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# Tm<sup>3+</sup>; Yb<sup>3+</sup>:Zn<sub>2</sub>TiO<sub>4</sub> near infrared to blue upconversion phosphors for anti-counterfeit applications

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Tm<sup>3+</sup>; Yb<sup>3+</sup>:Zn<sub>2</sub>TiO<sub>4</sub> samples have been synthesized using a solid state reaction route. The phase, lattice parameters, crystallite size has been examined using X-ray Diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). An intense peak of Yb<sup>3+</sup> codoped samples is observed near ~957 nm due to the <sup>2</sup>F<sub>7/2</sub> → <sup>2</sup>F<sub>5/2</sub> transition in diffuse reflectance spectra (DRS), which confirms the presence of Yb<sup>3+</sup> ion in the prepared compound. The optical band gap of Yb<sup>3+</sup> codoped samples has been calculated using Kubelka–Munk function. The Raman spectra corresponds to incorporation of Tm<sup>3+</sup>/Yb<sup>3+</sup> at the octahedral and tetrahedral site of the spinel host. The emission spectra recorded by using 370 nm excitation wavelength shows intense blue colour band corresponding to the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition of Tm<sup>3+</sup> ion. The upconversion (UC) emission spectra recorded by using 980 nm laser excitation source shows emission bands due to the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub>, <sup>1</sup>G<sub>4</sub> → <sup>3</sup>F<sub>4</sub> and <sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transitions of Tm<sup>3+</sup> ion in the host matrix lying in the blue, red and NIR regions respectively. There is effective enhancement of about ~35 times in the blue UC emission intensity with incorporation of Yb<sup>3+</sup> at 3% doping concentration in the prepared sample. The anti-counterfeit application of the optimized upconverting phosphor has been successfully demonstrated.

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## 1 Introduction

Studies of rare earths (REs) doped phosphors have gained considerable attention among material scientists due to their diversified applications in the field of *viz.* opto electronic devices, light emitting diodes, optical temperature sensors, high efficiency solar cells, anti-counterfeit security applications, finger print detection, *etc.*<sup>1–5</sup> As compared to research in organic luminescent materials, RE doped non-carbon oxides have several advantages *viz.* large Raman shifts, high optical stability, sharp emission spectra and cost-effective.<sup>6–8</sup> Doping RE in suitable luminescent hosts is always preferred for their multi-colour emission and colour tuning property.<sup>9,10</sup> Also, the lanthanide ions because of their large electronic configuration, consist of many energy states, some of which have longer life-time, hence by using the different external excitation sources, a series of optical transitions can be monitored.<sup>11,12</sup>

The luminescent property of a material is investigated by optical mechanism of upconversion (UC) and downshifting

(DS). UC is a non-linear optical process to create high energy photons using excitation from two or more lower energy photons. DS is the reverse process of UC in which a high frequency photon is converted into low frequency photons.<sup>3,4</sup> Through literature survey, it has been noticed that emission intensity of upconverting materials can be improved by codoping with suitable sensitizers.<sup>13,14</sup> One of the sensitizer widely used by researchers is Yb<sup>3+</sup> ion. Due to small shielding of the outer electrons, Yb<sup>3+</sup> ions strongly interact with neighbouring ions and the absorption cross-section of Yb<sup>3+</sup> ions in the near-infrared source is large, hence it easily transfers energy to activator ions in the host matrix.<sup>15,16</sup>

Nowadays, anti-counterfeit technology is widely used in classified documents, currency notes, identity cards verification, *etc.*<sup>17,18</sup> These applications are very relevant in public offices and business organizations.<sup>3</sup> Near infrared to visible luminescent materials explored as anti-counterfeit security ink are more reliable and difficult to replicate. Since upconverting materials can be designed to produce selective emission colours by suitable choice of host and dopants.<sup>19–21</sup>

Among the suitable hosts, Zn<sub>2</sub>TiO<sub>4</sub> have inverse spinel structure with the standard chemical formula B<sub>2</sub>AO<sub>4</sub>. It can also be written as B<sub>T</sub>(AB)<sub>O</sub>O<sub>4</sub>, where T in the subscript denotes tetrahedral sites and O signifies octahedral sites. Half of Zn<sup>2+</sup> cations and all of Ti<sup>4+</sup> cations occupy octahedral sites and another half of Zn<sup>2+</sup> cations occupy tetrahedral sites. O<sup>2–</sup> is an oxygen anion having six and four coordination with the cations

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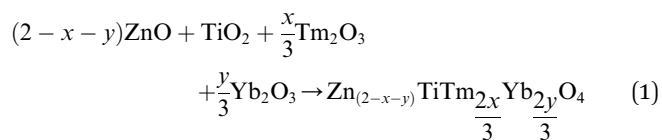

in the base compound.<sup>22</sup> The physical and electrical properties of  $\text{Zn}_2\text{TiO}_4$  have been investigated by various researchers.<sup>23,24</sup> But, studies of REs doped  $\text{Zn}_2\text{TiO}_4$  as luminescent material for applications in NIR to efficient blue frequency upconversion and anti-counterfeit is for the first time to the best of our knowledge.

In the present work,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}:\text{Zn}_2\text{TiO}_4$  luminescent materials have been synthesized by using the solid state reaction technique. The structural properties of the prepared samples have been explored using X-ray diffraction (XRD), High resolution transmission electron microscopy (HRTEM), Raman and diffuse-reflectance spectroscopy. The effect of  $\text{Yb}^{3+}$  codoping on UC and DS has been studied using UV and near-infrared excitation sources. The vacant states created due to doping and codoping of  $\text{RE}^{3+}$  ions ( $\text{Tm}^{3+}$ ;  $\text{Yb}^{3+}$ ) at the A-site and B-site of the spinel have been studied using electron paramagnetic resonance (EPR) spectroscopy. The anti-counterfeit security application has been demonstrated in the present investigation.

## 2 Experimental

### 2.1 Materials and methods for $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$ , $\text{Yb}^{3+}$ synthesis

The  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}:\text{Zn}_2\text{TiO}_4$  inverse spinel materials have been synthesized by using solid state reaction method. The precursors  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{Tm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  were mixed in stoichiometric proportion in agate mortar for 2 hours. The host raw materials *i.e.*  $\text{ZnO}$  and  $\text{TiO}_2$  have been taken from Merck (99.0% purity) and the dopants  $\text{Tm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  from Sigma Aldrich (99.9% purity). The homogeneous mixture was kept in the alumina crucible and the samples were annealed in an electric furnace at 800 °C for 24 hours. The annealed samples were again grind in the agate mortar for 30 minutes and used for structural, luminescence and EPR studies. The balanced chemical reaction is presented as follows:



For the synthesis of codoped  $\text{Zn}_2\text{TiO}_4$  crystals,  $\text{Tm}_2\text{O}_3$  ( $x$ ) optimized is fixed at 1 mol% and  $\text{Yb}_2\text{O}_3$  ( $y$ ) is varied as 1 mol%, 3 mol% and 5 mol%.

