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# Solution Combustion Synthesis of $ZrO_2$:$Tb^{3+}$ Nanophosphors Viable for WLEDs

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**Abstract**

$Tb^{3+}$ doped Zirconium oxide ($ZrO_2$) nanopowders were synthesized by solution combustion method using oxalyl di-hydrazide (ODH). The effect of dopant concentration on the crystal structure and photoluminescence properties of the nano phosphors were investigated. Band gap of the samples were obtained from Wood and Tauc plot. Scanning electron microscopy analysis reveals the formation of porous powders with large amount of voids. Room temperature photoluminescence shows visible luminescence of the phosphors under near UV excitation. The colour index of phosphors were calculated using CIE co-ordinates. These phosphors show bright green emission centered at 550 nm. The emission intensity increased with $Tb^{3+}$ concentration up-to 5 mol% and decreased thereon. All these samples were emitting green colour having colour coordinates at (0.25,0.65). The colour purity of the samples reveals that these phosphors are promising candidates as green emitting phosphors in the tricolor GaN based white light emitting diodes.


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*Keywords:* Phosphors; WLEDs; Zirconia; Terbium; Photoluminescence;

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## 1. Introduction

White light emitting diodes are new generation lighting systems because of their novel properties like high efficiency, durability, low power consumption and not containing toxic materials like mercury [1]. Yttrium-aluminium-garnet based material: $(Y,Gd)_3(Al,Ga)_5O_{12}:Ce^{3+}$ is the white light emitting diode currently used, it consists of a yellow emitting phosphor on a blue LED chip. Its main drawback is low colour rendering index [2]. Therefore, near UV and blue excited red, green and blue emitting phosphors are deliberately needed [3]. Presently, lot of europium based red emitting phosphors capable of being excited at near UV are being reported including, zinc sulfide ($ZnS:Eu^{3+}$), yttrium oxysulfide ($Y_2O_2S:Eu^{3+}$) -doped nitride/oxynitride, $Eu^{3+}$-doped titanate, molybdate and tungstate [4-6]. In case of green emitting phosphor, the classical phosphor materials that are used for the tricolor based white light emitting LEDs is ZnS: ($Cu^{+}$, $Al^{3+}$).

Especially green emitting phosphors are sulfide based materials, they exhibit low chemical and environmental stabilities, they are viable to be affected by rays from UV chip. Which may affect the durability of that particular LED. Also, they pose environmental issues both in application and production point of view as they contain toxic elements, particularly sulphur [7]. Therefore, there is an immediate requirement for green emitting phosphors with exceptional chemical and environmental stability, durability, high efficiency, eco-friendly without any environmental hazards and also possessing good chromaticity co-ordinates. It is well known that emission of rare earth materials depends on the surrounding environment, their photoluminescent behaviour greatly depends on the host matrix [8]. The site symmetry of the RE ions may vary even when they are doped in same matrices prepared in different methods.

In the current scenario, plenty of work are being done on zirconia, owing to their exceptional physical and chemical stability. They have high band gap and low phonon energy. Terbium based phosphors are good bet for green emitting materials. However, to the best of our knowledge, little report is available on the PL behaviour of $Tb^{3+}$ doped $ZrO_2$ nanoparticles. In this study, the photoluminescence properties of green emitting $Tb^{3+}$ doped $ZrO_2$ nanoparticles synthesized by the solution combustion method is reported. Terbium ions are expected to occupy zirconium site in the matrix.

## 2. Experimental section

Analar grade, high purity reagents were used without further purification. $Tb^{3+}$ ions doped $ZrO_2$ nanoparticles were synthesized by solution combustion method using ODH as fuel. Four $Tb^{3+}$ samples were prepared with molar concentrations namely 1%, 3%, 5% and 7%. For the preparation of terbium doped samples appropriate amount of $Tb(NO_3)_3$, $ZrO(NO_3)_2$ and ODH were dissolved in double distilled water to form a clear solution, later this solution was taken in crystalline dish and introduced in a muffle furnace preheated at 400 $^oC$. This solution thermally dehydrated and started smoldering with emission of large amount of gases. Entire reaction took place in about five minutes and white powders were formed in the crystalline dish. The powders were allowed to cool to room temperature and then collected. The powders were again calcined at 1000 $^oC$ for one hour to enhance the crystallinity.

