

# Effect of charge transfer band on luminescence properties of Yb doped Y<sub>2</sub>O<sub>3</sub> nanoparticles

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## Abstract

The photoluminescence properties of Yb doped Y<sub>2</sub>O<sub>3</sub> nanoparticles were investigated in visible region to resolve the origin of dissimilar fluorescence peaks at different excited wavelengths and to explore possible use of Yb: Y<sub>2</sub>O<sub>3</sub> for white light emission, excited by available near UV LED. The peak observed at 370 nm in photoluminescence excitation spectrum is due to expected transition of electrons from <sup>2</sup>F<sub>7/2</sub> to charge transfer band (CTB) associated with non-centrosymmetric C<sub>2</sub> centers however, the excitation peak at 335 nm is due to transition of electrons from <sup>2</sup>F<sub>7/2</sub> to the CTB associated with distorted centrosymmetric C<sub>3i</sub> centers. The Yb doping in nano Y<sub>2</sub>O<sub>3</sub> not only modify the CTB but also helps in transition of electron from these CTBs to ground <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> levels of Yb. Strong broad emission peak is observed at 503 nm which is assigned to transition from distorted CTB (C<sub>3i</sub>) to <sup>2</sup>F<sub>5/2</sub> energy levels. The findings are important because broad emission (from ~400 to ~650 nm) at 335 nm excitation (available AlGaIn LED wavelength) due to C<sub>2</sub> and C<sub>3i</sub> centers in Yb: Y<sub>2</sub>O<sub>3</sub> may be used for white light emission applications. Copyright © 2017 VBRI Press.

**Keywords:** Photoluminescence, nanophosphor, Yb: Y<sub>2</sub>O<sub>3</sub>, charge transfer band, TEM.

## Introduction

Charge transfer bands (CTB) are observed in several rare-earth (RE) oxide compounds and these are formed due to the transfer of electronic charge from the highest occupied orbital of the valence band in the host lattice, i. e. from the 2p orbitals of oxygen in the case of oxygen based hosts, to RE ions [1, 2]. The CTB transitions are usually observed as strong and broad absorption bands in the UV-visible region as they are not restricted by any selection rules [1]. The CTBs in Eu<sup>2+</sup> doped Sr<sub>2</sub>SiO<sub>4</sub> and Eu<sup>2+</sup> doped Sr<sub>3</sub>SiO<sub>5</sub> phosphors play an important role in photoluminescence (PL) process for wide range emission in visible region, make these materials suitable for white light emitting diodes [3-5]. The part of CTB absorption energy due to Eu<sup>2+</sup> in Sr (I) site transfer to Tb<sup>3+</sup> ion at Sr(II) site and consequently broad luminescence from both Eu<sup>2+</sup> and Tb<sup>3+</sup> is observed in Eu<sup>2+</sup> and Tb<sup>3+</sup> doped (Sr,Ba)<sub>2</sub>SiO<sub>4</sub> [6]. The broad emission in Sr<sub>2</sub>SiO<sub>4</sub>: Eu<sup>2+</sup> is associated with ligand (oxygen) distribution around two types of Sr sites (nine coordination Sr(I) site and ten coordination Sr(II) site). Similarly, the rare earth doped Y<sub>2</sub>O<sub>3</sub> is prone to CTB formation due to oxygen ligand environment around Y<sup>3+</sup> ions. The Y<sub>2</sub>O<sub>3</sub> as a promising optical material has excellent physical and chemical properties, such as high melting point (2430 °C), broad range of transparency (~ 0.2 - 8 μm) and high corrosion

resistance. The Y<sub>2</sub>O<sub>3</sub> has a cubic crystal structure with space group Ia3 and density of 5.04 g/cm<sup>3</sup> with refractive index ~1.9 at 1 μm wavelength [7, 8]. Due to its high effective atomic number and high density, i.e., 35 and 4.56 g cm<sup>-3</sup>, respectively, Y<sub>2</sub>O<sub>3</sub> can be a more effective scintillator than Yttrium aluminum garnet (YAG) [9].