### 2.2 Measurements and characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using Rigaku D/Max 2200 with Cu  $K_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the diffraction angle range of 20° to 80° at a scanning rate of 0.02° min<sup>-1</sup>. The surface morphology and particle size of the doped/codoped  $\text{Zn}_2\text{TiO}_4$  phosphors compound has been analyzed using high resolution transmission electron microscopy (HR-TEM) JEM-2100F. The energy dispersive X-ray (EDX) measurement has been recorded using Field emission scanning electron microscopy (FESEM) Supra 55 with an air lock chamber. The diffuse reflectance spectra of the prepared phosphors have been analysed employing Cary series (5000) UV-

vis-NIR spectrophotometer. UC emission study has been performed with a Princeton triple turret grating monochromator associated with a photomultiplier tube (PMT) upon excitation with a 980 nm continuous wave (CW) laser diode. The emission and excitation spectra are recorded by using a 'Lifetime Spectrometer' upon excitation with a Xenon arc lamp. Raman spectroscopy analysis has been carried out by Horiba scientific (LabRAM HR-UV-Open) Raman Spectrometer. EPR spectrum of the prepared phosphors has been performed by a conventional Bruker EMX spectrometer operating at X-band frequency of 9.446 GHz. All characterizations have been performed at room temperature (~28 °C). The lifetime measurement was recorded by Horiba PTI Quanta-master for the study of decay curves.

## 3 Results and discussion

### 3.1 XRD studies

The phase and lattice parameters of the prepared phosphors  $\text{Zn}_{(2-x-y)}\text{TiTm}_{\frac{2x}{3}}\text{Yb}_{\frac{2y}{3}}\text{O}_4$  have been investigated using XRD at room temperature. Fig. 1 depicts the XRD patterns of the prepared phosphors corresponding to Xpert High Score plus reference no. 98-010-9093 of tetragonal phase with space group  $P4_122$  and space group number 91. The most prominent peak observed for Yb-0%, Yb-1%, Yb-3% and Yb-5% near 35.29°, 35.29°, 36.35° and 35.23° respectively. No individual peaks of  $\text{Tm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  are observed in the XRD study of the prepared samples. This indicates single tetragonal phase of the prepared compound. The inset of Fig. 1 shows the shift in the most intense Bragg's diffraction angle ( $2\theta$ ) with increase in doping of  $\text{Yb}^{3+}$  ions in the host matrix. The shift in XRD peak and change in lattice parameters with incorporation of  $\text{Yb}^{3+}$  ion in the  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$  is due to difference in ionic radius of  $\text{Yb}^{3+}$  (0.97 Å) and  $\text{Zn}^{2+}$  (0.74 Å). Though the ionic radius of  $\text{Tm}^{3+}$  (0.96 Å) is comparable to  $\text{Yb}^{3+}$ , the increase in doping concentration of  $\text{Yb}^{3+}$  is attributed to lattice strain for the substitutional occupancy of  $\text{Yb}^{3+}$  ion in the tetrahedral and octahedral site of  $\text{Zn}^{2+}$  in the host. The calculated lattice parameters of the prepared samples are presented in Table 1. The crystallite size of the prepared samples are calculated using Scherrer formula<sup>25</sup>

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

where,  $\lambda = 0.154 \text{ nm}$  is the wavelength of Cu  $K_\alpha$  radiation,  $\theta$  denotes the Bragg's diffraction angle with respect to crystal plane and  $\beta$  is the full-width at half maximum for specific diffraction peak (Table 1). The crystallite sizes, calculated from Hall-Williamson (WH) relation,<sup>26</sup> are 32.71 nm, 36.45 nm, 41.67 nm, 32.14 nm for  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$  (1%) and  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$ (1%),  $\text{Yb}^{3+}$ (0%, 1%, 3%, 5%) samples.

It is clear from Table 1 that the average crystallite size increases with increase in doping concentration of  $\text{Yb}^{3+}$  from 0% to 3% and again decreases for 5% doping. The change in volume of the unit cell is related to density and optical transparency of the crystal.<sup>27</sup> The difference in cationic radius of  $\text{Yb}^{3+}$  and  $\text{Zn}^{2+}$  ions produces internal strain and this may shift crystal



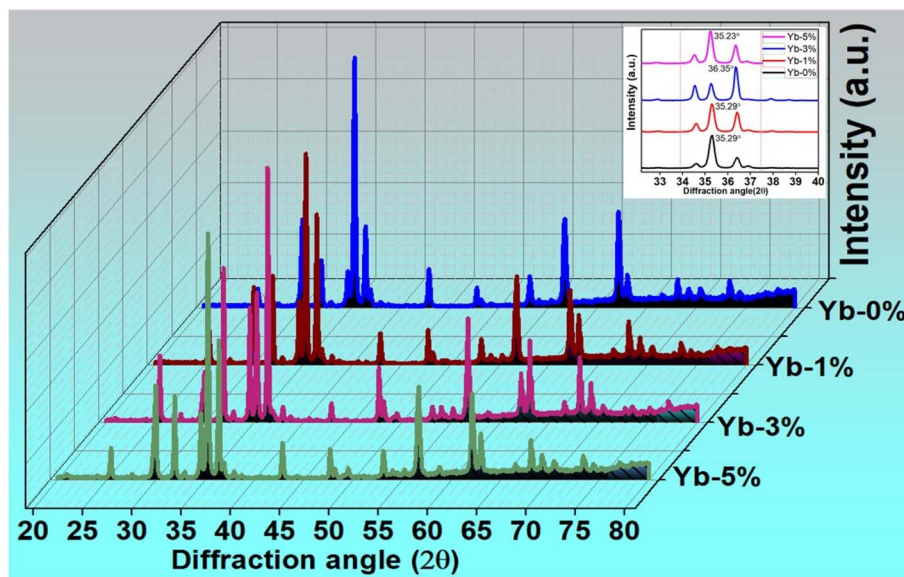


Fig. 1 XRD patterns of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoped  $\text{Zn}_2\text{TiO}_4$  phosphors. The inset shows the diffraction peak shift with increase in doping concentration of  $\text{Yb}^{3+}$  ion in the host.

Table 1 Lattice parameters, energy band gap within the parenthesis and average crystallite size for the optimized doped/codoped  $\text{Zn}_2\text{TiO}_4$ :-  $\text{Tm}^{3+}/\text{Yb}^{3+}$  phosphors

Phosphors	<i>a</i> (Å)	<i>c</i> (Å)	Cell volume (Å <sup>3</sup> )	Av. cryst. size (nm)
$\text{Zn}_{1.99}\text{TiTm}_{0.0067}\text{O}_4$ (3.88 eV)	6.042	8.409	306.977	32.21
$\text{Zn}_{1.98}\text{TiTm}_{0.0067}\text{Yb}_{0.0067}\text{O}_4$ (3.93 eV)	5.962	8.422	299.364	36.03
$\text{Zn}_{1.96}\text{TiTm}_{0.0067}\text{Yb}_{0.02}\text{O}_4$ (3.78 eV)	5.993	8.416	302.276	41.24
$\text{Zn}_{1.94}\text{TiTm}_{0.0067}\text{Yb}_{0.033}\text{O}_4$ (3.86 eV)	6.003	8.377	301.874	32.50

boundaries which rearranges the grain size of the system and alters the crystallite structure of the prepared phosphors.