PXRD studies were conducted to confirm the product formation and to identify the phase formed in the samples, on Philips PW 1050/70 instrument using Nickel – filtered Cu $K_\alpha$ radiation of emission wavelength 0.15418 nm. UV-Visible diffusive reflectance spectrum was recorded using a Jobin Varian Cary 5000 (USA) spectrometer. Morphological analysis was done using Scanning electron micrographs (SEM) in a JEOL (JSM-840A) instrument after coating the samples with gold. PL emission and PL excitation spectra were taken using a F-4500 “Hitachi fluorescence spectrophotometer” equipped with a xenon lamp for excitation.

## 3. Results and discussions

### *3.1. Structural characterization of $Tb^{3+}$ doped $ZrO_2$*

PXRD studies were carried out to study the crystal structure and to confirm phase purity of the products. Fig.1 shows the XRD pattern of the $Tb^{3+}$ doped $ZrO_2$ nanoparticles. Diffraction peaks observed in the PXRD spectra are

indexed to the cubic phase of $ZrO_2$ nanoparticles, that matches with the JCPDS file no. 81-1551 [9]. The sharp and strong peaks observed in diffraction pattern signifies good crystallinity of samples. Also, it has to be noted that other peaks which are characteristic of impurities and other phases of zirconia were not observed in the XRD pattern, indicating the quality of phase purity of the final products. Scherrer formula was adopted to calculate the average crystallite size [10]. The obtained crystallite sizes of the $ZrO_2$:x$Tb^{3+}$ nanoparticles were 10, 12, 13 and 18 nm, for x= 1, 3, 5 and 7 mol% respectively.

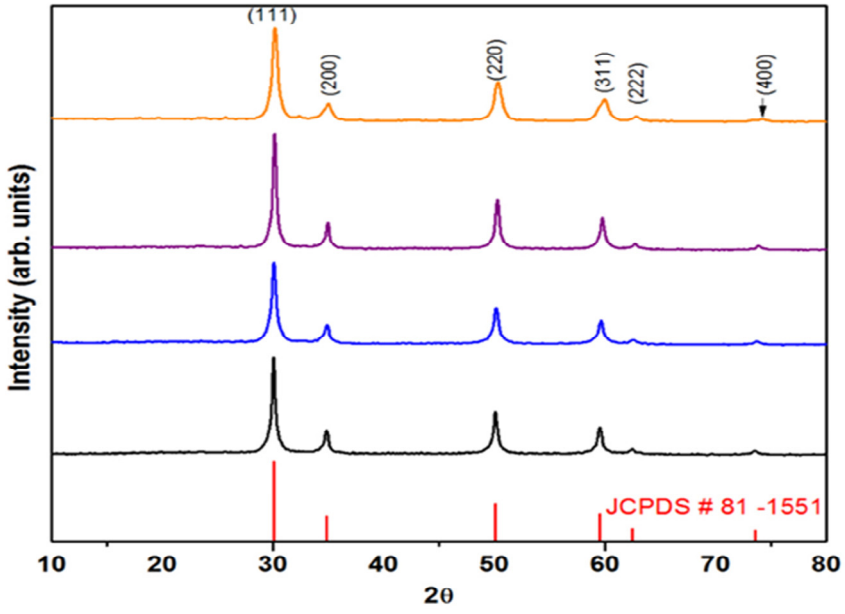


Fig. 1. PXRD spectrum of (a)1 (b)3 (c)5 and (d)7 mol% $Tb^{3+}$ doped $ZrO_2$ samples

*3.2. Bandgap*

Energy gap of the samples were calculated using the Wood and Tauc plot, derived from the UV-Visible spectra. A plot drawn between energy along the x- axis and $(\alpha h\nu)^2$ along the y- axis. X-intercept of the tangent drawn to that plot yields the energy gap in eV. Energy gap calculated based on this procedure are plotted in Fig.2, the values for the energy gap thus obtained samples were about 5.2 eV, which matches with the literature [11]. Same procedure was followed to calculate energy gap for all samples.

