

## Vật liệu huỳnh quang không pha tạp phát xạ ánh sáng toàn phổ ứng dụng trong đèn LED trắng

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### TÓM TẮT

Vật liệu huỳnh quang không pha tạp  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  kích thước cỡ vài  $\mu\text{m}$  đã được chế tạo thành công bằng phương pháp phản ứng pha rắn và nung ở nhiệt độ  $1100^\circ\text{C}$  trong bài báo này. Vật liệu huỳnh quang này phát ánh sáng trắng tương tự như phổ ánh sáng Mặt Trời với bước sóng phát xạ trong khoảng từ  $400\text{ nm} - 800\text{ nm}$ . Phổ phát xạ của mẫu được phân tích hàm Gauss cho các cực đại phát xạ ở các bước sóng khoảng  $450\text{ nm}$ ,  $515\text{ nm}$ ,  $580\text{ nm}$ ,  $680\text{ nm}$  và  $740\text{ nm}$ . Bài báo cũng giải thích nguồn gốc của các đỉnh phát xạ dựa trên lý thuyết phát xạ của các sai hỏng. Bên cạnh đó, bài báo cũng đề xuất sơ đồ giải thích nguồn gốc của các đỉnh phát xạ. Cuối cùng, khả năng ứng dụng của vật liệu trong chế tạo đèn LED chiếu ánh sáng trắng cũng được nghiên cứu trong bài báo này. Bột huỳnh quang sau khi chế tạo được phủ lên chip LED n-UV ( $310\text{ nm}$ ) cho kết quả đèn LED phát ánh sáng trắng với chỉ số hoàn màu (CRI) bằng 95. Kết quả nghiên cứu cho thấy, vật liệu huỳnh quang  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  có tiềm năng ứng dụng trong chế tạo LED trắng với giá thành rẻ và phương pháp đơn giản.

**Từ khóa:**  $\text{SnO}_2 - \text{Zn}_2\text{SnO}_4$ , vật liệu huỳnh quang  $\text{Zn}_2\text{SnO}_4$ , vật liệu huỳnh quang toàn phổ.

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# Full visible spectra of non-doped phosphor for WLED application

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## ABSTRACT

The  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  micro-composite has been successfully fabricated by the solid reaction technique followed by calcination at 1100 °C. The obtained powder gives a full visible range from 400 nm to 800 nm. The PL spectra were fitted into five Gaussian peaks in the blue to the far-red region centered about 450 nm, 515 nm, 580 nm, 680 nm, and 740 nm. The origin of these emissions was discussed in detail. The proposed diagram for explaining the PL mechanism has been given in this paper. Further, the prepared phosphors have been coated onto the n-UV LED chip, which shows white light with a high CRI of 95. The result approves that  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  micro composite is potential applications in white light-emitting diodes by a cheap and straightforward method.

**Keywords:**  $\text{SnO}_2$  -  $\text{Zn}_2\text{SnO}_4$  powders, photoluminescence of  $\text{Zn}_2\text{SnO}_4$ , full visible spectra.

## 1. INTRODUCTION

Light-emitting devices such as LEDs, WLED, and other optoelectronic devices based on wide band gap (WBG) semiconductor oxide materials are demonstrating their high efficiency and usefulness in recent years because of their regular physical, thermal and chemical properties.<sup>1,2</sup> One primary specification used in WLED and the lighting industry is the Color Rendering Index (CRI); thus, improving CRI for WLED is a significant and challenging task. One method commonly used to create WLED with high CRI is combining a semiconductor chip (blue or UV) with phosphors. Zinc oxide and tin dioxide are two of the most popular candidates for phosphors compared with others due to their simple synthesis and stable behavior.<sup>3</sup> Recently, many scientists have tried combining the two oxides

