

# Synthesis of Dy<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup> Activated Y<sub>2</sub>O<sub>2</sub>S Optoelectronic Phosphors for N-UV LED Applications



V. V. Shinde, S. J. Dhoble

Abstract: In this, a series of iso-structural  $Y_2O_2S$  ( $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  and  $Tb^{3+}$ ) phosphors were synthesized by high temperature solid state reaction method. All the phosphors exhibit strong line and broad excitation in the near ultraviolet (n-UV) region. Bright color emission in blue, green and red color region of electromagnetic hue cycle was noticed. The concentration of activator doped was optimized from the photoluminescence (PL) study. The quenching in luminescence intensity after particular concentration of dopant is discussed here. Y<sub>2</sub>O<sub>2</sub>S phosphor doped with Dy<sup>3+</sup>displays useful blue and yellow emission bands at 487nm and 574nm, when stimulated by 388nm excitation wavelength.  $Y_2O_2S:Eu^{3+}$  phosphor displays an orange and red emission at 594nm and 620nm, when stimulated at 396 nm. Whereas,  $Y_2O_2S:Tb^{3+}$  phosphor displays weak blue radiation in the range 485nm and strong green radiation at 545nm, when stimulated at 305 nm.

The excitation spectra used for the  $Y_2O_2S:RE^{3+}$  ( $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  and  $Tb^{3+}$ ) phosphor is in the near ultraviolet (n-UV) region spanning from 300 nm to 400 nm, which is a peculiarity of near ultraviolet stimulated LED. The outcome of the  $RE^{3+}$  ( $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  and  $Tb^{3+}$ ) absorption on the luminescence properties of  $Y_2O_2S:RE^{3+}$  phosphors was also studied.

Keywords: Oxy-sulphide, phosphor, lamp phosphor, light emitting diode, Rare earth.

#### I. INTRODUCTION

Light emitting diode (LED) industrial science is reaching towards fully developed stage by replacing the old technology of fluorescent lamps. During the last 20 years, improvements in phosphors have opened the new gateways for white LEDs, in which numerous wavelengths mix together to simulate the solar chromatic spectrum. There are two major approaches for achieving white light from LEDs. The first approach is to blend the light from particular electrically driven LEDs that radiate the primary colors, i.e., red, green and blue. The inadequacy of getting highly efficient green LEDs restricts the use of this approach to the generation of white light.

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In second approach the blue or UV emitting LEDs coated with a color converting phosphors which leads to the emission of white light. Majority of the research efforts on solid-state lighting (SSL) has focused on the development of light emitter and light extraction mechanisms to meet general illumination application requirements [1, 2].

The  $Y_2O_2S$  host is a prominent large band-gap (4.6-4.8eV) semiconductor [3]. The Y<sub>2</sub>O<sub>2</sub>S do not exist as usual mineral but was devised, firstly, as a host matrix for RE<sup>3+</sup> ions by Royce [4] and Yocom [5] in 1968. Since then this lattice has been subject of intensive research interest and utilized as a potential luminescence material for various application in lighting technology and display as a host. Y<sub>2</sub>O<sub>2</sub>S:Tb is known to be a X-ray phosphor used in practical X-ray display screens as well as a green phosphor for CRT displays. Y<sub>2</sub>O<sub>2</sub>S:Eu is one of the most crucial red-emitting phosphors used in industry. Some of the important applications of Y<sub>2</sub>O<sub>2</sub>S:Eu phosphor are in cathode-ray tubes (CRTs) and field emission displays (FEDs) [6-9]. The present investigations of rare earth doped Y<sub>2</sub>O<sub>2</sub>S phosphors into the visible emissions under near ultraviolet stimulation (excitation) were undertaken to examine the mechanism of emission process. The main aim of this study is to develop this phosphor and improve the PL properties for lighting applications when excited in the n-UV (near ultraviolet) region. In the present study we have used near ultraviolet excitation wavelength, as this range of excitation wavelength comes in the same region for the white LED excitation.

