

Band Gap and Photo luminescence studies of Sm^{3+} doped TiO_2 NP for wLED

Venkatesha Babu K R^{1*}, Renuka CG², Mohamed Zikriya³

¹Department of Physics, Nrupathunga University, Bangalore-560 001, India

^{2,3}Department of Physics, Bangalore University, Bangalore-560 056, India

Abstract: $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %) nano particles (NPs) were prepared by self-propagating solution combustion method (SC) using Neem leaf extract. PXRD study contributes the particle size, crystallinity etc., with phase transformation from rutile to anatase with the addition of dopant when calcinated for 2H. The energy band gap (E_g) of pure and doped samples was found to be in the range 3.10 - 3.23 eV. The Photo-luminescence points CIE and CCT results with chromaticity colour CIE-coordinates $x = 0.5310$, $y = 0.4601$ and average CCT as 2426K, suggests sample suitable for hot wLEDs which can be used for household applications.

Key words: CIE, CCT, Band Gap Energy

1. INTRODUCTION

Nano sized pure and Ce^{3+} doped TiO_2 particles have received significant interest owing to its wide range of applications. It was known that, TiO_2 was chemically stable, biocompatible with excellent physical and optical electrical properties. It has a polymorph showing rutile (tetragonal, $E_g=3.00$ eV), anatase (tetragonal $E_g =3.20$ eV) and brookite (orthorhombic $E_g= 1.90$ eV) phases. Further TiO_2 is non-toxic with high dielectric constant (~ 67.3) and high refractive index (~ 2.6). TiO_2 NPs have been prepared by various methods. Among them, SC technique was found to be simple, rapid and effective for the preparation of NPs. In this method, exothermic nature of the reduction-oxidation reaction was dominant for producing nano sized particles.

In the present work, $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %) NPs were prepared by SC technique using Neem leaf extract and the product was well characterized by utilizing PXRD, UV-visible, and PL for luminescence studies.

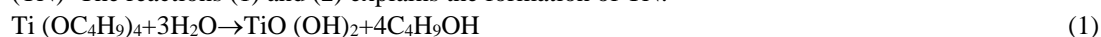
2. EXPERIMENTAL

2.1. Materials

The chemicals used are Ti $(\text{OC}_4\text{H}_9)_4$ MW=340.32 gmol^{-1} , 97%, (Sigma Aldrich), nitric acid (69%, HNO_3), Sm $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, MW=444.47 gmol^{-1} , 99.9%, (Sigma Aldrich) and Neem leaf.

2.2. Preparation of $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %)

The fresh Neem plant leaves are collected washed thrice with distilled water. The leaves were chopped and grounded to prepare the leave extract. The titanium butoxide treated with water and then HNO_3 gives titanyl nitrate $\text{Ti}(\text{NO}_3)_2$ (TN) The reactions (1) and (2) explains the formation of TN.



The stoichiometric compositions of the redox mixtures for combustion reaction were calculated using total oxidizing (O) and reducing (F) valencies of the components so that the equivalent ratio O:F is unity. The 20 minutes stirred mixtures are kept in the preheated muffle furnace maintained at 450 $^\circ\text{C}$ to get the pure TiO_2 . The same procedure was adopted to prepare the Sm^{3+} doped TiO_2 NPs with suitable stoichiometric calculations. The samples thus obtained are calcinated at 700 $^\circ\text{C}$ for 2H to remove the impurities present in the final products.

2.3. Characterization

The structural characterization was performed using powder X-ray diffractometer (PXRD) in the 2θ range 10 to 80 $^\circ$ with $\text{Cu-K}\alpha$ radiation (1.54178 \AA). Photoluminescence (PL) studies were carried out using Fluorolog-3 Jobin Yvon Spectro-fluorimeter equipped with 540W Xenon source.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

Fig.1 shows the PXRD profiles of pure and doped TiO_2 NPs. All the peaks were well matched to pure rutile phase of TiO_2 . When the product was calcined at 700 $^\circ\text{C}$ for 2H, the pure rutile phase was obtained. However, with the addition

of Sm^{3+} ions, rutile phase ($2\theta \approx 27^\circ$) was converted to anatase phase ($2\theta \approx 25^\circ$). Also, the strong peaks of anatase were matched to JCPDS card no. 84-1286 and 87-920 for rutile phase. Further, no impurity peaks were observed indicating that Sm^{3+} ions were successfully existed in the lattice sites rather than interstitial sites.