### 3.2 Surface morphological and EDX study

The surface morphology of the optimized sample  $\text{Zn}_{1.96}\text{TiTm}_{0.0067}\text{Yb}_{0.02}\text{O}_4$  ( $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%/Yb}^{3+}\text{-3\%}$ ) is presented in Fig. 2. The high resolution transmission electron microscopy (HR-TEM) images in two scales are depicted in Fig. 2 (a) 50 nm (b) 0.2  $\mu\text{m}$ . It is clear from these images that some dark spot is observed which confirms the presence of dopants  $\text{Tm}^{3+}$  ions and  $\text{Yb}^{3+}$  ions in the prepared compound. Fig. 2c shows the particle size distribution of the optimized sample. The average particle size calculated using image J software employing normal distribution in histogram is 145.66 nm. The crystallinity of the prepared phosphor is investigated from selected area electron diffraction (SAED) pattern shown in Fig. 2d. The circular white spots corresponding to different diameters of the circle is formed by the electron beam's diffraction at regular lattice points of the unit cell. The miller indices of the different planes of the crystal structure are labelled in Fig. 2d. The miller indices calculated using image J software resembles XRD analysis discussed in the section 3.1. The *d*-spacing of the plane (1 2 1) evaluated using integral

transformation property of direct and inverse fast Fourier transform (FFT) in the SAED pattern illustrated in Fig. 2e is 3.37 Å. The elements present in the prepared phosphors can be detected by studying EDX spectrum. The EDX spectra, colour mapping of the corresponding spectra and elemental distribution of the prepared phosphors  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%}$  (a)  $\text{Yb}^{3+}\text{-0\%}$  (b)  $\text{Yb}^{3+}\text{-1\%}$  (c)  $\text{Yb}^{3+}\text{-3\%}$  and (d)  $\text{Yb}^{3+}\text{-5\%}$  is presented in Fig. 3. It is evident that Zn, Ti, Tm, Yb and O elements are present in the doped/codoped phosphors. The inset table in Fig. 3a–d reflects the elemental compositions in wt% and at% observed in the scanning region of the EDX instrument. It is evident from at% values shown in the inset of Fig. 3b–d that Tm : Yb are nearly of the ratios 1 : 1, 1 : 3 and 1 : 5 respectively which confirms the homogeneity and molar mixing composition of the dopants/codopants in the host.

### 3.3 Optical diffuse reflectance and Raman analysis

The diffuse reflectance spectra (DRS) of the prepared phosphors are recorded in the range of 200–1600 nm with respect to the reference of  $\text{BaSO}_4$  (Fig. 4a). In the prepared phosphors peak bands for  $\text{Tm}^{3+}$  ion are observed at  $\sim 296$  nm,  $\sim 688$  nm,  $\sim 787$  nm and  $\sim 1202$  nm corresponding to the  $^3\text{H}_6 \rightarrow ^1\text{D}_2$ ,  $^3\text{H}_6 \rightarrow ^3\text{F}_{2,3}$ ,  $^3\text{H}_6 \rightarrow ^3\text{H}_4$  and  $^3\text{H}_6 \rightarrow ^3\text{H}_5$  transitions respectively.<sup>28</sup>





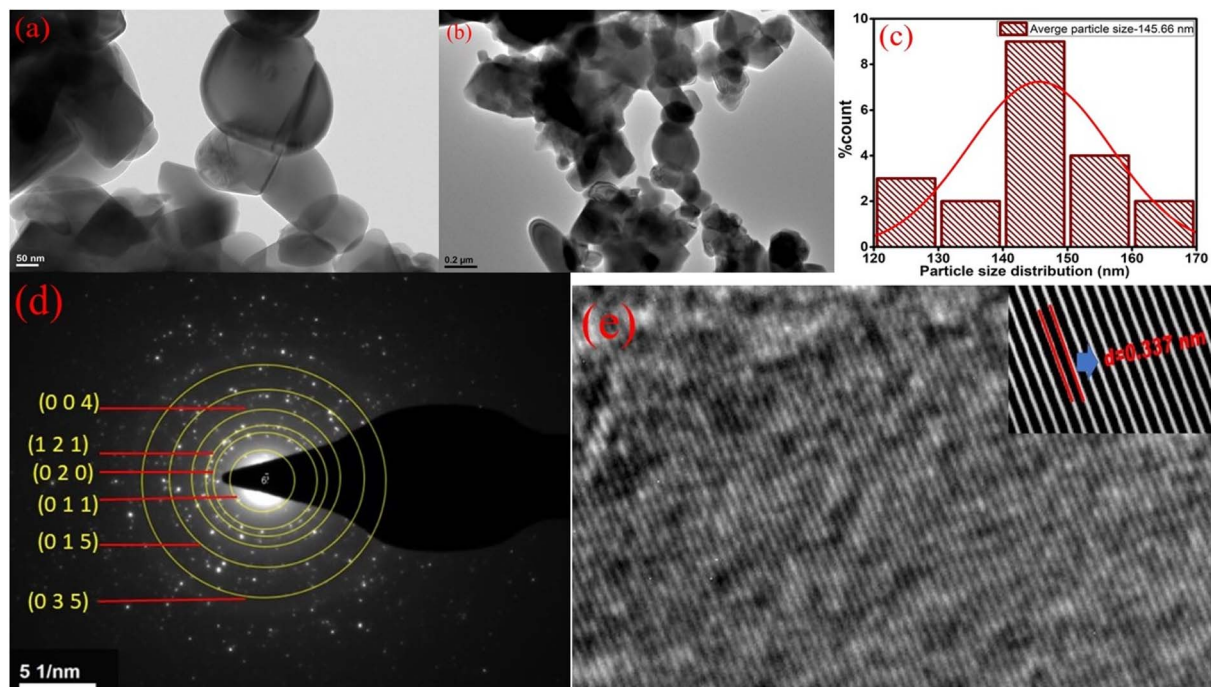


Fig. 2 HR-TEM images of the optimized sample  $\text{Zn}_{1.96}\text{TiTm}_{0.0067}\text{Yb}_{0.02}\text{O}_4$  in (a) 50 nm (b) 0.2  $\mu\text{m}$  resolution (c) Histogram depicts the particle size distribution (d) SAED pattern with miller indices labelled across different planes (e) FFT pattern representing  $d$ -spacing of the (1 2 1) plane.