#### **II. EXPERIMENTAL METHOD**

In the present work,  $Y_2O_2S:RE^{3+}$  ( $RE^{3+}$  =,  $Dy^{3+}$ ,  $Eu^{3+}$  and  $Tb^{3+}$ ) phosphors were synthesized by solid flux fusion reaction method. The starting materials used were yttrium oxide ( $Y_2O_3$ ), sulphur powder (S), Sodium carbonate ( $Na_2CO_3$ ), tri-potassium Phosphate ( $K_3PO_4$ ) as fluxes. Different flux materials such as sodium carbonate ( $Na_2CO_3$ ) and tri-potassium phosphate ( $K_3PO_4$ ) are used to increase the rate of reaction and lower down the reaction temperature. These raw materials have melting point below the melting temperature of  $Y_2O_2S$  material. These fluxes dissolve partially and remain inactive in the solid state reaction. During synthesis, the quantity of flux used was 20 weight % for  $K_3PO_4$  and 30 to 50 weight % for both sulphur powder and  $Na_2CO_3$ , of the total weight.

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The rare earth dopants used were ammonium hexanitratocerate  $(NH_4)_2Ce(NO_3)_6$ , dysprosium oxide  $(Dy_2O_3)$ , Europium oxide  $(Eu_2O_3)$ , and terbium oxide  $(Tb_2O_3)$ .

In this synthesis the stoichiometric quantities of raw materials were weighted and mixed in homogeneous form by crushing mechanically for 1 hour in mortar pastel. These crushed powders were preheated in a muffle furnace at around  $100^{0}$ C and then again crushed all these samples and placed in muffle furnace for annealing at  $1150^{\circ}$ C for 10 hours. After that prepared samples were taken out from the furnace and washed with distilled water several times then finally washed with diluted HCl acid. The prepared samples were again placed in for drying then crushed in mortar pastel [10]. The preparation of  $Y_2O_2S$ :RE phosphor follows the chemical reaction:

 $Y_2O_3 + RE_2O_3 + Flux \left(S + Na_2CO_3 + K_3PO_4\right) \rightarrow Y_2O_2S:RE$ 

## + flux residues $(Na_2S_x + Na_2SO_4)$ + gaseous products

The phase purity and crystallinity of prepared host lattice  $Y_2O_2S$  was characterized by X-ray powder diffraction method using Cu K $\alpha$  radiation. The particle size and morphological behaviour of synthesized powder were analyzed by scanning electron microscope (SEM). Brucker Fourier transform infrared spectrometer was used to record infrared spectra. The spectroscopic properties of synthesized phosphors were measured at room temperature by using Shimadzu make RF5301PC spectro-fluorometer. At measurement time slit width of the instrument was fixed at 1.5nm. The co-ordinations in the xy-chromaticity diagram are directly calculated from the fluorescent spectra (CIE 1931) [11].

#### **III. RESULTS AND DISCUSSION**

#### A. X-ray Diffraction (XRD)

Figure 1 shows XRD pattern of synthesized  $Y_2O_2S$  phosphor. It is found that diffraction peaks of the phosphor are in well accordance with the standard ICDD File No. 24–1424. The XRD diffraction pattern of prepared  $Y_2O_2S$  host did not indicate presence of any constituent and other likely phases. All the diffraction peaks were evidence of the high purity and crystallinity of  $Y_2O_2S$ .

The sample was found to be non-hygroscopic, stable and whitish in nature. The diffraction pattern acknowledges that the  $Y_2O_2S$  phosphor was prepared without any impurity and it confirms  $Y_2O_2S$  phosphor were successfully prepared in the homogeneous form.



Figure 1: XRD pattern of pure Y<sub>2</sub>O<sub>2</sub>S.