ZnO and  $\text{SnO}_2$  as a composite or compound to create new properties that suit their applications. For instance, the coupling may slow down the recombination of electron-hole pairs or improve performance in photocatalytic experiments.<sup>4</sup>  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  composite and other phases based on ZnO and  $\text{SnO}_2$  have been produced by various methods and applied for many purposes. Abdessalem et al. synthesized the ZnO- $\text{SnO}_2$  nanocomposites using the sol-gel method and application on photocatalytic.<sup>3</sup> Precipitation – decomposition method was used to prepare the ZnO- $\text{SnO}_2$  composite by V.kuzhalosai et al.<sup>5</sup> Also,  $\text{Eu}^{3+}$  and  $\text{Ca}^{2+}$  co-doped  $\text{Zn}_2\text{SnO}_4$  were synthesized by the hydrothermal method, and its emission was in the red band as reported by Krishna Sagar *et al.* in 2018.<sup>6</sup> In the same method, S. Dinesh et al. produced zinc stannate

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( $\text{Zn}_2\text{SnO}_4$ ) and applied it in photocatalytic and antibacterial activity.<sup>7</sup> In addition, other shapes of  $\text{Zn}_2\text{SnO}_4$ , like nanobelts and nanorings, have been synthesized using thermal evaporation or simple chemical vapor deposition methods.<sup>8,9</sup> High energy milling method, electrospinning, and combustion method were also applied in the synthesis of  $\text{ZnO-SnO}_2$  composite and  $\text{Zn}_2\text{SnO}_4$ .<sup>10-12</sup>  $\text{Zn}_2\text{SnO}_4$  has a wide band gap (3.6 eV) with good potential for phosphor applications. However, only a small number of reports focus on the optical properties of these host materials.<sup>13</sup> Furthermore, the application of these phosphors on White LED has not been much regarded.

Normally, a phosphor consists of a host lattice and doping ions such as rare-earth ions. Specifically,  $\text{Eu}^{3+}$  and  $\text{Ca}^{2+}$  co-doped  $\text{Zn}_2\text{SnO}_4$  was synthesized using a hydrothermal method and its emission was in the red band as reported by Krishna Sagar et al. in 2018.<sup>12</sup> In 2016, Dimitrievska et al. reported that  $\text{Eu}^{3+}$  doped  $\text{Zn}_2\text{SnO}_4$ , generated by a solid-state reaction method, showed several emission bands, including narrow bands of magnetic dipole emission at 595 nm and electric dipole emission at 615 nm.<sup>13</sup> However, phosphors based on rare-earth are not cheap and unsafe.

In this paper, the undoped phosphor  $\text{SnO}_2$  -  $\text{Zn}_2\text{SnO}_4$  has been successfully produced by a simple method – solid reaction. The PL spectra show a full visible range like the sunlight spectrum from 400 nm to 800 nm. When the prepared phosphor is coated onto the surface of an n-UV LED chip, the device shows warm white color with a CRI of 95. Other parameters related to the quality of WLED have been calculated. Further, the origin of PL emission and the proposed diagram for explaining the PL mechanism have been given in this research.

## 2. EXPERIMENTIAL

The sample synthesized by solid reaction in this work follows the below process:

i. Pure  $\text{ZnO}$  (99.99%, Sigma-Aldrich) and  $\text{SnO}_2$  (99.99%, Sigma-Aldrich) powders were used as starting materials. The starting materials were weighed according to the stoichiometric

weight ratio of 1:1 of  $\text{ZnO} : \text{SnO}_2$  (5g  $\text{ZnO}$  and 5g  $\text{SnO}_2$ ). After that, the mixture is grounded coarsely for 1 hour and further grounded by high-energy planetary ball milling (Restch PM400) at a speed of 200 rpm for 60 hours. The next step is putting the mixture into a furnace and annealing at 1100 °C.

ii. The powder was coated on to UV LED Chip.

iii. The parameters of WLED will be measured and compared with commercial products.