An intense peak of  $\text{Yb}^{3+}$  ion in the codoped samples is observed in Fig. 3a(ii), (iii) and (iv)) near  $\sim 957$  nm due to the  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition.<sup>29</sup>

The optical band gap of the  $\text{Yb}^{3+}$  doped and undoped  $\text{Zn}_2\text{-TiO}_4\text{:Tm}^{3+}$  phosphor can be evaluated from the DRS spectra using the well-known Kubelka–Munk (KM) theory.<sup>30</sup> The KM

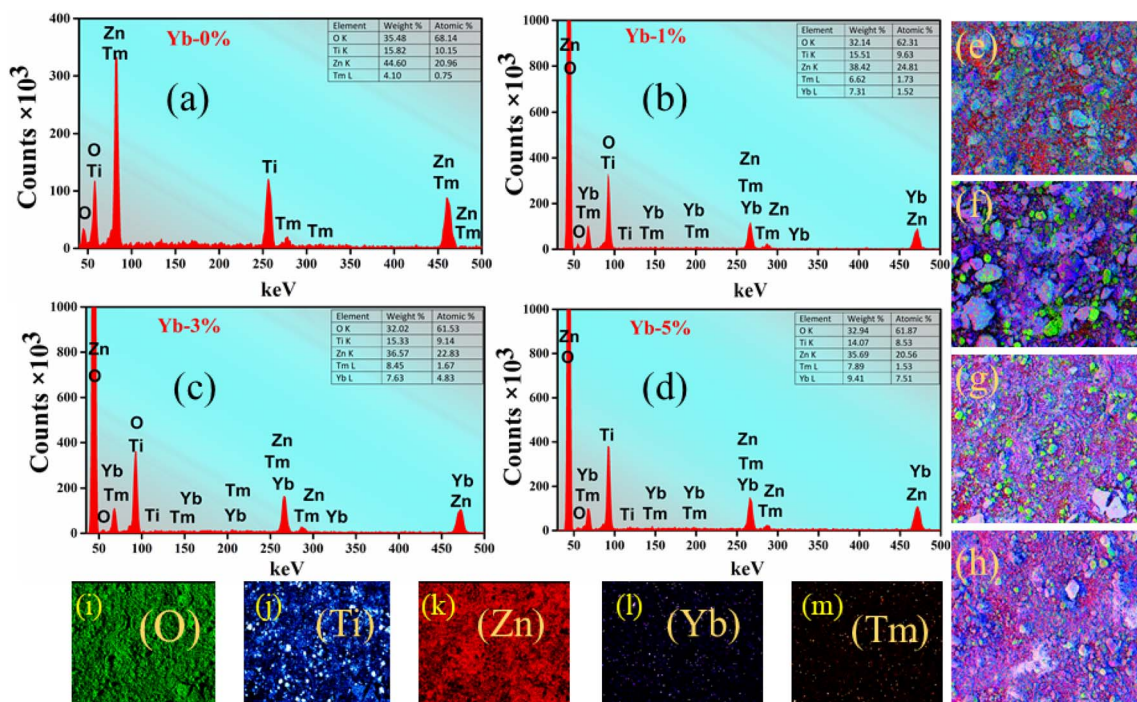


Fig. 3 (a)–(d): EDX spectrum of the prepared phosphors; (e)–(h): corresponding EDX colour mapping; (i)–(m): elemental distribution represented in parenthesis of the prepared phosphors  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}$ ,  $\text{Yb}^{3+}$ .

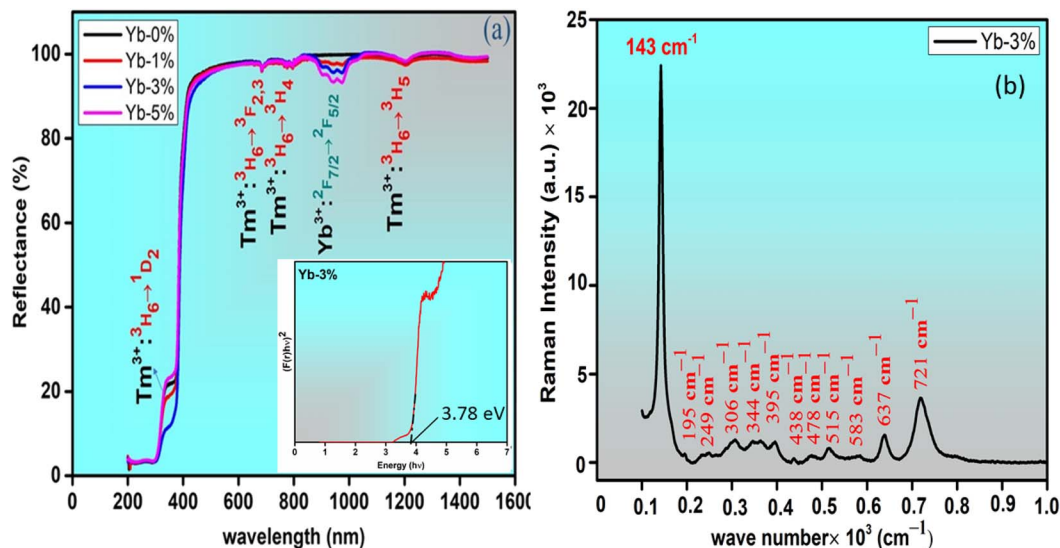


Fig. 4 (a) Diffuse reflectance spectra of (i) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-0% (ii) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-1% (iii) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-3% (iv) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-5%. The inset shows the optical band gap of the optimized phosphors Zn<sub>1.96</sub>TiTm<sub>0.0067</sub>Yb<sub>0.02</sub>O<sub>4</sub> (Yb-3%) using Kubelka-Munk function (b) Raman spectrum of the optimized sample.

function  $F(R_{\infty})$  i.e. the reflectance with respect to a reference for each observed wavelength can be mathematically expressed as,

$$F(R_{\infty}) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \quad (3)$$

where, 'R' is the diffuse reflectance ratio of the observed spectrum, 'K' is the absorption coefficient and 'S' denotes coefficient of scattering. The well known Tauc relation<sup>31</sup> used to evaluate the optical band gap 'E<sub>g</sub>' is given by,