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#### **B.** Surface Morphology

Figure 2 shows the SEM micrograph of  $Y_2O_2S$  powders. During annealing at high temperature, the crystallites come closer and form an agglomerated structure which is consist of small sintered clusters. The morphology of the  $Y_2O_2S$ powders found to be irregular in shape and the grain size is significantly varying. The approximate particle size ranges from 1 to 5 µm. The particle size strongly depends on the type of synthesis method and synthesis conditions. Phosphors synthesized by solid state method generally have particle size within this range.



Figure 2: SEM image of synthesized Y<sub>2</sub>O<sub>2</sub>S.

#### C. Crystal Structure

Schematic crystal structure of  $Y_2O_2S$  is shown in figure 3. The  $Y_2O_2S$  lattice has trigonal crystal symmetry with  $P3^-m1$  space group. The  $Y_2O_2S$  lattice found to be *A*-type rare-earth oxide structure, and analyzed that the one of the three oxygen sites is occupied by a sulphur atom. Figure clearly illustrate that the every metal ions bonded with four oxygen atoms and three sulphur atoms. In presented crystal structure investigation found to form a seven coordinated geometry with the oxygen and the metal in the same plane. The  $Y_2O_2S$  crystal structure shows Ln and oxygen atoms have the same site symmetry of  $C_{3v}$  and the S site has symmetry of  $D_{3d}[10]$ .



Figure 3: Schematic crystal structure of Y<sub>2</sub>O<sub>2</sub>S.

#### **D. FT-IR Analysis**

FT-IR is the characterization tool which gives information about the vibrations of bonds present in prepared host. FT-IR spectroscopy gives the information about molecules frequencies, their vibrations and stretching corresponding to distinct energy levels.

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An obtained spectrogram provides valuable knowledge about type of bonding present in the sample, the strength of the bonding and bonding percentage present in the sample. Fourier transform infrared spectrometer was used for measurement of FT-IR spectra of the pure  $Y_2O_2S$  phosphor. The spectrum was measured in the range of 500 to 4000 cm-1. Figure 4 shows the FTIR spectrum of  $Y_2O_2S$ .



Figure 4: FT-IR spectrum of Y<sub>2</sub>O<sub>2</sub>S phosphor.

In this no absorption deep was observed around 3500 cm-1 which suggest complete removal of O-H molecules from the sample after annealing. The absorption deep of cubic phase of  $Y_2O_2S$  appears at 561 cm-1. Strong deeps at 1540 and 1072 cm-1 were due to Y-O symmetric stretching mode. The stretching modes due Y-S and S-O bonding were not witnessed in the FTIR spectrum [10, 11].

## E. PL Emission Of $RE^{3+}$ In Y<sub>2</sub>O<sub>2</sub>S ( $RE^{3+} = Dy^{3+}$ , $Eu^{3+}$ and $Tb^{3+}$ )

Photoluminescence studies of  $RE^{3+}$  ( $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  or  $Tb^{3+}$ ) doped Y<sub>2</sub>O<sub>2</sub>S oxy-sulphides phosphors are investigated here. This work gives the optimum quantity of activator required for getting maximum lighting efficiency and light emission of dopant in particular region.

## i) PL Emission Of Dy3+ In Y2O2S

The excitation spectra of  $Y_2O_2S:2mol\%Dy^{3^+}$  phosphor was recorded under 574 nm emission wavelengths as shown in figure 5. The excitation spectrum consists of several peaks varying from 220 nm to 450 nm. The excitation peaks in the range 275 to 450nm, which are ascribed due to f-f transition of the Dy<sup>3+</sup> ion. The prominent excitation peaks recorded at 351 nm, 368 nm and 388 nm, which are due observed due to the  ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$ ,  ${}^{6}H_{15/2} \rightarrow {}^{6}P_{5/2}$ , and  ${}^{6}H_{15/2} \rightarrow {}^{6}I_{13/2}$  transitions Dy<sup>3+</sup> ion, respectively[12,13].