The diffraction peaks were linked to the parameters such as crystallite size, stress, dislocation density, stacking fault (SF), texture coefficient (TC) and lattice cell parameters. The crystallite sizes of pure and doped were estimated using the Scherrer's relation (3) and were found to be around 26 nm.

$$D = \frac{k \lambda}{\beta \cos \theta} \tag{3}$$

where k: the shape factor (0.9 for spherical shape particles), β : full width at half maximum (FWHM) of the peak.

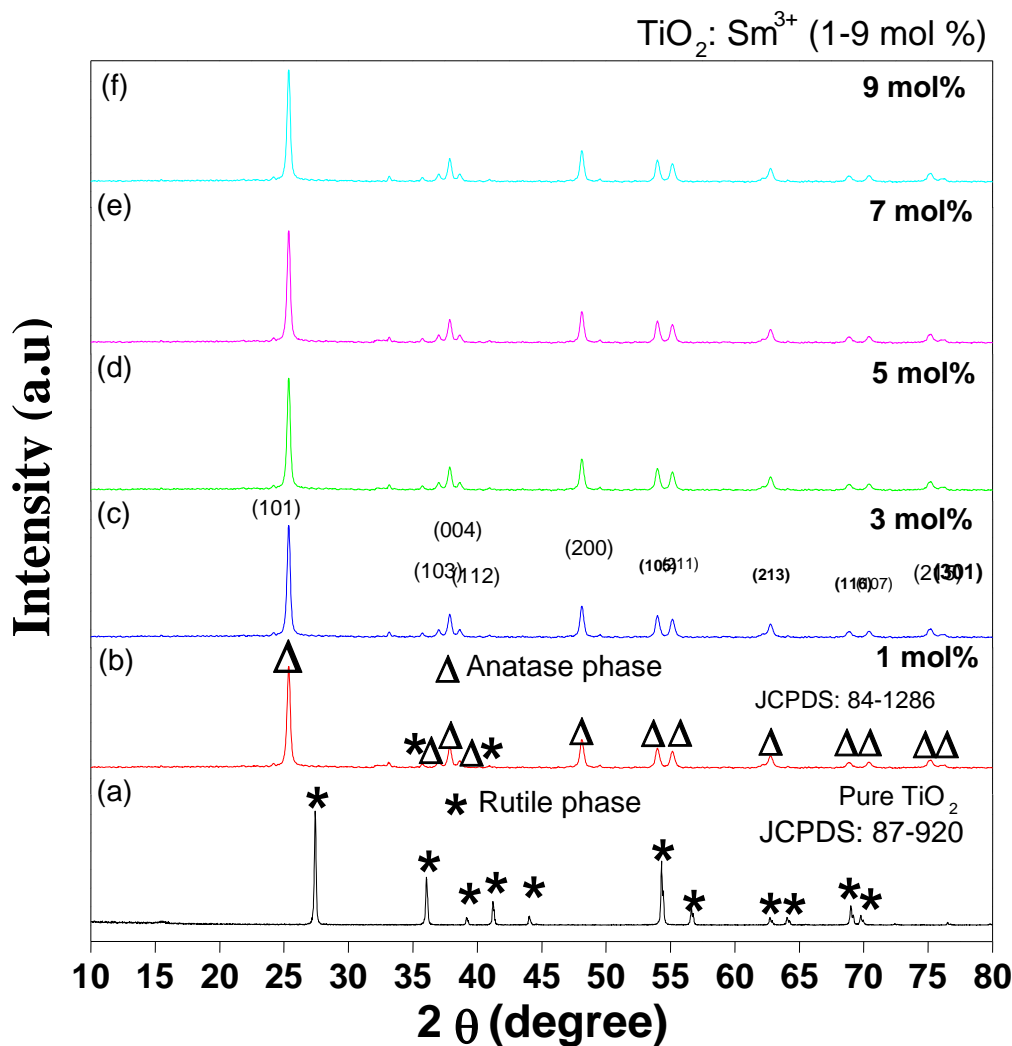


Fig 1: PXRD patterns of (a) pure TiO_2 and (b-f) calcinated $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %) NPs

3.2. Diffuse reflectance (DR) spectral studies

The optical properties of the $\text{TiO}_2:\text{Sm}^{3+}$ (1-9mol %) were studied by Diffused reflectance (DR). The DR spectra at RT recorded in the range 200 – 1100 nm wavelength Kubelka-Munk (K-M) method was adopted to find the E_g of pure and doped TiO_2 using following relation (4).

$$F(R) = (1 - R^2) / 2R = K / S \tag{4}$$

where, R: reflectance, K: absorption co-efficient and S: scattering co-efficient. The relation between E_g and the absorption co-efficient (α) of phosphor Wood-Tauc relation is given by equation (5).

$$\alpha h\nu = A(\alpha h\nu - E_g)^{1/2} \tag{5}$$

Where, the factor ‘ $h\nu$ ’ represents the energy of the light beam and A : constant.