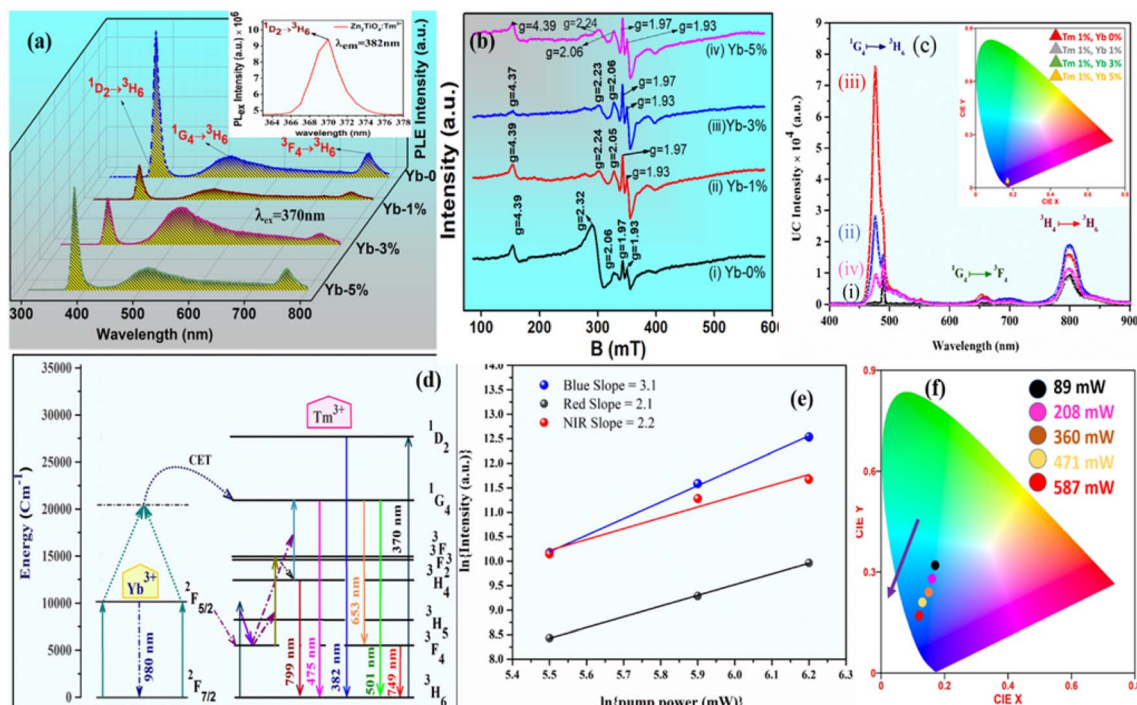


Fig. 5 (a) PL emission spectra at 370 nm excitation wavelength. The inset represents the excitation spectrum of Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup> phosphor at 382 nm emission. (b) and (c) represents the EPR intensity and UC emission spectra of the powder samples (i) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-0% (ii) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-1% (iii) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-3% (iv) Zn<sub>2</sub>TiO<sub>4</sub>:Tm<sup>3+</sup>-1%, Yb<sup>3+</sup>-5% respectively recorded at room temperature. The inset of (c) shows the CIE plot of UC emission intensity. (d) Schematic energy level diagram (e) pump power dependence study of Tm<sup>3+</sup>-Yb<sup>3+</sup> codoped Zn<sub>2</sub>TiO<sub>4</sub> phosphors (f) The corresponding CIE plot of the pump power variation in the optimized sample.



$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

where, ' $\alpha$ ' is the absorption coefficient. ' $A$ ' is the constant of proportionality and ' $h\nu$ ' is the energy of incident light in eV, ' $n$ ' is the exponential constant which depends upon the nature of electronic transitions. Using eqn (3) and (4), the diffuse reflectance spectrum can be expressed in terms of following KM function  $F(R_\infty)$ ,

$$[h\nu F(R_\infty)]^2 = A(h\nu - E_g) \quad (5)$$

Using eqn (5), the band gaps  $E_g$  for (i)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-0\%}$  (ii)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-1\%}$  (iii)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  (iv)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-5\%}$  are 3.88 eV, 3.93 eV, 3.78 eV and 3.86 eV respectively (Table 1). It is clear from Table 1 that there is no direct correlation between average crystallite size and energy band gap of the prepared samples. The decrease in band gap is related to increase in crystallinity of the prepared samples and increase in band gap may be due to higher values of direct and/or indirect band gap of  $\text{Yb}_2\text{O}_3$ .<sup>31</sup> This may be due to interstitial occupancy or agglomeration of  $\text{Yb}^{3+}$  ion about the grain boundary in the host matrix. This is consistent with the observations of the HR-TEM images presented in different resolutions in Fig. 2.

The Raman intensity as a function of Raman frequency ( $\text{cm}^{-1}$ ) of the optimized sample  $\text{Zn}_{1.96}\text{TiTm}_{0.0067}\text{Yb}_{0.02}\text{O}_4$  is illustrated in Fig. 4b. The intensity is plotted in the range of 100 to  $1200\text{ cm}^{-1}$ . The inverse spinel zinc titanate of the form  $\text{B}_2\text{AO}_4$  has the chemical formula  $\text{Zn}_2\text{TiO}_4$  which can also be written as  $[(\text{ZnTi})\text{ZnO}_4]$  with 56 atom unit cell. All Zn ions and half of Ti ions within the parenthesis occupy octahedral site and other half of Ti ions occupy tetrahedral site.

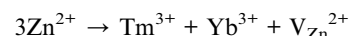
The most intense mode near  $\sim 143\text{ cm}^{-1}$  is due to  $\text{B}_{1g}$  mode of rutile  $\text{TiO}_2$ .<sup>32</sup> A low intense mode near  $\sim 195\text{ cm}^{-1}$  may be due to translation motion/free rotation of  $\text{Tm}^{3+}$  ion at the octahedral site of the crystal structure.<sup>33</sup> The  $\text{E}_g$  mode near  $\sim 306\text{ cm}^{-1}$  may be due to vibration of  $\text{TiO}_6/\text{ZnO}_6$  which signifies local lattice effects in the octahedral sites.<sup>34</sup> The intense peak near  $\sim 438\text{ cm}^{-1}$  is due to  $\text{E}_2$  mode of  $\text{ZnO}$ .<sup>32</sup> Similarly, the peak at  $\sim 583\text{ cm}^{-1}$  is due to  $\text{E}_1$  mode of  $\text{ZnO}$ .<sup>32</sup> The peak near  $\sim 438\text{ cm}^{-1}$  is attributed to  $\text{A}_{1g}$  mode of tetragonal  $\text{Zn}_2\text{TiO}_4$ . It corresponds to vibration of  $\text{ZnO}_4$  mode which reflects the local lattice effects in the tetrahedral sublattice.<sup>32,34</sup> The peaks near  $(395, 515, 637)\text{ cm}^{-1}$  is related to  $\text{Tm-O}$  stretching.<sup>33</sup> Unlike in other Raman studies, the peak of  $\text{B}_{2g}$  mode of rutile  $\text{TiO}_2$  near  $\sim 826\text{ cm}^{-1}$  is absent in the present investigation. The different Raman active modes observed in the present study of the optimized sample confirms the incorporation of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  in the host  $\text{Zn}_2\text{TiO}_4$ .

### 3.4 Photoluminescence and EPR studies

The photoluminescence (PL) emission spectra of the prepared phosphors at (i)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-0\%}$  (ii)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-1\%}$  (iii)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  (iv)  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-5\%}$  observed at excitation wavelength  $\sim 370\text{ nm}$  is depicted in Fig. 5a. The emission spectra exhibit peaks near  $\sim 382\text{ nm}$ ,  $\sim 501\text{ nm}$  and  $\sim 749\text{ nm}$  corresponding to the  $^1\text{D}_2 \rightarrow$

$^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  and  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  transitions of the  $\text{Tm}^{3+}$  ion.<sup>35</sup> The excitation spectra consists of band peaking near  $\sim 370\text{ nm}$  related to the  $^1\text{D}_2 \rightarrow ^3\text{H}_6$  transition.<sup>35</sup> The maximum photoluminescence emission (PLE) intensity is observed for  $\text{Tm-1\%, Yb-0\%}$  sample. This confirms self-quenching of the activator  $\text{Tm}^{3+}$  ions in the host. There can be various reasons for quenching phenomenon in the present investigation.<sup>36</sup>

(i) The ionic radius of  $\text{Tm}^{3+}$  is comparable with  $\text{Yb}^{3+}$  ion. With increase in doping concentration of  $\text{Yb}^{3+}$  ion from 0% to 5%, electron captured zinc vacancies are created in the host matrix. The well known phenomenon of self-trapping of electrons may be induced to maintain charge neutrality of the compound which ultimately decrease the PLE intensity.



(ii) The non-radiative energy transfer among  $\text{Yb}^{3+}\text{-Yb}^{3+}$  ions due to exchange interaction, radiative reabsorption or multipole-multipole interaction adversely affect the PLE intensity.