In cubic Y<sub>2</sub>O<sub>3</sub> the Y<sup>3+</sup> ion occupies 24 noncentrosymmetric (C<sub>2</sub>) and 8 centrosymmetric (C<sub>3i</sub>) sites in an elementary cell. The luminescence of the Y<sub>2</sub>O<sub>3</sub> is predominantly connected with noncentrosymmetric (C<sub>2</sub>) site. Since C<sub>3i</sub> site has an inversion centre, according to the selection rules electric dipole transitions are not allowed for ions occupying this site, because these sites cannot provide odd terms in the crystal field [10]. Y<sub>2</sub>O<sub>3</sub> crystallizes in monoclinic phase (space group C2/m) and possesses three crystallographically distinct cation sites with seven-fold coordination, each having point group symmetry C<sub>s</sub> [11]. However, Y<sub>2</sub>O<sub>3</sub> crystallizes in cubic phase in majority of synthesis method. The C<sub>2</sub> and C<sub>3i</sub> cation sites associated with two different centers of distorted octahedrons which changes the electron distribution between Y<sup>3+</sup> and oxygen ligands giving rise to two types of CTBs. Y<sub>2</sub>O<sub>3</sub> is used as host for many rare earth dopants like Eu<sup>3+</sup>, Tb<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Er<sup>3+</sup>, Nd<sup>3+</sup> and Sm<sup>3+</sup> for applications in illumination, colour display, biomedical imaging and heavy ion dosimetry [12-16]. The co-doping of rare earth ions in Y<sub>2</sub>O<sub>3</sub> (like Yb & Er and

Tm & Yb and so on) is used for upconversion phosphor application, fluorescence imaging etc. [17, 18]. The Er doped  $Y_2O_3$  nano crystalline powder also shows upconversion green emission following excitation with low energy near infrared radiation ( $\lambda=980$  nm) [19, 20]. The Yb doped  $Y_2O_3$  (Yb:  $Y_2O_3$ ) is a well-studied material for IR laser application (absorption at 940 and 976 nm; lasing action at 1030 and 1070 nm) [21, 22]. Above studies on rare earth doped  $Y_2O_3$  shows the emission in visible region which is due to characteristic electronic transition of dopant elements. However, very few reports are available on PL studies of Yb:  $Y_2O_3$  in visible region because of low integrated emission intensity due to transition from CTB to ground level. Two broad emission bands are observed at 368 and 533 nm in Yb:  $Y_2O_3$  for excitation wavelength 215 nm at 10K which are associated with  $CT-^2F_{7/2}$  and  $CT-^2F_{5/2}$  transitions but there is no differentiation between the CTBs associated with  $C_2$  and  $C_{3i}$  centers [23]. The electronic transition arises due to  $Yb^{3+}$  in different host materials are extensively studied by L. V. Pieterse [23] and the emission due to  $Yb^{2+}$  is extensively reported by Dorenbos [2]. The  $Yb^{3+}$  ion in  $Y_2O_3$  occupies any of the two sites i. e. either  $C_2$  or  $C_{3i}$  sites and hence modifies the electronic distribution in  $Y_2O_3$  which in turn changes the energies of CTBs associated with  $C_2$  and  $C_{3i}$  [24]. A clear picture on CTBs associated with  $C_2$  and  $C_{3i}$  centers is still matter of investigation.

In the present work, the luminescence properties of nano Yb:  $Y_2O_3$  was studied at different doping percentage of Yb. The dopant Yb is chosen because  $Yb^{3+}$  ions possess high quantum efficiency, relatively long fluorescence lifetime, wide absorption and emission bands and these ions were already demonstrated as a suitable active candidate for high intensity fluorescence [25-27]. Moreover, the effective ionic radius of  $Yb^{3+}$  is very close to  $Y^{3+}$  ( $Yb^{3+}$  (0.087 nm),  $Y^{3+}$  (0.09 nm)) which replace host lattice cation without changing crystal structure [28]. The aim of this work is to study the change in charge transfer band related luminescence in Yb doped  $Y_2O_3$  due to near UV excitation (available LED). It is found that the excitation and emission wavelengths of nano Yb:  $Y_2O_3$  are correlated using CTB associated with  $C_{3i}$  and  $C_2$  sites. The energy level diagram of nano Yb:  $Y_2O_3$  for visible emission is presented to explain broad emission in visible region. The luminescence spectra of nano and bulk Yb:  $Y_2O_3$  particles were compared with each other and also with bulk  $Y_2O_3$ . The possible use of Yb:  $Y_2O_3$  nanoparticles have also been emphasized because of its broad emission in visible range.