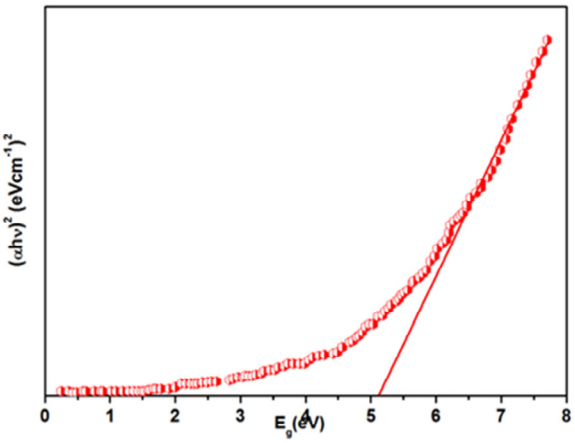


Fig. 2. Wood and Tauc Plot for 5 mol% $Tb^{3+}$doped $ZrO_2$

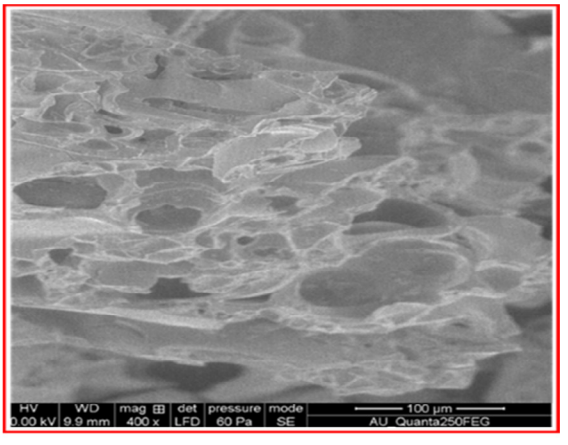


Fig. 3. SEM micrograph of 5 mol% $Tb^{3+}$ doped $ZrO_2$.

### *3.3. SEM analysis*

It is well known that the morphology of the samples plays a vital role in deciding the field of application. Scanning electron microscopy was used to study the morphology of the combustion derived nano phosphors. Fig.3 show the SEM micrograph 5 mol% terbium doped samples under x400 magnification, at a pressure of 60 Pascal. It revels mesoporous nature of the samples. Almost all samples were showing same morphology, doping concentration hardly effected the morphology of the samples. The fluffy nature with lots of voids observed can be assigned to the escape of gaseous combustion products that formed at the time of combustion.

### *3.4. Luminescence properties of $Tb^{3+}$-doped $ZrO_2$ nanoparticles*

Fig.4 shows a broad excitation peak at 375 nm, spread over 368 nm and 385 nm which is due to the $^7F_6 \rightarrow {}^5G_6$ transition of $Tb^{3+}$ ions [12]. This peak makes this phosphor an excellent candidate for the GaN based light emitting diodes which has the emission between 370 to 410 nm. Room temperature PL emission spectra of $Tb^{3+}$ doped $ZrO_2$ nanophosphors is shown in Fig.5. They show a strong emission peak at 560 nm arising due to $^5D_4 \rightarrow {}^7F_5$ and three shoulder peaks at 500 nm due to ($^5D_4 \rightarrow {}^7F_6$), 590 nm due to ($^5D_4 \rightarrow {}^7F_4$) and 620 nm due to ($^5D_4 \rightarrow {}^7F_3$) [13].

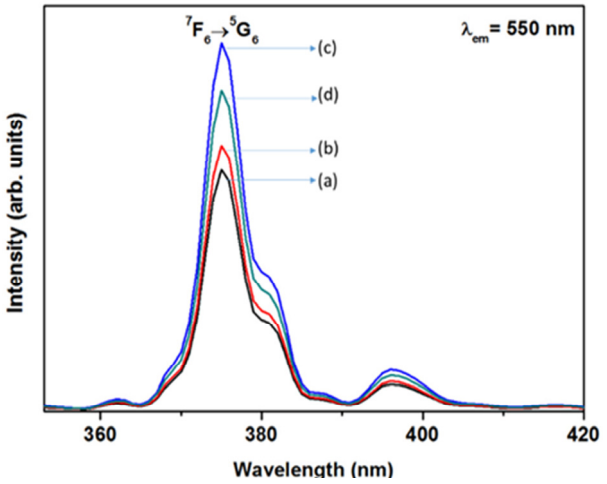


Fig. 4. PL excitation spectra of (a)1 (b) 3 (c) 5 and (d) 7 mol% $Tb^{3+}$ doped $ZrO_2$