The excitation spectra for  $Y_2O_2S:Dy^{3+}$  phosphor has three prominent peaks in the near UV region at 351nm, 368nm and 388nm. The PL emission of  $Y_2O_2S:Dy^{3+}$  phosphor for all these excitations is shown in figure 6. The excitation peak shows highest intensity at 351nm compared to other peaks. The excitation spectra shows highest intensity at 351nm wavelength but 388nm excitation peak is more promising for solid state lighting because it is well matched with UV excitation range [14].



Figure 5: Excitation spectrum of Y<sub>2</sub>O<sub>2</sub>S:Dy<sup>3+</sup> phosphor.



Figure 6: Emission spectra of Y<sub>2</sub>O<sub>2</sub>S:Dy<sup>3+</sup> phosphor at 2 mole% for various excitation wavelengths.

Under 388nm excitation, the emission spectrum was recorded for  $Y_2O_2S:Dy^{3+}$ , phosphors as shown in the figure 7. The PL emission spectrum shows two prominent emission peaks at blue (487nm) and yellow (574nm) regions, which are ascribed due to the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  electronic transitions of  $Dy^{3+}$  ions, respectively [15]. According to available literature,  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  (487nm) and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  (574nm) transition occurred due to magnetic dipole transition and hypertensive (forced dipole) transition, respectively.

The optical properties of the material are often affected by the structure of the matrix and synthesis technique [16]. According to literature it is well known that  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (magnetic dipole transition) occurred because of insensitivity to the crystal field around the Dy<sup>3+</sup> ions and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (hyper sensitive transition) occurred because of strongly influenced by the outside environment surrounding of Dy<sup>3+</sup>. When the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  transition is stronger than the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transition then Dy<sup>3+</sup> is located at a low symmetry site (without inversion symmetry) [10, 17]. Thus, from emission spectra shown in figure 7, it can be concluded that Dy<sup>3+</sup> has occupied low symmetry site that too without inversion symmetry.

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Figure 7: Emission spectra of Y<sub>2</sub>O<sub>2</sub>S:Dy<sup>3+</sup> phosphor.

Photoluminescence properties of a phosphor is fully depends on the concentration of dopants [18]. It is well known that the pattern of emission peak does not change with doping of rare earth ions, only the emission intensity vary with increasing the concentration of rare earth ions [19]. Fig. 7 shows that when concentration of Dy<sup>3+</sup> increases then PL emission intensity increased up to 2mol%. PL emission spectrum shows maximum value of intensity at 2mole % and then decreases with an increase of dopant concentration due to concentration quenching. This happens when the concentration of  $Dy^{3+}$  increases continuously which increases the interaction among  $Dy^{3+}$  ions. The interaction between  $Dy^{3+}$  ions is such that they transfer energy to nearest  $Dy^{3+}$  ion through non-radiative transfer. With increase in Dy concentration the probability of non-radiative energy transfer increases which leads to further decrease in emission intensity. In the process of cross relaxation among two dopants, the excitation energy from an ion decaying from an excited state stimulates a nearby ion from the ground state to the metastable level. In case of Dy<sup>3+</sup> the energy of the ( ${}^{4}F_{9/2} \rightarrow$  ${}^{6}\text{H}_{11/2} + {}^{6}\text{H}_{9/2}$ ) transition matches that of the  $({}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{F}_{11/2} +$  ${}^{6}\text{H}_{9/2}$ ) transition. In the present work, concentration quenching occurred due to cross relaxation process i.e. energy transfers from one  $Dy^{3+}$  to another neighboring  $Dy^{3+}$  [20]. The 300 to 400 nm is Hg free excitation and it is very important for solid state lighting phosphors. All these outcomes shows our synthesized Y<sub>2</sub>O<sub>2</sub>S:Dy<sup>3+</sup> phosphors have potential application in field of solid state lighting devices as well as in white LED.