By rewriting relation (5), that is $[F(R)h\nu]^2 = A(h\nu - E_g)$, where F(R) is the Kubelka-Munk function F(R), value of E_g was determined by extrapolating the linear fitted region to $F(R)^2=0$ of the curve drawn for $[F(R) h\nu]^2$ and ‘ $h\nu$ ’. Fig. 2 shows the E_g values obtained for pure and doped NPs. The values of E_g are tabulated in the table (1). It is noticed from the table that, there was a gradual rise in E_g value with increase in conc. of the Sm^{3+} ions, exhibiting a red shift. The variation of E_g was due to increase in the number of crystal defects with increase of Sm^{3+} ions concentration in the host matrix.

It was evident from the literature survey that, the structural order and disorder due to doping in the matrix of the host material leads the changes in E_g as well as distribution of energy levels within the band gap. The order-disorder in the matrix was mainly due to the factors such as preparation methods and experimental conditions.

Table 1: E_g values for different conc. of Sm^{3+} in TiO_2

Conc. Of Sm^{3+} in TiO_2	pure	1	3	5	7	9
Band gap energy (E_g) (eV)	3.10	3.13	3.14	3.17	3.20	3.23

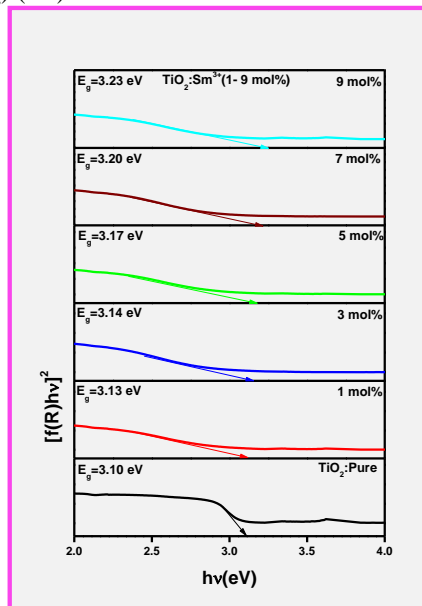


Fig.2. Energy band gap plots of pure and $TiO_2:Sm^{3+}$ (1 – 9 mol %) NPs

4. PHOTOLUMINESCENCE STUDIES

The excitation spectrum monitored at 490 nm emission wavelength. The spectra consist of an intense peak at ~600nm. The emission spectrum was obtained due to excitation of $TiO_2:Sm^{3+}$ (1-9 mol %) by radiation of wavelength ~ 490 nm. The emission spectrum consists of peaks at 564,579,595,601,647,698 and 777 nm. PL intensity was found to be increases up to 1 mol% of Sm^{3+} ions and thereafter it decreases due to well-known phenomenon known as concentration quenching.

Further, the three mechanisms may be responsible for the non-radiative energy transfer such as exchange interaction, radiation re-absorption and multi-polar interaction.

4.1. Photometric properties

Fig. 3 shows the 1931 CIE system based CIE diagram for $TiO_2: Sm^{3+}$ (1-9 mol%) nanophosphor. The obtained CIE colour chromaticity coordinates (Table 2) lies in the yellow region and were indicated as a star ‘★’ mark. The coordinates were in accordance with NTSC reference. With increase of the Sm^{3+} ions conc. from 1 to 9 mol%, the movement of ‘★’ can also be noticed.