## Experimental

### Materials synthesis

The Yb:  $Y_2O_3$  nanoparticles were prepared by co-precipitation method [29]. High purity  $Y_2O_3$  and  $Yb_2O_3$  (Alfa Aesar make, 99.999% purity, product no: 11182) were used as starting materials. The steps involved in preparation of Yb:  $Y_2O_3$  nanopowders from its salts are: (1) preparation of the Yb doped yttrium nitrate

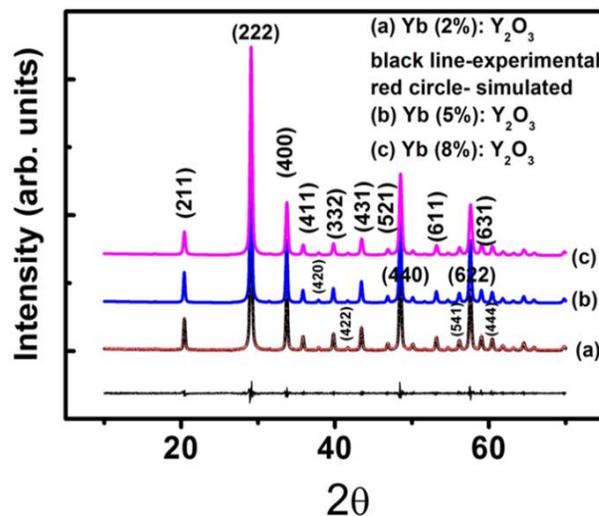
(mother solution), (2) addition of  $NH_4OH$  into mother solution till formation of  $Y(OH)_3$  precipitate, (3) filtration and washing of precipitate with water, (4) drying and (5) calcinations of precursor powder. The dried Yb doped  $Y(OH)_3$  precursor was calcined at 900 °C to get nano powders of Yb:  $Y_2O_3$ . Using above procedure, Yb:  $Y_2O_3$  nano powders were synthesized with 2, 5 and 8 mole percentage of Yb.

### Characterization

The phase and crystallite size of powders calcined at 900 °C were determined using X-ray diffractometer (Rigaku X-ray diffractometer with a Ni filtered  $Cu K\alpha$  radiation source and wavelength  $\lambda$  of the source being 1.54 Å). The size and morphology of nanoparticles were determined using transmission microscopy (TEM). Nanoparticles dissolved in chloroform are placed on the grid drop wise and the excess liquid is allowed to evaporate. The grids are examined in Philips CM200 electron microscope equipped with a tungsten cathode and operated at 200 kV. The photoluminescence (PL) measurement of nanoparticles was carried out at different absorption wavelength using PL spectrometer (FLS920-s, Edinburgh Instruments Ltd.) at room temperature. The background excitation source used for this purpose was a 450 W ozone-free Xenon arc lamp with continuous output. A calibrated photodiode and a R928P photomultiplier are used as excitation and emission detectors in visible range.

## Results and discussion

The X-ray diffraction patterns of (2-8 mol %)Yb:  $Y_2O_3$  nano powders are shown in Fig. 1.



**Fig. 1.** X-ray diffraction pattern of the Yb:  $Y_2O_3$  nanoparticles; (a) 2%Yb, (b) 5% Yb and (c) 8% Yb. In figure (a) the black line represents experimental, the red circle represents simulated and the difference line is shown below XRD patterns.

The XRD patterns were simulated and the calculated structural parameters are listed in **Table 1**. The structure of Yb:  $Y_2O_3$  samples were found to be cubic ( $Ia-3$ ) with

slight change in their lattice parameter with no phase change compared to  $Y_2O_3$  [30].

The lattice constants and the lattice volume were decreased with subsequent Yb doping due to smaller ionic radius of  $Yb^{3+}$  (0.087 nm) compared to ionic radius of  $Y^{3+}$  (0.09 nm) [28]. The lattice parameters of Yb doped  $Y_2O_3$  nanopowders were also calculated using Vegard's law (by using lattice parameters of  $Y_2O_3 = 10.601$ ; JCPDS No. 41-1105 and  $Yb_2O_3 = 10.43$ ; JCPDS No.78-1690, 82-2417). The calculated lattice parameters for 2, 5 and 8 percentage Yb:  $Y_2O_3$  are 10.597, 10.592 and 10.587 Å respectively which are well matched with experimental results. Debye Scherrer formula was utilized to determine the crystallite size (by subtracting instrumental broadening from FWHM of peaks) of nano Yb:  $Y_2O_3$ . The average size of crystallites is found to be 45-70 nm (Table 1) and it is found that the crystallite size decreases with increasing Yb content.

The TEM bright field images of nanocrystalline (2-8 mol%) Yb:  $Y_2O_3$  are shown in Fig. 2. The average particle size obtained from TEM micrographs for 2, 5 and 8mol% Yb:  $Y_2O_3$  were 65-70 nm, 60-65 nm and 55-45 nm respectively. Particle size was found to decrease with increasing Yb mole percentage in  $Y_2O_3$  and the morphology of the particles was almost remains same for all Yb:  $Y_2O_3$  nanopowders.