The critical distance ( $R_c$ ) evaluated using Blasse equation<sup>36</sup> is found to be  $29.99\text{ \AA}$ . This value of  $R_c$  indicates multipolar interaction. Further, after using the Dexter and Schulman theory to investigate the type of multipolar interaction,<sup>2,36</sup> the value of  $q$  obtained from graphical interpretation is about  $\sim 7.6$  which is near to 8. This shows that the dipole-quadrupole interaction is dominant among  $\text{Yb}^{3+}$  ions.

Fig. 5b shows the EPR spectra of the powder samples  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}/\text{Yb}^{3+}$  recorded at room temperature. The EPR spectra of  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}$  phosphors exhibit a number of resonance signals of varying intensity with effective  $g$ -values near  $\sim 4.39, 2.32, 2.06, 1.97$  and  $1.93$  shown in Fig. 5b(i). With incorporation of  $\text{Yb}^{3+}$  ion in the host, shift of resonant peaks is noticed attributed to  $g$ -values near  $\sim 4.39, 2.24, 2.05$ . No change has been seen in the position of EPR peaks for  $g \sim 1.97$  and  $1.93$ . Interestingly there is no change in peak position with increase in doping concentration of  $\text{Yb}^{3+}$  ion from 1 mol% to 5 mol%. It is ascertain from Fig. 4b that there are large number of resonance signals with different  $g$ -values due to diversified crystal field interaction of the rare earth (RE) dopants  $\text{Tm}^{3+}/\text{Yb}^{3+}$  at different site-symmetry with different coordination numbers in the host.<sup>37</sup> The EPR signals of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  ions remain unresolved at room temperature due to short spin-lattice relaxation time.<sup>38</sup> Hence all resonance signals observed in Fig. 5b are related to zinc and oxygen vacancies created by RE dopants at the Zn-site of the inverse spinel structure  $\text{Zn}_2\text{TiO}_4$ . Further, the peak shift observed in Fig. 5b(ii) is only for  $g$  values greater than 2. This is due to increase in Zn vacancies with doping of  $\text{Yb}^{3+}$  ion at the Zn site of the host, which modifies the crystal field interaction of the RE dopants and/or exchange interaction of  $\text{Yb}^{3+}\text{-Yb}^{3+}$  ions in the host matrix.<sup>39-41</sup> The  $g$  values less than 2 are related to oxygen vacancies.<sup>42</sup> There is no evidence of dipolar broadening with increase in doping concentration of  $\text{Yb}^{3+}$  ions in the host. This is coexistent with the experimental findings of the PL study discussed earlier. There is strong correlation between  $g$  values near  $\sim 4.39$  with the average crystallite size calculated in Table 1. The resonant intensity of the EPR signals



decrease at this  $g$ -value from Yb-0% to Yb-3% and again starts to increase for Yb-5%, similar to the change in crystallite size with doping concentration of  $\text{Yb}^{3+}$  ion. As the crystallite size increases, there is decrement in  $d$ -spacing and EPR signal intensity also follows the same. This is consistent with the structural studies discussed in Section 3.1, that with increase in average crystallite size, relative concentration of vacancies decreases.<sup>43</sup>

### 3.5 Upconversion, pump power studies, lifetime measurements and demonstration of security ink for anti-counterfeit applications

The upconversion (UC) emission spectra for all the developed  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$  phosphors upon 980 nm laser diode excitation have been recorded and represented in Fig. 4c. For all the prepared doped and codoped phosphors three UC emission bands peaking at  $\sim 476$  nm (blue),  $\sim 662$  nm (red),  $\sim 799$  nm (NIR) corresponding to the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$  and  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transitions respectively have been observed in the 400–900 nm wavelength range.<sup>35</sup> It is worthwhile to mention that the intense blue UC emission coming from the  $\text{Tm}^{3+}\text{-Yb}^{3+}$  codoped phosphors can be clearly visible in the natural environment. From Fig. 5c, it is clear that the blue UC emission band for  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  codoped phosphors is more intense as compared to the other doped/codoped phosphors.

An improvement in the blue UC emission intensity around  $\sim 35$  times for  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  as compared to  $\text{Zn}_2\text{-TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-0\%}$  codoped phosphors has been observed in the present investigation. No additional peaks were observed in the emission study on the codoping of  $\text{Yb}^{3+}$  ions to the doped  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}$  ions system. The strongest blue UC emission produced by  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  phosphors is due to the better environment produced by the  $\text{Zn}_2\text{TiO}_4$  host around the dopants  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$  which avoid quenching process by preventing the creation of large number of RE ions clusters.<sup>5,35,44</sup>

This is compatible with the EPR investigation Fig. 5b reported in Section 3.4 of the present study. The schematic energy level diagram for the  $\text{Tm}^{3+}\text{-Yb}^{3+}$  ions to describe the complete information about the UC emission mechanism is shown in Fig. 5d. In the  $\text{Tm}^{3+}\text{-Yb}^{3+}$  codoped system upon 980 nm laser excitation;  $\text{Yb}^{3+}$  ion effectively absorbs 980 nm photons. Since the  $\text{Yb}^{3+}$  ion have large absorption cross-section corresponding to the  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition, it can effectively transfer its excitation energy to the  $\text{Tm}^{3+}$  ion through cooperative energy transfer (CET) process.<sup>44</sup> The  $\text{Yb}^{3+}$  ions after absorbing the 980 nm photons are excited from the ground state  $^2\text{F}_{7/2}$  to the excited state  $^2\text{F}_{5/2}$ . These excited  $\text{Yb}^{3+}$  ions transfers their excitation energy to the  $\text{Tm}^{3+}$  ions through ground state absorption (GSA). The  $\text{Tm}^{3+}$  ion present in the  $^3\text{F}_4$  state through excited state absorption (ESA) process gets promoted to  $^3\text{F}_2$  and then again to  $^1\text{G}_4$  energy levels. A part of the excited ions at  $^3\text{F}_2$  energy levels gets depopulated by non-radiative relaxation to the  $^3\text{H}_4$  state and then again radiatively relax by emitting a photon to the ground state ( $^3\text{H}_6$ ) at wavelength  $\sim 799$  nm. Further, a radiative transition of intense blue emission by depopulating the  $^1\text{G}_4$  state corresponding to  $\sim 475$  nm is observed. Some part of

the excited ions at  $^1\text{G}_4$  levels also radiatively relax by emitting photon of wavelength  $\sim 653$  nm to the  $^3\text{F}_4$  state. The  $\text{Yb}^{3+}$  ion may also absorb the pump excitation energy from 980 nm source and transit upward to a virtual state and then it may transfer the energy to populate the excited state at  $^1\text{G}_4$  level of the activator  $\text{Tm}^{3+}$  ion.

The CIE colour coordinate studies have been done for all the  $\text{Tm}^{3+}\text{-Yb}^{3+}$  doped/codoped  $\text{Zn}_2\text{TiO}_4$  phosphors. GoCIE software has been used to evaluate the colour co-ordinates with the help of recorded UC and PL emission spectra. The calculated colour coordinates for all the phosphors are presented in Table 2. All the coordinates of the prepared phosphors lie in the intense blue colour region. The CIE chromaticity diagram study suggests that the  $\text{Tm}^{3+}\text{-Yb}^{3+}$  codoped  $\text{Zn}_2\text{TiO}_4$  upconverting phosphors can be applied in blue colour light emitting devices.