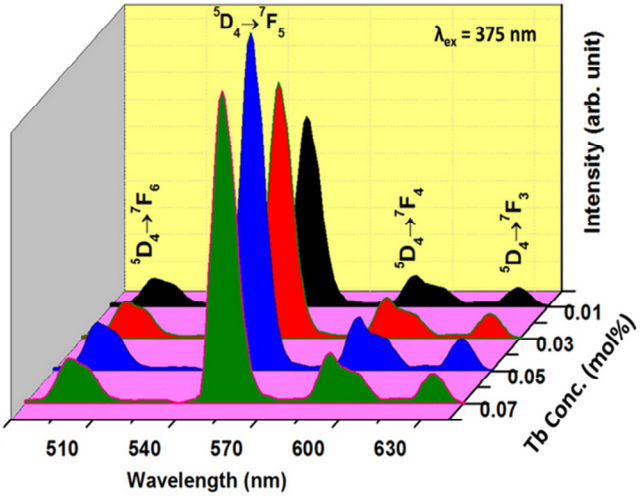


Fig. 5. PL emission spectra of (a)1 (b) 3 (c) 5 and (d) 7 mol% $Tb^{3+}$ doped $ZrO_2$

These phosphors exhibits concentration quenching. Ran Li et al. [14] observed a maximum luminescence intensity for a 1 mol% doping concentration of $Tb^{3+}$ in $SrSi_2O_2N_2$. K. Joy [15] observed a maximum luminescence at a doping concentration of 5 mol% in the $Tb^{3+}$-doped $ZrO_2$. Patha et al. [16] reported a maximum emission intensity for a doping concentration of 0.50 wt% in the $Tb^{3+}$-doped ZnO nanorods. In this present study emission intensity at 600 nm due to $^5D_4 \rightarrow {}^7F_5$ transition of $Tb^{3+}$ in $ZrO_2$:$Tb^{3+}$ nanoparticles significantly increased with $Tb^{3+}$ concentration and the emission intensity was maximum when $Tb^{3+}$ doping concentration was 5 mol%. If $Tb^{3+}$ concentration continued to increase, beyond 5 mol%, the emission intensity was decreasing.

### *3.5. CIE Co-ordinates*

Calculated CIE co-ordinates for the trivalent terbium doped zirconia samples is shown in Fig.6. Terbium doped samples were emitting green colour having colour coordinates at (0.25, 0.65). The colour purity of the samples reveals that these phosphors are promising candidates as green emitting phosphors in the tricolor GaN based white light emitting diodes under 375 nm excitation.

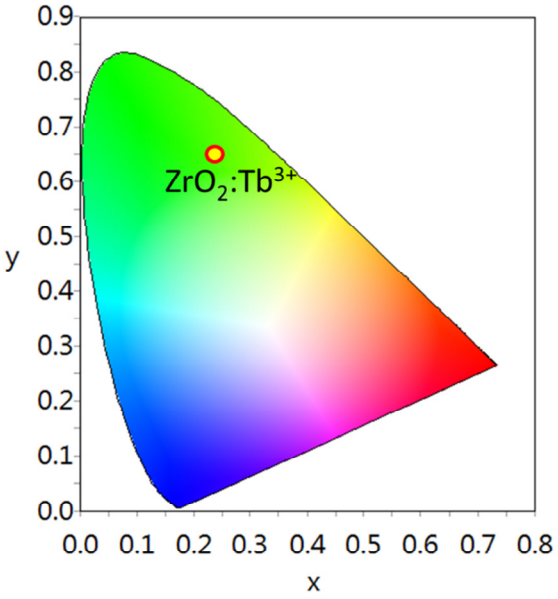


Fig. 6. CIE coordinates calculated for $Tb^{3+}$ doped $ZrO_2$.

## 4. Conclusion

$Tb^{3+}$ doped $ZrO_2$ nanoparticles were synthesized by one step solution combustion method. PXRD results revealed good crystallinity and phase purity of the samples. Fluffy nature of the products revealed by the SEM images suggests that these samples can be used as a coating with increased surface area. The band gap obtained from Wood and tauc plot was about 5.2 eV. It was found that the optimum $Tb^{3+}$ content in $ZrO_2$ nanoparticles was 5 mol %. $Tb^{3+}$ samples exhibited strong excitation maxima at 375 nm and an intense emission peak at 560 nm arising due to $^5D_4 \rightarrow {}^7F_5$ and three shoulder peaks at 500 ($^5D_4 \rightarrow {}^7F_6$), 590 ($^5D_4 \rightarrow {}^7F_4$) and 620 nm ($^5D_4 \rightarrow {}^7F_3$). Color rendering index of the samples were calculated to be (0.25,0.65) for trivalent terbium ions in zirconia (green emission). Based on these values we can strongly recommend these phosphors for W-LED applications based on three colour emitting systems.

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