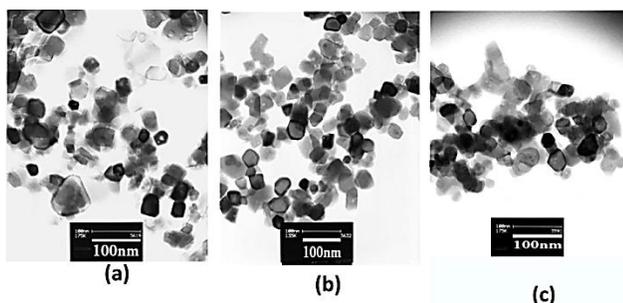


Fig. 2. Transmission electron microscopic images of Yb:  $Y_2O_3$  nano powders; (a) 2% Yb, (b) 5% Yb and (c) 8% Yb.

The excitation and emission spectra for 2, 5 and 8% Yb:  $Y_2O_3$  nano powders are shown in Fig. 3, 4 and 5 respectively. The excitation spectra for (2%) Yb:  $Y_2O_3$  nano powder was recorded by keeping detector at 420 nm and two broad excitation peaks were observed at 335 nm and 370 nm (Fig. 3(a)).

Table 1. Structural parameters and crystallite size for nano Yb (2, 5 and 8%):  $Y_2O_3$ .

Materials name	Lattice Parameters			Space group	Volume of Unit Cell(A <sup>3</sup> )	Crystallite size			
	a	b	c				α	β	γ
Yb: $Y_2O_3$ (2%)	10.595	10.595	10.595	90	90	90	Ia-3	1.1894*10 <sup>3</sup>	69.966
Yb: $Y_2O_3$ (5%)	10.592	10.592	10.592	90	90	90	Ia-3	1.1884*10 <sup>3</sup>	67.370
Yb: $Y_2O_3$ (8%)	10.588	10.588	10.588	90	90	90	Ia-3	1.1870*10 <sup>3</sup>	46.745

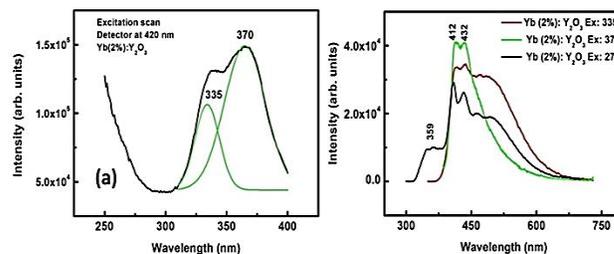


Fig. 3. Photoluminescent spectra of Yb(2%):  $Y_2O_3$ ; (a) excitation spectra keeping detector at 420 nm and (b) emission spectra at excitation 335 nm (Red), 370 nm (green), 270 nm (black) and 420 nm (blue).

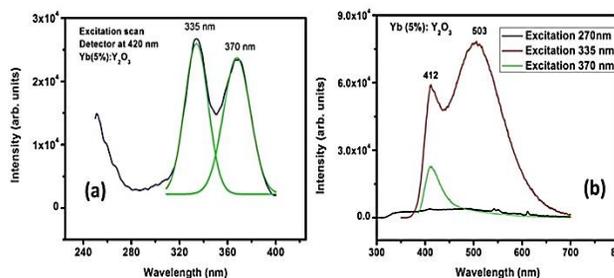


Fig. 4. Photoluminescent spectra of Yb(5%):  $Y_2O_3$ ; (a) excitation spectra keeping detector at 420 nm and (b) emission spectra at excitation 335 nm (Red), 370 nm (green), 270 nm (black).

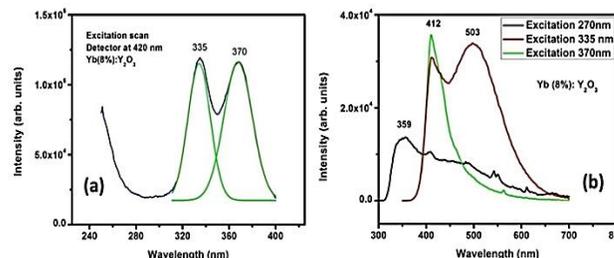


Fig. 5. Photoluminescent spectra of Yb(8%):  $Y_2O_3$ ; (a) excitation spectra keeping detector at 420 nm and (b) emission spectra at excitation 335 nm (Red), 370 nm (green), 270 nm (black).