## ii) PL Emission Of Eu<sup>3+</sup> In Y<sub>2</sub>O<sub>2</sub>S

The excitation spectra of  $Y_2O_2S:Eu^{3+}$  phosphor monitored at 594 nm emission wavelength is shown in figure 8. The excitation spectra observed in the range of 200nm to 500nm. In this range we have observed charge transfer band at 255nm and several narrow excitation peaks in the range of 350nm and 400nm are due to the typical f-f transition of  $Eu^{3+}$ . The strongest excitation peaks observed at 396 nm and 468nm, which are ascribed due to  ${}^7F_0 \rightarrow {}^5L_6$  and  ${}^7F_0 \rightarrow {}^5D_2$  transitions of  $Eu^{3+}$  ions, respectively [21]. Besides this, due to the charge transfer band ( $Eu^{3+} \rightarrow O^{2-}$ ) broad excitation peak at 255 nm is also observed. Figure 9 and 10 show the emission spectra of  $Y_2O_2S:Eu^{3+}$  phosphors excited by 396 nm and 468 nm wavelengths, respectively. The  $Y_2O_2S:Eu^{3+}$  phosphor when excited by  $\lambda_{ex}$ =396 nm and  $\lambda_{ex}$ =468 nm shows prominent emission peaks at 594 nm, 620 nm 589 nm and 613 nm respectively. The characteristic emission peaks in region of  $Eu^{3+}$ . A strong red emission of  $Eu^{3+}$  in the region 610 to 620 nm was due to the  ${}^5D_0 \rightarrow {}^7F_2$  transition and emission in the region 589 to 596 nm was due to  ${}^5D_0 \rightarrow {}^7F_1$  transition. It is observed that at  $\lambda_{ex}$ =396, 594 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 620 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ) whereas at  $\lambda_{ex}$ =468 nm, 613 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ) emission is dominant compared to 589 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is dominant compared to 520 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ) emission is do



Figure 8: Excitation spectrum of Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> phosphor.



Figure 9: Emission spectra of  $Y_2O_2S:Eu^{3+}$  phosphor at  $\lambda ex=396$  nm.

580 to 640 nm corresponds to intra 4f shell transitions of  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J=0, 1, 2, 3, 4) of The emission spectra of Eu<sup>3+</sup> particle is marginally impacted by encompassing ligands of the host material because the transition of Eu<sup>3+</sup> include just a redistribution of electrons inside the internal 4f subshells. A less transitions are delicate to the environment and turn out to be increasingly extreme and such advances are known as hypersensitive transitions. For Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> phosphor the emission in the range 610 - 620 nm is because of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is electric dipole transition and considered as hypersensitive transition.



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In the present work, prepared material gives bright emission because its transition obey the selection rule  $\Delta J=2$ . The orange emission observed in the range of 590 to 596 nm is because of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, with the selection rule  $\Delta J=1$  is a magnetic-dipole transition. According to literature, inversion symmetry occurred in  $Eu^{3+}$  when  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is dominant. On the contrary, if Eu<sup>3+</sup> does not occupy the inversion symmetry site, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is dominant. The luminescence property of material depends on the concentration of the dopants. In the present study, when concentration of Eu<sup>3+</sup> ions increased then the distance between Eu<sup>3+</sup> ions becomes less and this results in the migration of excitation energy among Eu<sup>3+</sup> ions leading to quenching of the emission. The maximum emission intensity is observed at 5mol% of Eu<sup>3+</sup> concentration and decreases with further increase in concentration of  $Eu^{3+}$  ions [10].



Figure 10: Emission spectra of  $Y_2O_2S:Eu^{3+}$ phosphor at  $\lambda ex=468$  nm.