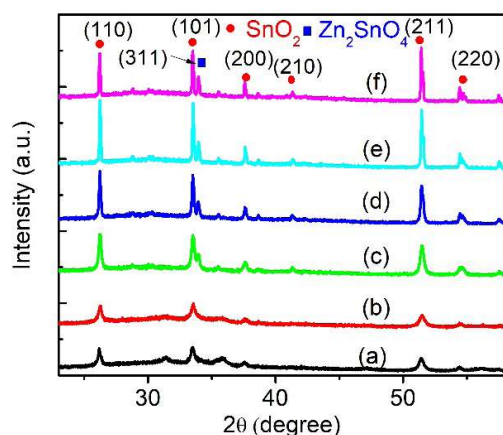
The prepared powders have been analyzed by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation (Bruker D8 Advance) in the  $2\theta$  range of 100 – 800. The surface morphology and average size of particles are determined by ultra-high resolution scanning Electron Microscopy (SEM – Jeol JSM-7600F). In addition, the elemental analysis of the sample is studied by energy dispersive spectrometry (EDS) carried out on the Jeol JSM-7600F detector on the SEM over the range 0-20KeV. Horiba Jobin Yvon equipment was taken to investigate the luminescence characteristics at room temperature. Further, the i-DR S320A Desktop Dispensing system was used to cover the phosphor on to UV LED Chip, and the chromaticity coordinates of the phosphors were calculated by a LED testing system (Gamma Scientific).

## 3. RESULTS AND DISCUSSION

### 3.1. X-ray diffraction

Figure 1 illustrates X-ray diffraction (XRD) patterns of  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  composites prepared by solid reaction and annealed at different temperatures: unannealing (a); 500 °C (b); 900 °C (c); 1000 °C (d); 1100 °C (e) and 1200 °C (f) for 2 hours in air. As shown in Figure 1, the XRD peaks of the sample annealed at 1100 °C show the highest intensity and sharpest summit. All the diffraction peaks are indexed to the cubic phase  $\text{Zn}_2\text{SnO}_4$  (JCPDS card no. 00-024-1470, space group  $\text{Fd-3m}$  (227) and cell parameters  $a = b = c = 8.657 \text{ \AA}$ <sup>14</sup> (Figure 4a) and Tetragonal phase  $\text{SnO}_2$  (JCPDS card no. 00-021-1250, space group

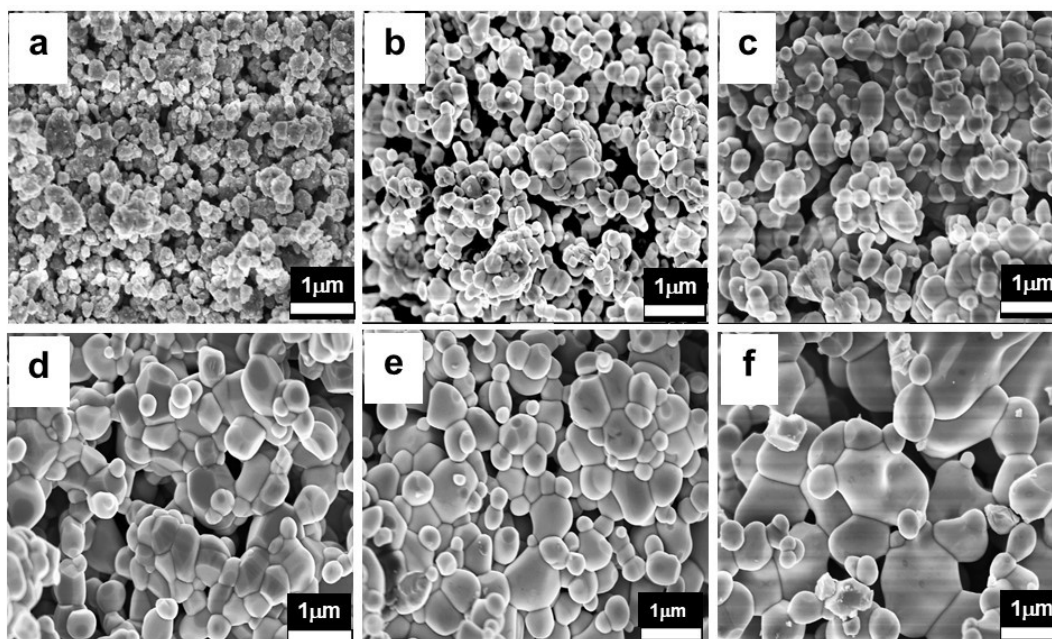
P42/mm (136) and cell constants  $a = b = 4.738 \text{ \AA}$  and  $c = 3.188 \text{ \AA}$ <sup>15</sup> (Figure 4b). Furthermore, as can be seen in Figure 1f, the peak (101) of the  $\text{SnO}_2$  phase begins to separate into two peaks and form a new peak (311) of  $\text{Zn}_2\text{SnO}_4$  at  $900^\circ\text{C}$ . The same phenomenon happens at the (422) peak of  $\text{Zn}_2\text{SnO}_4$  at  $1200^\circ\text{C}$ . The formation of the second phase may cause a decrease in the photoluminescence intensity of the sample, so we chose the optimal temperature of  $1100^\circ\text{C}$  in this work.