The peak at 370 nm is more intense compared to peak 335 nm for 2%Yb:  $Y_2O_3$ ; however, intensity of the peak at 335 nm is more as compared to that at 370 nm ( Fig. 4a) for 5%Yb:  $Y_2O_3$ . We have observed two excitation bands at 335 and 370 nm for 8% Yb:  $Y_2O_3$  similar to 5%Yb:  $Y_2O_3$  except the decrease in intensity of peak at 335 nm (Fig. 5a). It confirms the existence of two strong

bands in between valence and conduction band of Yb: Y<sub>2</sub>O<sub>3</sub> from which transition of electron takes place at particular excitations i.e. 370 and 335 nm. In order to find the origin of these transitions in nano Yb: Y<sub>2</sub>O<sub>3</sub> powder, the PL studies of pure Y<sub>2</sub>O<sub>3</sub> (bulk powder) and Yb: Y<sub>2</sub>O<sub>3</sub> (transparent ceramic pellet) were also carried out and are shown in Fig. 6 and Fig. 7 respectively. We observed only one broad peak (maximum at 324 nm) in the excitation spectra of bulk Y<sub>2</sub>O<sub>3</sub> (Fig. 6(a)) while for bulk Yb: Y<sub>2</sub>O<sub>3</sub> two excitation peaks at 335 and 370 nm (Fig. 7(a)) similar to that of nano Yb: Y<sub>2</sub>O<sub>3</sub> powders. Therefore it is confirmed that the presence of 335 nm and 370 nm peaks in the excitation spectra of bulk and nano Yb: Y<sub>2</sub>O<sub>3</sub> is due to Yb<sup>3+</sup> dopant.

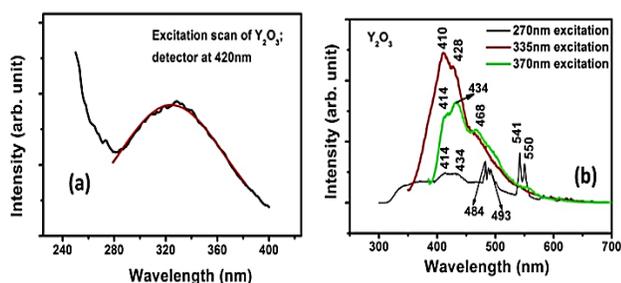


Fig. 6. Photoluminescent spectra of Y<sub>2</sub>O<sub>3</sub> bulk powder (a) excitation spectra keeping detector at 420 nm and (b) emission spectra at excitation 335 nm (Red), 370 nm (green), 270 nm (black).

Fig. 3(b) shows the emission spectra of 2% Yb: Y<sub>2</sub>O<sub>3</sub> excited at 270, 335 and 370 nm. Broad emission bands centered at ~359 nm, ~400 nm and ~503 nm were observed in emission spectrum of 2% Yb: Y<sub>2</sub>O<sub>3</sub> for 270 nm excitation. The broad emission peak at ~503 nm is less intense compared to the peak at ~400 nm. The broad peak at ~400 nm splits into two sub peaks centered at 412 nm and 432 nm. When 2% Yb: Y<sub>2</sub>O<sub>3</sub> nano powders are excited at 335 nm, the PL intensity of broad emission peaks i.e. at ~400 nm and ~503 nm was increased as compared to 270 nm excitation. The emission spectra of 5% Yb: Y<sub>2</sub>O<sub>3</sub> excited at different wavelengths is shown in Fig. 4(b).

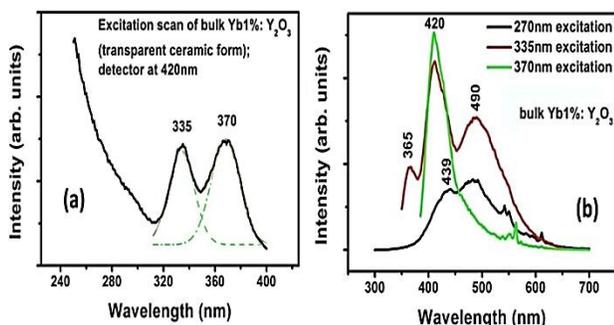


Fig. 7. Photoluminescent spectra of Yb(1%): Y<sub>2</sub>O<sub>3</sub> bulk transparent ceramic (a) excitation spectra keeping detector at 420 nm and (b) emission spectra at excitation 335 nm (Red), 370 nm (green), 270 nm (black).

A broad emission band in the range from 335 nm to 600 nm was observed with less PL intensity (as compared to

that of 2% Yb: Y<sub>2</sub>O<sub>3</sub>) for 270 nm excitation. The emission spectrum consists of two broad bands centered at ~412 and ~503 nm and extended in a range between ~390 nm to 600 nm for 335 nm excitation. The energy gap between two bands amounts to ~4500 cm<sup>-1</sup> which is very less as compared to the energy difference between <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> of Yb<sup>3+</sup>. The stoke shifts for ~412 and ~503 bands are 5460 and 9976 cm<sup>-1</sup> respectively. The broad emission peak at ~412 nm appears for all excitation wave lengths; however, the broad peak at ~503 nm is absent for 370 nm excitation. Fig. 5(b) shows emission spectra of 8% Yb: Y<sub>2</sub>O<sub>3</sub> at excitation wave lengths 270 nm, 335 nm and 370 nm.