In  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$  codoped  $\text{Zn}_2\text{TiO}_4$  phosphors, three UC emission bands at  $\sim 476$  nm (blue),  $\sim 662$  nm (red),  $\sim 799$  nm (NIR) corresponding to the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$ ,  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transitions respectively have been observed. The number of NIR photons responsible for these UC emissions can be evaluated

Table 2 Colour coordinates of the upconversion (UC) and downshifting (DS) fluorescence computed using CIE software of the prepared optical phosphors

Phosphors	Upconversion (UC)		Downshifting (DS)	
	X	Y	X	Y
$\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-0\%}$	0.15	0.31	0.22	0.59
$\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-1\%}$	0.12	0.16	0.23	0.66
$\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$	0.13	0.19	0.27	0.68
$\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-5\%}$	0.13	0.23	0.24	0.71

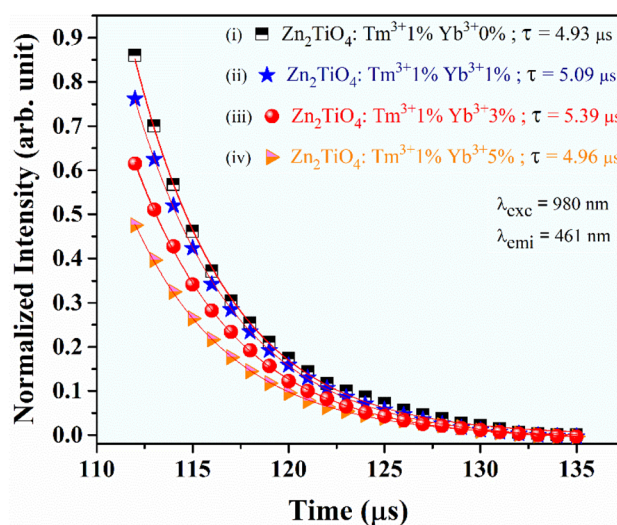


Fig. 6 Lifetime spectra of the  $^1\text{G}_4$  level of  $\text{Tm}^{3+}$  for the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  (461 nm) transition ( $\lambda_{\text{emi}} = 461$  nm) for all the doped/codoped (i)  $\text{Zn}_2\text{-TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-0\%}$  (ii)  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-1\%}$  (iii)  $\text{Zn}_2\text{TiO}_4:\text{-Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  (iv)  $\text{Zn}_2\text{TiO}_4:\text{Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-5\%}$  phosphors at 980 nm pulsed laser radiation.



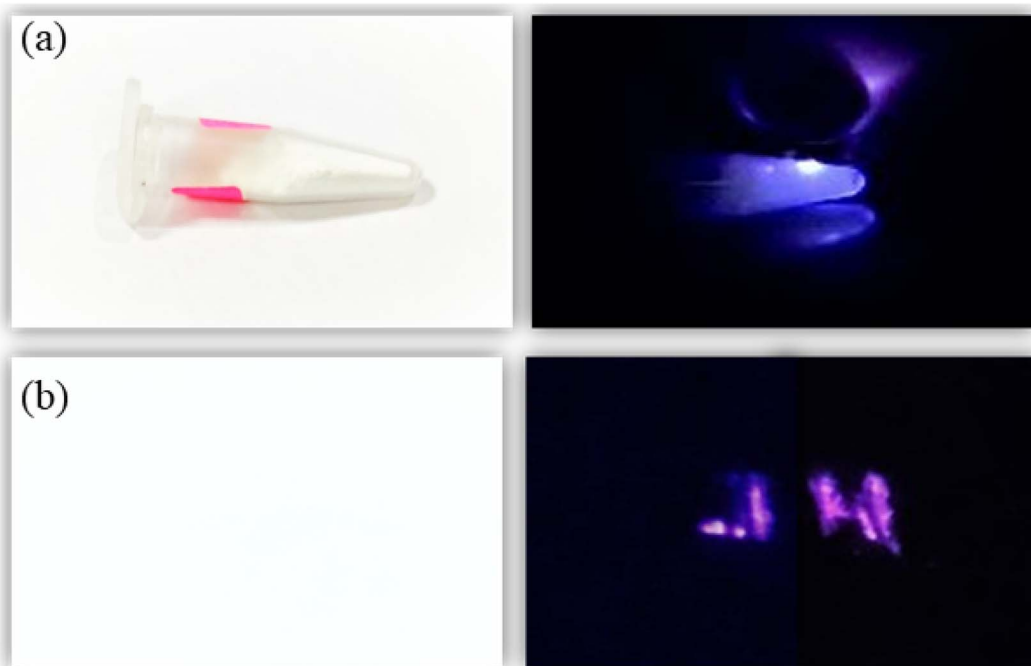


Fig. 7 (a) Optical image of the optimized  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  UC phosphors in day light condition, (b) anti-counterfeit illustration of some classified document coded with 'JH' under 980 nm CW laser excitation source.

graphically from the slope of the variation of UC intensity with respect to pump power using the well known mathematical relation<sup>45</sup>

$$I \propto p^n \quad (6)$$

where, ' $I$ ' is the UC emission intensity, ' $p$ ' is the pump power and ' $n$ ' is the number of NIR photons responsible for UC emission.

The slope values for the blue, red and NIR emissions are 3.1, 2.1 and 2.2 respectively and represented in Fig. 5e. In  $\text{Tm}^{3+}$ ;  $\text{Yb}^{3+}$  codoped phosphors,  $^3\text{H}_4$  and  $^1\text{G}_4$  levels of  $\text{Tm}^{3+}$  ions are populated by the active participation of two and three NIR photons respectively.<sup>45,46</sup> It is evident from the chromaticity diagram of Fig. 5f that with increase in pump power the colour coordinate shifts towards the blue region. Hence the prepared upconverting materials can be employed to develop blue emitting display devices.

To monitor the effect of  $\text{Yb}^{3+}$  ion on the luminescence dynamics, decay time behaviour of the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  (461 nm) transition of  $\text{Tm}^{3+}$  ions for the doped/codoped phosphors has been measured using the 980 nm pulsed laser excitation. Fig. 6 shows the fit of the experimental data to a first order exponential decay equation as<sup>47</sup>

$$I = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) \quad (7)$$

where ' $I$ ' is luminescence intensity at time ' $t$ ' and ' $I_0$ ' is the initial luminescence intensity, ' $A_1$ ' is constant and ' $\tau_1$ ' is the decay time.