**Figure 1.** XRD patterns of  $\text{SnO}_2\text{-Zn}_2\text{SnO}_4$  sample unannealed (a) and annealed at different temperature of  $500^\circ\text{C}$  (b);  $900^\circ\text{C}$  (c);  $1000^\circ\text{C}$  (d);  $1100^\circ\text{C}$  (e) and  $1200^\circ\text{C}$  (f).

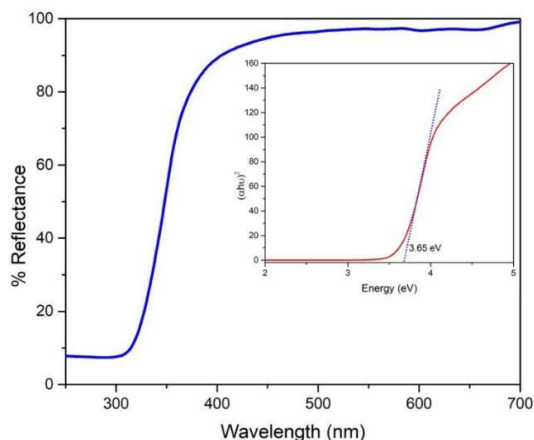
### 3.2. Phosphor morphology

In order to determine phosphor morphology and size of the sample, a typical scanning electron microscope (SEM) has been carried out by ultra-high resolution scanning Electron Microscopy (SEM – Jeol JSM-7600F). Figure 2 illustrates a typical scanning electron microscope image of the prepared  $\text{Zn}_2\text{SnO}_4\text{-SnO}_2$  at different annealing temperature un-calcinated (a);  $500^\circ\text{C}$  (b);  $900^\circ\text{C}$  (c);  $1000^\circ\text{C}$  (d);  $1100^\circ\text{C}$  (e) and  $1200^\circ\text{C}$  (f). Both particle shape and size are affected by changing calcination temperature dramatically. The powder particles of the unannealed sample (a) have an average size of about  $10 \text{ nm}$  with irregular spherical particles. When the annealing temperature increases to  $1000^\circ\text{C}$ , the sample particle sizes are bigger and spherical morphology with particle bounds can be observed clearly. This result is well-matched with the XRD analysis mentioned above. The average particle size of the sample at  $1100^\circ\text{C}$  is about  $10 \text{ nm}$  to  $1 \mu\text{m}$ , which is a suitable size for LED applications. However, under the high of temperature  $1200^\circ\text{C}$ , a re-crystallization or particles cluster together to form massive or tiny particles.



**Figure 2.** FESEM images of  $\text{SnO}_2\text{-Zn}_2\text{SnO}_4$  sample: unannealed (a) and annealed at different temperature of  $500^\circ\text{C}$  (b);  $900^\circ\text{C}$  (c);  $1000^\circ\text{C}$  (d);  $1100^\circ\text{C}$  (e) and  $1200^\circ\text{C}$  (f).

### 3.3. Optical properties



**Figure 3.** UV-Vis spectra of the sample  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  at calcination temperature of 1100 °C.

The UV – vis spectroscopy was used to examine optical properties and estimate the band gap  $E_g$  of the prepared sample as shown in Figure 3. As seen from the Figure 3, there is a significant rise in strong light reflection around over 310 nm and the most substantial absorption at about 310 nm, which can be assigned to intrinsic band gap absorption. The K-M formula<sup>16</sup> has been used to estimate the optical absorption band gap of the prepared sample as shown in the inset of the Figure. The estimated value of the bandgap  $E_g$  is about 3.65 eV, which is slightly higher than the band gap value of bulk  $\text{Zn}_2\text{SnO}_4$  (3.6 eV), but it is just under in comparison with the  $\text{SnO}_2$  band gap (3.7 eV) reported by a previous report.<sup>17</sup> The two-band gaps may correspond to 3.6 eV of  $\text{Zn}_2\text{SnO}_4$  and 3.7 eV of  $\text{SnO}_2$  phosphor. Furthermore, based on the XRD estimated result, the two phases,  $\text{Zn}_2\text{SnO}_4$  and  $\text{SnO}_2$ , are nearly identical.