The spectrum is similar to that of 5% Yb: Y<sub>2</sub>O<sub>3</sub> except the decrease in integrated emission peak intensity. The decrease in PL intensity for 8% Yb: Y<sub>2</sub>O<sub>3</sub> compared to 5% Yb: Y<sub>2</sub>O<sub>3</sub> may be explained on the basis of creation of more defect states due to smaller ionic radius of Yb which leads to decrease in the lattice parameters. Since more defect states are created for 8% Yb: Y<sub>2</sub>O<sub>3</sub> which may lead to high non-radiative relaxation [31]; hence decrease in PL intensity as compared to 5% Yb: Y<sub>2</sub>O<sub>3</sub>. It is also reported that the decrease in crystallite size reduces the PL intensity in rare earth doped Y<sub>2</sub>O<sub>3</sub> [32]. The crystallites in 8% Yb: Y<sub>2</sub>O<sub>3</sub> are very small as compared to that of 5% Yb: Y<sub>2</sub>O<sub>3</sub>. This may be one of the cause of decrease in PL intensity. In addition to broad peaks, very small peaks at 483, 488, 493, 541, 555 and 612 nm are present in PL spectra of Yb: Y<sub>2</sub>O<sub>3</sub> for 270 nm excitation. Small intensity peaks observed at 483, 488, 493 and 612 nm are attributed to the presence of Yb in Y<sub>2</sub>O<sub>3</sub> [33].

The emission spectrum of bulk Y<sub>2</sub>O<sub>3</sub> and Yb: Y<sub>2</sub>O<sub>3</sub> are shown in Fig. 6(b) and 7(b) respectively. In bulk Y<sub>2</sub>O<sub>3</sub> we observed two broad emission peaks at ~410 nm and ~468 nm for both 335 and 370 nm excitations. In bulk Yb: Y<sub>2</sub>O<sub>3</sub> two broad peaks at ~420 nm and ~490 nm was also observed for 335 nm excitation; however, one broad emission peak at 420 nm was observed for 370 nm excitation. The presence of high intense broad peak at ~ (410 – 440 nm) in all the samples with or without Yb doping and in bulk as well as in nano form of Yb: Y<sub>2</sub>O<sub>3</sub> confirms that this band is associated with stable CTB due to non centrosymmetric C<sub>2</sub> sites. The peak position of this band is slightly changed due to Yb doping in Y<sub>2</sub>O<sub>3</sub> as compared to pure Y<sub>2</sub>O<sub>3</sub>.

The broad emission peak observed at ~503 nm for nano Yb: Y<sub>2</sub>O<sub>3</sub> and emission peak at ~490 nm for bulk Yb: Y<sub>2</sub>O<sub>3</sub> may correspond to a CTB and its position depends on the doping percentage of Yb in Y<sub>2</sub>O<sub>3</sub>. Therefore, this CTB may be assigned to centrosymmetric C<sub>3i</sub> centres whose appearance depends on size of particles and percentage of dopant in the matrix. In Y<sub>2</sub>O<sub>3</sub> the intensity of peak due to CTB associated C<sub>3i</sub> centers is very less as compared to the intensity of peak associated with C<sub>2</sub> centers which may be attributed to very small distortion of centrosymmetry of C<sub>3i</sub> centres. In bulk Yb: Y<sub>2</sub>O<sub>3</sub> the emission peak associated with distorted C<sub>3i</sub> centres are shifted towards higher wave lengths as compared to Y<sub>2</sub>O<sub>3</sub> and the intensity becomes prominent due to creation of

more distortion at  $C_{3i}$  sites due to Yb doping. In case of nano Yb:  $Y_2O_3$  further distortions occur at  $C_{3i}$  sites to break centrosymmetry and more transitions are allowed so as to observe intense emission at  $\sim 503$  nm. The emission band at  $\sim 503$  nm mainly appears for 335 nm or small wave length excitation made it clear that the CTB associated with  $C_{3i}$  centers must have higher energy compared to the CTB associated with  $C_2$  centers. From the above discussion, it is confirmed that two types of CTBs associated with  $C_2$  and  $C_{3i}$  symmetry centers of  $Y_2O_3$  are present in Yb:  $Y_2O_3$ . The position of CTB associated with  $C_{3i}$  depends on type of dopant, percentage of dopant and size of the particles etc. These two charge transfer states correspond to ligand interactions at two different  $Y^{3+}$  positions in nano  $Y_2O_3$  [16]. The separation between two CTBs is around  $2823\text{ cm}^{-1}$ .