## iii) PL Emission Of Tb<sup>3+</sup> In Y<sub>2</sub>O<sub>2</sub>S

Figure 11 show the excitation spectra of  $Y_2O_2S:Tb^{3+}$ phosphor in the 220–500 nm range, monitored at 545 nm emission wavelength. The overall excitation spectrum of  $Tb^{3+}$ can be divided into two parts. First part is in the wavelength range from 220-320 nm comprising of  $4f^8 \rightarrow 4f^75d^1$  transitions and other part of the excitation spectrum in the wavelength range 320–500 nm which is due to  $4f^8 \rightarrow 4f^8$  transitions of the  $Tb^{3+}$  ions [24].



Figure 11: Excitation spectrum of  $Y_2O_2S:Tb^{3+}$  phosphor. There are several excitation peaks in the 320 to 400 nm region corresponding to transitions between  ${}^7F_6$  and the

Retrieval Number: D1412029420 /2020©BEIESP DOI: 10.35940/ijitee.D1412.029420 Journal Website: <u>www.ijitee.org</u> various excited states belonging to the 4f<sup>8</sup> electronic configuration of Tb<sup>3+</sup> ions. The excitation peaks at 352 nm ( ${}^{7}F_{6}\rightarrow{}^{5}L_{9}$ ) and 380 nm ( ${}^{7}F_{6}\rightarrow{}^{5}G_{6}$ ) were due to forbidden 4f-4f transition of Tb<sup>3+</sup> ions. Though there were significant absorption at 260 nm for Y<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup> we have chosen  $\lambda_{ex}$ =305 nm as excitation for Y<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup>, as it is more suitable for near UV excitation in white LED and therefore, Y<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup> has potential to be used as near-UV LED phosphor. The emission spectra of Y<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup> is determined by the transitions of electrons from an upper ( ${}^{5}D_{3}$ ) and a lower ( ${}^{5}D_{4}$ ) excited level to the multiple levels  ${}^{7}F_{J}$  (J = 0, 1, 2, 3, 4, 5, 6) of the 4f<sup>8</sup> configuration. The emission of terbium doped phosphor is mainly in the green region due to the  ${}^{5}D_{4}\rightarrow{}^{7}F_{J}$  transitions and the blue emission contributes to the emission from the higher level transitions  ${}^{5}D_{3}\rightarrow{}^{7}F_{J}$  [25].

Figure 12 shows the emission spectra of  $Y_2O_2S:Tb^{3+}$  phosphors under the excitation wavelength of 305 nm. The emission peaks were found in the region 485-495, 545 and 580-600 nm, which were assigned to the  ${}^5D_4 \rightarrow {}^7F_J$  (J = 6, 5, 4) transition of Tb<sup>3+</sup> ions.



Figure 12: Emission spectra of  $Y_2O_2S$ :Tb<sup>3+</sup>phosphor at  $\lambda ex=305$  nm.

As expected, the spectral shift was not observed because the 4f shell of  $Tb^{3+}$  was well shielded by 5s and 5p shells. Moreover, the emission from  ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$  level are quenched by the cross relaxation  $[Tb^3({}^5D_3) + Tb^3({}^7F_6) \rightarrow Tb^3({}^5D_4) + Tb^3$  $({}^{7}F_{1})$ ]. The cross relaxation process produces the rapid population of the  ${}^{5}D_{4}$  level at the expense of  ${}^{5}D_{3}$ , resulting in a strong emission from the  ${}^{5}D_{4}$  to the  ${}^{7}F_{J}$  level [26–27]. Generally, the cross relaxation is observed at higher Tb<sup>3+</sup> concentration. The occurrence of PL emission quenching at higher concentration of Tb was witnessed, which is due to the cross relaxation. This is in good agreement with the results reported in literature. The luminescent mechanism of phosphor is due to competition between the optical activation of Tb<sup>3+</sup> ions which results in increase of PL intensity and the clustering of Tb<sup>3+</sup> causes concentration quenching. At lower concentration of  $Tb^{3+}$ , the first mechanism is dominant in the luminescence process and the PL intensity increases with the increase in concentration of Tb<sup>3+</sup> [28].