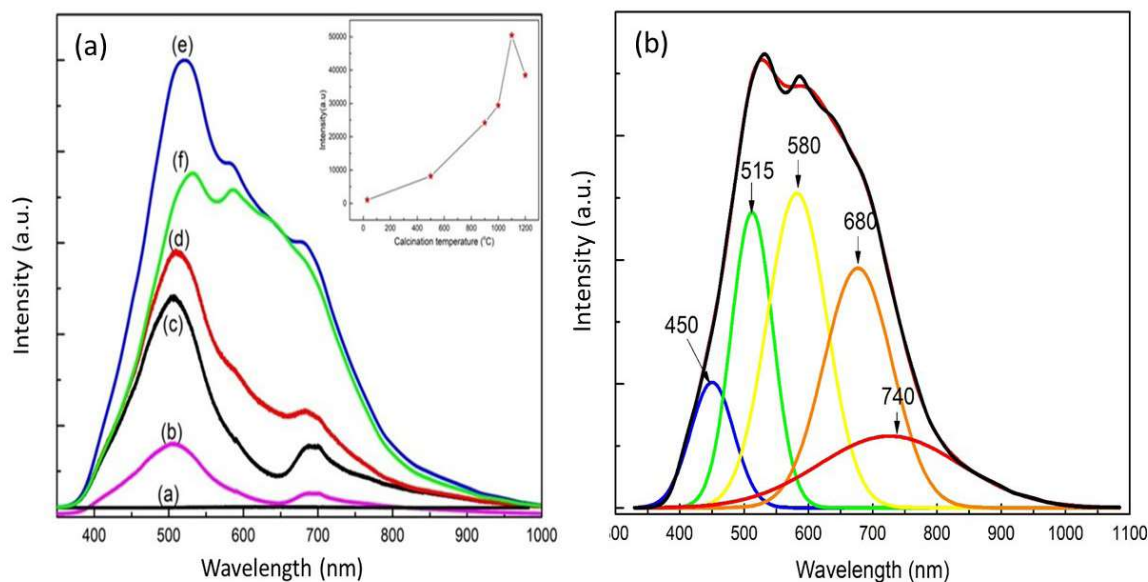
Figure 4 illustrates the photoluminescence (PL) spectrum of the  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  sample annealed with different temperature: uncalcinated (a); 500 °C (b); 900 °C (c); 1000 °C (d); 1100 °C (e) and 1200 °C (f). The spectra was recorded with the excitation wavelength 310 nm at room temperature by Nanolog - Horiba Jobin Yvon equipment. Overall, PL spectra of all samples annealed over 500 °C