Small intensity peaks are also observed in bulk  $Y_2O_3$  (as purchased micron size powder; Alfa Aesar; product no 11182) and bulk Yb:  $Y_2O_3$  at 483, 488, 493 and 612 nm for above band gap excitation i. e. 270 nm. These are attributed to the presence of Yb in the bulk material [34].

The characteristic peaks at 541 and 555 nm confirms the presence of Er impurity in the bulk  $Y_2O_3$ . Since nano powders of Yb:  $Y_2O_3$  are prepared using these  $Y_2O_3$  powders, small extra characteristic peaks of Er are also present in the PL spectra of Yb:  $Y_2O_3$ .

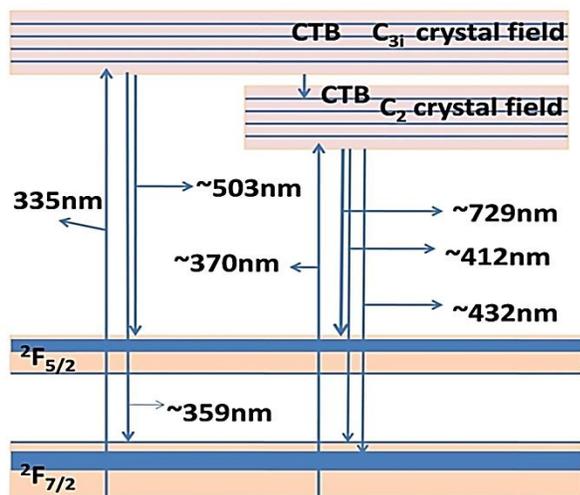


Fig. 8. Schematic energy level model of Yb:  $Y_2O_3$  nano phosphor.

The observed excitation and emission spectra has been summarized in the energy level diagram as shown in Fig. 8. The electronic transitions occur between CTB (associated with  $C_2$  and  $C_{3i}$  centres of host  $Y_2O_3$ ) and ground level ( $^2F_{5/2}$  and  $^2F_{7/2}$  created due to Yb doping). Here it worth to note that the 4f-4f transition and CTB-4f are two different types of transitions of the  $Yb^{3+}$  ions in crystals. The 4f orbital is shielded from the surrounding by the filled  $5s^2$  and  $5p^6$  orbital. Therefore, the influence of host lattice on the optical transitions within the  $4f^n$  configuration is small and 4f-4f transitions occur in IR

region, while the CTB absorption shows a broad band character and intense than that of 4f-4f transition and lies in visible region.

The excitation peak at 370 nm corresponds to transition of electron from ground level ( $^2F_{7/2}$ ) to CTB associated with  $C_2$  charge centre and the peak at 335 nm corresponds to excitation of electron to CTB associated with  $C_{3i}$  charge centre from  $^2F_{7/2}$  level because the absorption energy level of  $C_{3i}$  centers is at higher energy than that of the  $C_2$  centers.<sup>34</sup>The intensity of 335nm peak in excitation spectra depends on doping percentage of Yb in  $Y_2O_3$  because this transition depends on the number of  $C_{3i}$  charge centres at which there is broken of centre of symmetry (i. e. for 2% Yb doped  $Y_2O_3$  nano powder the number of  $C_{3i}$  centres for which the centrosymmetry was broken is less compared to 5% and 8% Yb doped  $Y_2O_3$  nano powders).

The possible broad emission peaks  $\sim 359$  nm,  $\sim 400$  nm (centered at 412 nm & 430 nm) and  $\sim 503$  nm observed for 270 nm excitation correspond to CTB ( $C_{3i}$ ) -  $^2F_{7/2}$ , CTB ( $C_2$ ) -  $^2F_{7/2}$  and CTB ( $C_{3i}$ ) -  $^2F_{5/2}$  ( $\sim 503$ nm) transitions respectively. According to the energy level diagram, for 335 nm excitation (i. e. from  $^2F_{7/2}$  to CTB ( $C_{3i}$ )) the possible strong emission bands at  $\sim 503$  nm, 412 nm, 359 nm and 729 nm are due to CTB ( $C_{3i}$ ) -  $^2F_{5/2}$ , CTB ( $C_2$ ) -  $^2F_{7/2}$ , CTB ( $C_{3i}$ ) -  $^2F_{7/2}$  and CTB ( $C_2$ ) -  $^2F_{5/2}$  transition respectively. The peak at 729 nm was not observed in PL spectra due to limitation of PL scan range (to avoid 1<sup>st</sup> and 2<sup>nd</sup> order excitation diffraction peak). Similarly, for 370 nm excitation the strong possible broad emission peak was observed at  $\sim 412$  nm due to electron transition from CTB ( $C_2$ ) to  $^2F_{7/2}$ . From above discussion, it is understood that due to activation of centrosymmetric ( $C_{3i}$ ) sites in nano Yb:  $Y_2O_3$  powders strong broad PL in the range from  $\sim 400$  to  $\sim 650$  nm is observed.