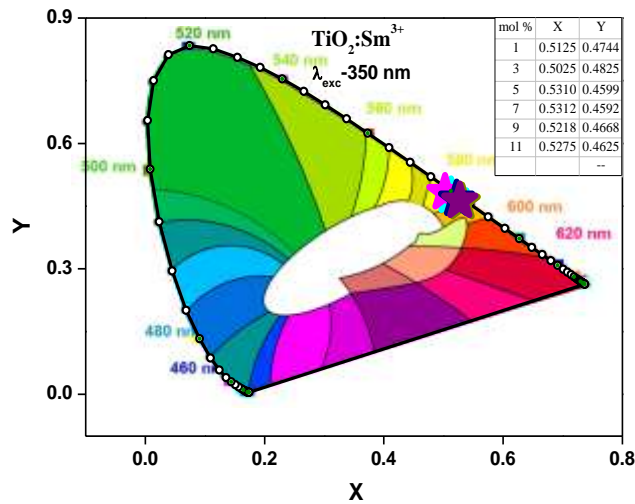


Fig 3: CIE diagram of $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %)

Table 2: CIE color coordinates of $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %) NPs

Sm ³⁺ conc. In TiO ₂	CIE colour coordinates	
	X	Y
Pure	0.5125	0.4744
1	0.5025	0.4825
3	0.5310	0.4599
5	0.5312	0.4592
7	0.5218	0.4668
9	0.5275	0.4625

The correlated colour temperature (CCT) was one of the important parameters to understand the appearance of the colour of the light being emitted by the source, relating its colour with respect to a reference light source when heated up to a specific temperature. The CCT was estimated from the concept of Planckian locus; it was a small portion of the chromaticity diagram. The equations (6) and (7) mentioned below, were used to transform the CIE coordinates (x, y) in to CCT coordinates (U^1, V^1). It was observed that the average temperature estimated was ~ 2426 K indicated by again a star mark '★'. The '★' was very close to Planckian locus. The estimated CCT coordinates were also indicated in the same diagram.

$$U^1 = \frac{4x}{-2x + 12y + 3} \quad (6)$$

$$V^1 = \frac{9y}{-2x + 12y + 3} \quad (7)$$

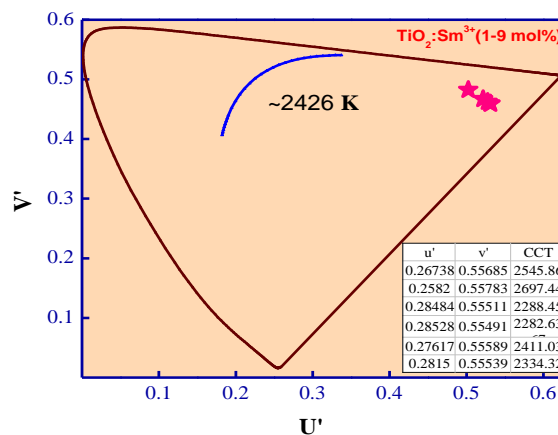


Fig 4: CCT diagram of $\text{TiO}_2:\text{Sm}^{3+}$ (1-9 mol %)

The quality of light emitted was suggested by Mc Camy for CCT from CIE 1931 (x,y) was given by the relation $CCT = -437n^3 + 3601n^2 - 6861n + 5514.31$ where $n = (x - x_c)/(y - y_c)$ was the inverse of the slope and with chromaticity epicenter at $x_c = 0.3320$ and $y_c = 0.1858$. The average CCT value estimated from Mc Camy method was in good agreement with the value estimated from CIE method (4563K). The CCT values obtained from two methods were tabulated in the Table 3.

Table 3: CCT values of $TiO_2:Sm^{3+}$ (1- 9 mol %) NPs

Sm³⁺ Conc. (mol %)	CCT (K)	MacCamy theoretical CCT (K)
Pure	2545.86	2524.98
1	2697.44	2677.99
3	2288.45	2264.0
5	2282.63	2257.98
7	2411.03	2388.40
9	2334.32	2310.32

5. CONCLUSIONS

A series of $TiO_2:Sm^{3+}$ (1-9 mol%) NPs were prepared by self-propagating solution combustion method by leaf extract. The PXRD pattern of TiO_2 confirms anatase phase while rutile when doped and calcinated for 2H. The energy gap (E_g) values of the pure and doped TiO_2 vary from 3.10 to 3.23 eV. The phosphor exhibit yellow emission at a wavelength 490 nm. PL intensity was found to be maximum for 1 mol% of Sm^{3+} in the TiO_2 and then diminishes due to concentration quenching phenomena. The phosphor showed CIE chromaticity co-ordinates (0.5310, 0.4601) and average value of CCT as 2426 K. The CIE values were on par with the values of standard phosphors. The samples doped can be used for house hold applications.

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