shows a broad visible band from 400 nm to 900 nm and nearly covers the full visible range blue – far-red emission. However, there are different intensities among them. It is observed that the PL intensity of the sample increases when the calcination temperature increases, and the highest intensity belongs to the sample with an annealing temperature of 1100 °C (the inset of Figure 4). This result is suitable with XRD and SEM results. In order to clear the origin of PL peaks emission, the broadband emission has been fitted by Gaussian function as given in Figure 4b, which indicates that the PL spectrum was fitted into five Gaussian peaks when the Gaussian was applied. Overall, there is no direct recombination process of a hole in the valence band to an electron in the conductor band because all five peaks' emission is smaller than the band gap of the prepared sample (3.65 eV). The first peak is in the blue region centered around 450 nm. Based on the calculated band gap of 3.65 eV, it is well-known from previous reports<sup>6, 11, 18, 19</sup> that the band gap of bulk  $\text{SnO}_2$  and  $\text{Zn}_2\text{SnO}_4$  are around 3.87eV and 3.6 eV, respectively. So the peak emission at 450 nm is not due to the band-to-band gap emission of neither  $\text{SnO}_2$  nor  $\text{Zn}_2\text{SnO}_4$  phosphor. According to a former investigation,<sup>1, 7</sup> the PL mechanisms have always been ascribed to other luminescent centers, such as oxygen vacancies and residual strain during the growth process. Hence, this work supports that the blue in the PL spectra can be attributed to oxygen vacancy defects in the  $\text{SnO}_2$ . The second band emission centered around 515 nm. This peak's origin was also discussed in Fu et al. research<sup>20</sup> and Baruah et al. report.<sup>21</sup> According to them, the similar broad green emission centered at 520 nm in  $\text{Zn}_2\text{SnO}_4$  under Xenon lamp excitation was caused by oxygen vacancy in  $\text{Zn}_2\text{SnO}_4$  during the growth process. Moreover, Smilja et al. said that the 546 nm emission in  $\text{ZnO/SnO}_2$  spectra were that green emission implicates surface defects, as well as the defects just below the crystalline surface.<sup>22</sup> So we suggest that the emission centered at 515 nm observed in PL spectra relates to oxygen

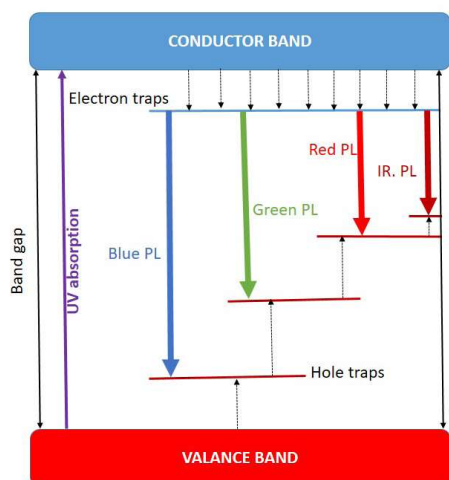
vacancies in  $\text{Zn}_2\text{SnO}_4$ . Next, the third peak is in the yellow-orange region centered at 580 nm, which may attribute to  $\text{SnO}_2$  defects such as Zn interstitials ( $\text{Zn}_{\text{ni}}$ ) or oxygen interstitials ( $\text{O}_{\text{i}}$ ).<sup>8</sup> The two final peaks are red and far-red, centered at 680 nm and 740 nm, which have not been observed and discussed in previous reports. We suggest that they may relate to surface defects of the obtained sample,<sup>23</sup> but the exact type and number of defect states depend on the method and parameters changing in the process.

Regarding the origin of the red emission band, Fu et al.<sup>20</sup> approved that stoichiometry Zn/Sn played a role in this emission. Furthermore, the red emission centered at 630 nm in  $\text{SnO}_2$  PL spectra reported by Smilja et al.<sup>22</sup> was considered related to deep-level defects within the gap of  $\text{SnO}_2$ , associated with oxygen vacancies and Sn interstitial formed during the synthesis procedure. The origin of this emission is still unclear and needs another measurement. Nevertheless, we agree with Chih-Hsien Cheng

et al.<sup>23</sup> that the origin of the infrared 700 nm in his research is related to the transition states between neutral and ionized oxygen. In addition, from what is discussed above and what is shown in PL spectra, we propose a diagram to explain the PL mechanism as shown in Figure 5. We believe defects formed during the calcination process play as energy states within the band gap. Hole traps are states that exit just over the valance band and fill holes, whereas electron traps are formed just under the conductor band and fill with electrons. The PL mechanism can be proposed as the following explanation. First, electrons from the valance band absorb excited energy as large as band gap energy and move to the conductor band to become excited electrons. Because the electron traps are just under the conductor band, excited electrons are trapped in electron traps easily without light-emitting. After that, these electrons release to lower energy states and depend on the gap between the two states that emit blue, green, red, or infrared.<sup>24</sup>



**Figure 4.** PL spectra of the  $\text{Zn}_2\text{SnO}_4-\text{SnO}_2$  phosphor annealed at different calcination temperatures (a) and PL of the sample annealed at 1100 °C fitted by Gaussian peak (b). The inset of the Figure a is the relative intensity of the  $\text{Zn}_2\text{SnO}_4-\text{SnO}_2$  phosphor annealed at different calcination temperatures.