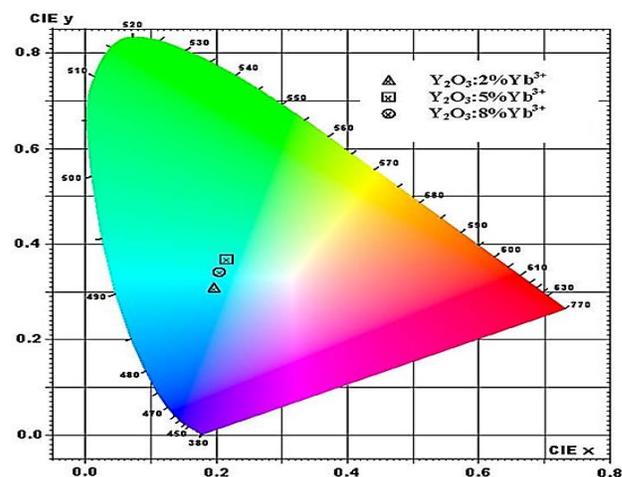


Fig. 9. The color coordinate diagram for  $Y_2O_3:Yb^{3+}$  nanophosphors for different  $Yb^{3+}$  concentration.

The CIE (International Commission on Illumination) chromaticity illustration of  $Y_2O_3:Yb^{3+}$  nanophosphor for various molar concentration of  $Yb^{3+}$  is shown in Fig. 9. From the chromaticity diagram (Fig. 9), it can be seen that colour coordinates transverse from bluish white to

greenish white region with increase in Yb<sup>3+</sup> doping concentration. The CIE colour coordinates (x, y) are shown in **Table 2**.

The CIE parameter colour purity of emitted colour is useful for narrow banded light sources and for broad band light sources CCT (Correlated Color Temperature) is more useful [35]. The CCT were calculated by the McCamy empirical formula and are summarized in **Table 2**; [36, 37]

$$\text{CCT} = -437n^3 + 360n^2 - 6861n + 5514.31 \quad (1)$$

where,  $n = (x-x_e)/(y-y_e)$  and chromaticity epicenter is at  $x_e = 0.3320$  and  $y_e = 0.1858$ . The CCT values shows the color temperatures correspond to bluish white for Yb: Y<sub>2</sub>O<sub>3</sub> nanophosphors.

**Table 2.** Photometric parameters of nano Yb (2, 5 and 8%): Y<sub>2</sub>O<sub>3</sub>.

Nano-phosphor	Concentration (mol%)	Colour Coordinates		CCT (K)
		x	y	
Y <sub>2</sub> O <sub>3</sub> :Yb <sub>3+</sub>	2	0.195	0.304	18984.603
	5	0.215	0.365	11650.510
	8	0.206	0.339	13836.115

## Conclusion

In the present work, we have investigated the photoluminescence properties of nano Yb: Y<sub>2</sub>O<sub>3</sub> with different doping percentage of Yb in visible region. The nano Yb: Y<sub>2</sub>O<sub>3</sub> shows intense and broad excitation peaks at 335 nm and 370 nm. The excitation peak at 370 nm is obvious due to transition of electrons from <sup>2</sup>F<sub>7/2</sub> to CTB associated with non-centrosymmetric C<sub>2</sub> centers but the excitation peak at 335 nm is due to transition of electrons from <sup>2</sup>F<sub>7/2</sub> to the CTB associated with distorted centrosymmetric C<sub>3i</sub> centers. A broad intense emission peak observed at ~503 nm is assigned to transition from CTB (C<sub>3i</sub>) to <sup>2</sup>F<sub>5/2</sub> energy levels. The Yb doping in Y<sub>2</sub>O<sub>3</sub> not only modify the charge transfer bands but also provides ground energy levels to the emitted electron which results in strong intense broad emission ranging from ~400 to ~650 nm. Among various doping percentage of Yb in Y<sub>2</sub>O<sub>3</sub>, the 5% Yb doped Y<sub>2</sub>O<sub>3</sub> nano phosphor shows high integrated emission intensity at ~503 nm for ~335 nm excitation. Therefore by using AlGaIn based LED (output peak at ~335 nm with FWHM 10 nm, commercially available) the 5% Yb: Y<sub>2</sub>O<sub>3</sub> nano phosphor may use to produce bluish white light.

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## Author's contributions

All have equal contribution. Authors have no competing financial interests.

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