Tb_xAl_5O_{12}:Ce_{0.03}$ with various Tb concentrations (10 to 30 mol%) for an excitation of 460 nm shows in Fig.(6). The addition of Tb ions at the Y^{3+} site resulted in a significant red shift of the emission maxima from 528 to 542.5 nm. The inset curve shows the relation between the relative intensity for various Tb^{3+} doped concentration in YAG:Ce.

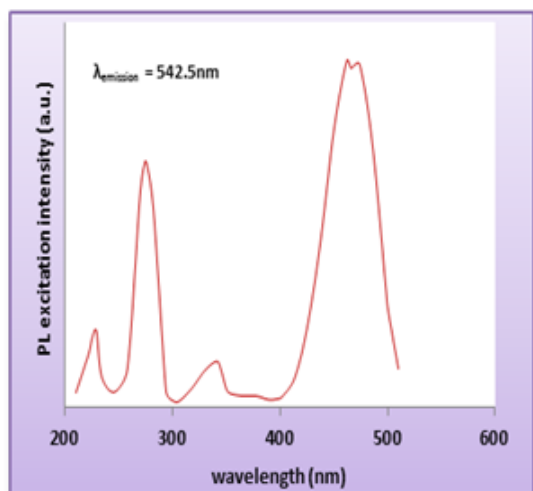


Figure 5: PL excitation spectra for YAG: Ce, Tb

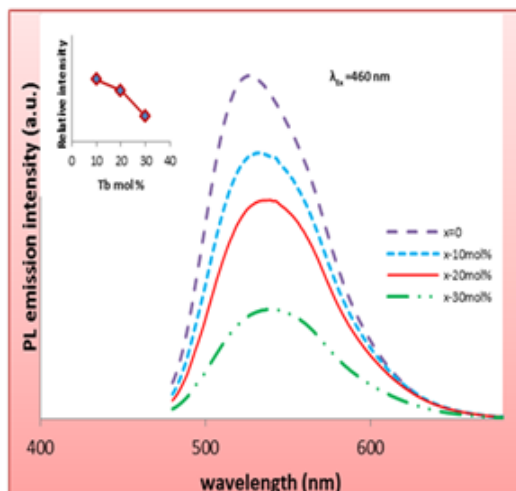


Figure 6: PL emission spectra of $Y_{2.97-x}Tb_xAl_5O_{12}:Ce_{0.03}$ phosphors with various x values.

Thus at the same activator concentration and excitation light ($\lambda_{ex} = 460$ nm), the emission wavelength is shifted to the longer wavelength in the YAG lattice after codoping by Gd or Tb ions with Ce ions is possible even at low temperature by this method. The variation of intensity and wavelength with content of codoping Gd/Tb in YAG:Ce is shown in Fig.(7).

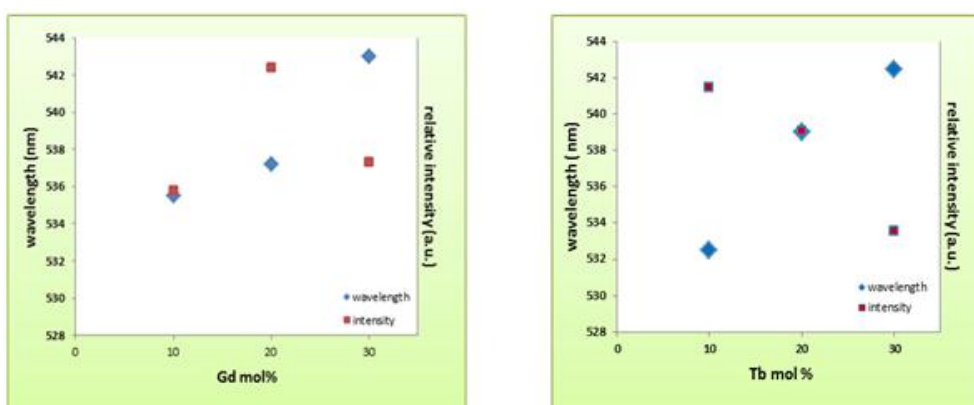


Figure 7 : variation of intensity and wavelength with codopent Gd/Tb in YAG:Ce

These results are in conformity with that reported by Yang et al [31], Blasse and Brill [2]. They reported that the emission band shift was due to lowering of the 5d energy level of Ce^{3+} . For Ce^{3+} the lowest excited state is derived from the 5d configuration. Due to tetragonal symmetry of the dodecahedral yttrium site in YAG, the 5d state splits due to the symmetry and spin-orbit interaction into five levels. This result into five absorption bands 460, 340, 261, 224, and 205 nm, but 460nm and 340 nm are commonly observed at RT. In Ce^{3+} the interaction between the 5d-electron and the chemical surrounding affects the level energies. The crystal field splitting is the energy difference between the lowest 5d₁ and highest energy 5d₅ level and almost entirely determined by the shape and the size of the first anion coordination polyhedron around Ce^{3+} . It is almost independent on the type of anions and the bonding with Ce^{3+} . The centroid shift is the average energy of the five 5d-levels and independent on the shape and symmetry of the coordination polyhedron but it is entirely determined by the chemical properties of the surrounding ligands [32]. The combination of crystal field splitting, spin-orbit splitting, and centroid shift leads to lowering of the 5d₁ level by an amount that was named as the redshift. When Y^{3+} (0.102 nm) site was substituted by a larger Tb^{3+}/Gd^{3+} ion (0.104 /0.106 nm), distance between Ce^{3+} and O^{2-} become shorter. Since crystal field splitting is proportional to $1/R^5$, where R is the bond length of activator cation–ligand anion [33], this shorter distance between Ce^{3+} and O^{2-} increases the magnitude of crystal field, and lowers of the 5d band of Ce^{3+} which outcomes in redshift. However, it should be noted that the emission intensity of Gd^{3+}/Tb^{3+} doped YAG:Ce³⁺ phosphors decreased remarkably with the increase of Gd^{3+}/Tb^{3+} content.

IV. Conclusion

In this paper, Ce³⁺ doped, Gd³⁺/Tb³⁺ co-doped YAG:Ce³⁺ phosphors were prepared successfully by combustion synthesis by mixed fuel at low temperature and without further sintering process. Their photoluminescence properties were studied. Gd³⁺/Tb³⁺ substitution shifts the Ce³⁺ emission to the longer wavelength, at the expense of emission intensity. This longer wavelength shift is suitable for high power w-LEDs applied in general illumination field. However shift is not enough to compensate for the absence of red color in the phosphor and emission intensity also reduces considerably. Thus to obtain white LEDs with higher color rendering further efforts are required to arrive at a high sensitive phosphor for blue LED excitation.

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