**Figure 5.** Proposed energy band diagram for expalination PL machanism of  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  sample showing the defect states and the transitions between the states.

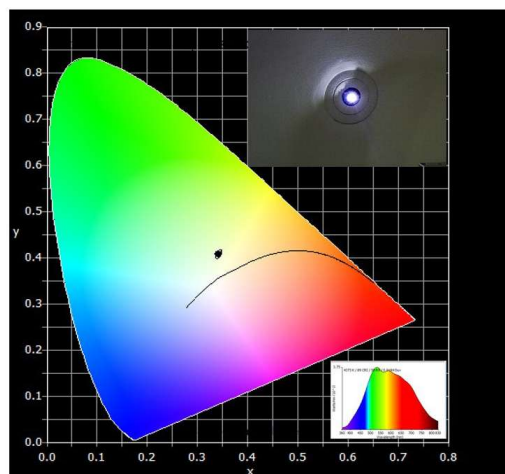
### 3.4. Electroluminescence properties of $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$ micro composite

In order to explore the potential application of  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  powder annealed at  $1100^\circ\text{C}$ ,

white emission LED is assembled by coating 5 mg of  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  phosphor on an LED chip 310 nm by the i-DR S320A Desktop Dispensing system. The image of the white LED device underdrive current of 0.2004 A and a voltage of 8.029 V during the process, and its CIE chromaticity coordination is displayed in Figure 6. The  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  powder annealed at  $1100^\circ\text{C}$  was covered on. The device was then introduced into an integrating sphere system to calculate parameters related to the quality of WLED as shown in Table 1. Figure 6 demonstrates that the CIE coordinates and CRI of White LED are (0.3755; 0.4173) and 95, respectively, which are very close to natural light. The colour temperature is 4273 K, which is energizing and most closely mimics natural daylight; it helps with tasks requiring focused attention, such as reading, computer work, carpentry, and drawing. These results demonstrate that  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  micro composite phosphor shows a potential application in producing high both CRI and LER White LED.

**Table 1.** The WLED parameters ( $D_{uv}$ ; Correlated colour temperature (CCT); Colour rendering index (CRI); Luminous efficacy of radiation (LER);  $R_9$  and CIE coordinates(x,y)) of LED covered phosphor.

| Sample                                   | LED parameters |         |     |            |       |        |        |
|------------------------------------------|----------------|---------|-----|------------|-------|--------|--------|
|                                          | $D_{uv}$       | CCT (K) | CRI | LER (lm/W) | $R_9$ | x      | y      |
| $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$ | 0.0194         | 4273    | 95  | 85         | 94    | 0.3755 | 0.4173 |



**Figure 6.** CIE 2015-10° xy color chromaticity coordinates of the spectral emission from UV LED chip coated by prepared phosphor. The insets is the electroluminescence spectrum and the image captured by a digital camera of the white-emitting LED.

#### 4. CONCLUSION

The  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  micro composite was produced successfully by solid-state reaction followed by calcination at 1100 °C in air. The crystalline structure of samples was mixed of the cubic phase  $\text{Zn}_2\text{SnO}_4$  (JCPDS card no. 00-024-1470, space group Fd-3m (227) and cell parameters  $a = b = c = 8.657 \text{ \AA}$ ) and Tetragonal phase  $\text{SnO}_2$  (JCPDS card no. 00-021-1250, space group P42/mm (136) and cell constants  $a = b = 4.738 \text{ \AA}$  and  $c = 3.188 \text{ \AA}$ ). PL spectra of all samples show a broad visible band from 400 to 900 nm, nearly covering the full visible range of blue–far–red emission with peaks at around 450, 515, 580, 680, and 740 nm. A PL mechanism diagram has been proposed to explain the emission's origin. The LED chip 310 was used to cover obtained phosphor, getting a white LED. The CIE coordinates and CRI of White LED are (0.3755;0.4173) and 95, respectively. These results demonstrate that  $\text{Zn}_2\text{SnO}_4 - \text{SnO}_2$  micro composite phosphor is potentially applicable in producing high CRI White LED.

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