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Figure 12 also shows the relative PL intensities of 545 nm under 305nm excitation for  $Y_2O_2S:Tb^{3+}$  phosphors. Up to 2mol% concentration of  $Tb^{3+}$  ion the PL intensity of 545 nm emission peak increases with increase of  $Tb^{3+}$  ion concentration after that the PL intensity of 545 nm emissions decreases. As the concentration of  $Tb^{3+}$  exceed the critical concentration, distance between  $Tb^{3+}$  ions become shorter, which cause activator to form pairs and thus results in concentration quenching. The emission intensity reached its maximum value at about 2 mole% doping concentration in the  $Y_2O_2S:Tb^{3+}$  phosphor [24].

#### F. Chromatic Properties

The Commission International de l Eclairage (CIE) 1931 diagram of the prepared  $Y_2O_2S:RE^{3+}$  phosphor (Where  $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  or  $Tb^{3+}$ ) is shown in figure 13.



The chromatic co-ordinates (X, Y) are calculated using the color calculator radiant imaging software and are summarized Figure 13: Chromatic graph of  $Y_2O_2S$ : RE<sup>3+</sup> phosphor (RE<sup>3+</sup> = Dy<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup>).

 $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$  emission in table 1 given on page 10. The emitting color of the phosphor can be tuned in the respective color region either by changing the concentration of dopant or by changing the excitation wavelength [29, 30].

#### **IV. CONCLUSION**

In summary, we have successfully synthesized and investigated the luminescent properties of the  $Y_2O_2S:RE^{3+}(RE^{3+} = Dy^{3+}, Eu^{3+} \text{ or } Tb^{3+})$  phosphors. The use of flux reduces the reaction temperature and enhances the reaction rate, finally results in single phase Y<sub>2</sub>O<sub>2</sub>S compound. The emission color of the obtained phosphors can be modulated either by controlling the doping content of the rare earth ions or by fixing the doping content and varying the excitation wavelength. The developed  $Y_2O_2S:RE^{3+}(RE^{3+} =$  $Dy^{3+}$ ,  $Eu^{3+}$  or  $Tb^{3+}$ ) phosphor can be stimulated (excited) in n-UV domain which is most desired requirement for commercially producing white light emitting diodes. The synthesized phosphor emits bright color in the blue, yellow, green and red region. Hence, it has likely potential to be used in phosphor converted light emitting diodes as a primary color emitter in 3 band pc-LEDs or red spectrum enhancer in yellow phosphor converted white light emitting diodes and therefore results indicate that these phosphors may be a promising candidates for white LEDs.

Table I: The (X, Y) chromatic co-ordinates for  $Y_2O_2S$ :  $RE^{3+}$  phosphor ( $RE^{3+} = Dy^{3+}$ ,  $Eu^{3+}$  and  $Tb^{3+}$ ).

Name of sample	Excitation (nm)	Emission (nm)	(X,Y) Coordinates	Color region
$Y_2O_2S: Dy^{3+}$	388	487	(0.059, 0.235)	Blue
		574	(0.472, 0.527)	Yellow
$Y_2O_2S: Eu^{3+}$	396	594	(0.598, 0.402)	Orange
		620	(0.692, 0.308)	Red
$Y_2O_2S: Tb^{3+}$	305	485	(0.069, 0.201)	Blue
		545	(0.265, 0.724)	Green

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- 2. Nanomaterials for Green Energy (Publisher: Elsevier)
- 3. Spectroscopy of Lanthanide Doped Oxide Materials (Publisher: Elsevier)
- 4. Phosphate phosphors for solid state lighting (Publisher: Springer)
- 5. Phosphors for energy saving and conversion technology (Publisher:Taylor & Francis Group)
- 6. Phosphors: Synthesis and Applications (Publisher: Pan Stanford).

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