The decay time of the  $^1\text{G}_4$  level corresponding to the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transition of  $\text{Tm}^{3+}$  ion is  $\sim 4.93 \mu\text{s}$ ,  $\sim 5.09 \mu\text{s}$ ,  $\sim 5.39 \mu\text{s}$  and

$\sim 4.96 \mu\text{s}$  for  $\text{Zn}_2\text{TiO}_4\text{:Tm}^{3+}\text{-1\%; Yb}^{3+}\text{-0\%, Yb}^{3+}\text{-1\%, Yb}^{3+}\text{-3\%}$  and  $\text{Yb}^{3+}\text{-5\%}$  respectively. The decay time of the  $^1\text{G}_4$  level thus increases with incorporation of  $\text{Yb}^{3+}$  ion from 1% to 3% doping in the host matrix. This is coexistent with the structural studies (Table 1) and experimental findings of the EPR observations studied in earlier sections. This confirms that along with the energy transfer process the improvement in average crystallite size is also responsible for an enhancement in the emission intensity of the codoped phosphors.<sup>30,47,48</sup>

Further, to demonstrate the anti-counterfeit security ink application, the optimized UC phosphor 20 mg ( $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}\text{:Zn}_2\text{TiO}_4$ ) is dissolved in 10 ml ethanol and sonicated at 50 kHz for 2 hours by ultra sonic probe to form good dispersion solution. After that 1 ml of aminopropyltriethoxysilane (APTES) is slowly added to the solution with continuous stirring at 400 rpm, 60 °C for 2 hours and then cooled at RT. After 12 hours aging, the solution was used to write as a security ink (Fig. 7). The letter "JH" which appears to be white is clearly visible upon 980 nm diode laser excitation. Thus, these unique security inks could also be used in printing labels of pharmaceuticals or in printing important documents, other than making our currency notes more secure.

## 4 Conclusion

$\text{Tm}^{3+}$ ;  $\text{Yb}^{3+}\text{:Zn}_2\text{TiO}_4$  have been successfully synthesized with tetragonal phase by solid state reaction method. The change in average crystallite size of the prepared samples is related to lattice strain developed due to incompatible ionic radii of  $\text{Tm}^{3+}$ /  $\text{Yb}^{3+}$  and  $\text{Zn}^{2+}$  ions in the host matrix. The average particle size 145.66 nm has been calculated from the HR-TEM analysis of the





prepared phosphors using image J software. Miller index from SAED pattern and *d*-spacing of the optimized sample has been evaluated in the present investigation. An intense peak of Yb<sup>3+</sup> ions for Yb-codoped samples near ~957 nm is observed in the DRS spectra which indicate the successful incorporation of Yb<sup>3+</sup> ion in the host matrix. Self-quenching of the activator Tm<sup>3+</sup> ions in the host is observed in photoluminescence studies. All resonance signals observed in EPR investigation at room temperature are related to zinc and oxygen vacancies created by Tm<sup>3+</sup>/Yb<sup>3+</sup> dopants at the Zn-site of the host. Upon excitation with a 980 nm laser CW excitation source, the blue upconversion intensity of Yb<sup>3+</sup> codoped samples at 3% doping concentration increases several times. The enhancement in intensity has been explained using efficient energy transfer process on codoping of rare-earth ions in the host. The anti-counterfeit application of the prepared sample has been successfully demonstrated. The colour coordinates of the upconverting phosphors indicates blue emission display device applications.

## Author contributions

Joydip Dutta: conceptualization, investigation, data curation, formal analysis, methodology. Mitesh Chakraborty: conceptualization, data curation, formal analysis, investigation, methodology, validation. Vineet Kumar Rai: conceptualization, formal analysis, investigation, supervision, validation, visualization.

## Conflicts of interest

The authors declare no conflict of interest.

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## References

- 1 E. D. Martinez, C. D. S. Brites, L. D. Carlos, R. R. Urbano, *et al.*, *Front. Chem.*, 2019, **7**, 83.
- 2 A. Kumari, L. Mukhopadhyay and V. K. Rai, *J. Rare Earths*, 2019, **37**, 242.
- 3 Y. Cui, R. S. Hedge, I. Y. Phang, H. K. Lee, *et al.*, *Nanoscale*, 2014, **6**, 282.
- 4 S. Gai, C. Li, P. Yang and J. Lin, *Chem. Rev.*, 2014, **114**, 2343.
- 5 A. Kumari, M. Mondal, V. K. Rai and S. N. Singh, *Methods Appl. Fluoresc.*, 2017, **6**, 0150003.
- 6 Y. Wang, R. Deng, X. Xie, L. Huang, *et al.*, *Nanoscale*, 2016, **8**, 6666.
- 7 R. S. Yadav, R. K. Verma and S. B. Rai, *J. Phys. D: Appl. Phys.*, 2013, **46**, 275101.
- 8 F. Auzel, *Chem. Rev.*, 2004, **104**, 139.
- 9 S. Pattnaik and V. K. Rai, *Mater. Sci. Eng., B*, 2021, **272**, 115318.
- 10 D. Manzani, J. F. D. S. Petrucci, K. Nigoghossian, A. A. Cardos, *et al.*, *Sci. Rep.*, 2017, **7**, 1.
- 11 Y. Q. Chen, H. P. Wang, X. T. Zhang, Z. Xiao, *et al.*, *J. Rare Earths*, 2018, **36**, 468.
- 12 H. Y. Hao, H. Y. Lu, Y. L. Song and Y. X. Wang, *Luminescence*, 2017, **32**, 1.
- 13 J. Tang, J. Gou, G. Li, Y. Li, *et al.*, *RSC Adv.*, 2016, **6**, 54435.
- 14 Y. Tian, X. Qi, X. Wu, R. Hua, *et al.*, *J. Phys. Chem. C*, 2009, **113**, 10767.
- 15 A. K. Soni and V. K. Rai, *Dalton Trans.*, 2014, **43**, 13563.
- 16 P. Gluchowski and W. Strek, *Opt. Mater.*, 2013, **35**, 731.
- 17 Y. Lu, K. Ai and L. Lu, *Nanoscale*, 2011, **3**, 4804.
- 18 B. Yoon, J. Lee, I. S. Park, S. Jeon, *et al.*, *J. Mater. Chem. C*, 2013, **1**, 2388.
- 19 J. Zhao, Z. Lu, Y. Yin, C. McRae, *et al.*, *Nanoscale*, 2013, **5**, 944.
- 20 H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, *et al.*, *Science*, 2000, **290**, 2123.
- 21 J. Zhao, D. Jin, E. P. Schartner, Y. Lu, *et al.*, *Nat. Nanotechnol.*, 2013, **8**, 729.
- 22 K. Sarkar, E. V. Braden, T. Froschl, N. Husing, *et al.*, *J. Mater. Chem. A*, 2014, **2**, 15008.
- 23 S. Ayyed, H. Abdelkefi, H. Khamakhem and A. Matoussi, *J. Alloys Compd.*, 2016, **677**, 185.
- 24 K. Jotimurugesan and S. K. Gangwal, *Ind. Eng. Res.*, 1998, **37**, 1929.
- 25 P. Scherrer, *Mathematisch-Physikalische Klasse*, 1918, vol. 26, p. 98.
- 26 S. Pattnaik and V. K. Rai, *J. Alloys Compd.*, 2022, **929**, 167237.
- 27 M. Mazhdi and M. J. Tafreshi, *Appl. Phys. A*, 2018, **124**, 863.
- 28 L. Li, Y. Wang, J. Shen, W. Chang, *et al.*, *J. Nanosci. Nanotechnol.*, 2016, **16**, 3511.
- 29 L. Li, Y. Pan, W. Chang, Z. Feng, *et al.*, *Mater. Res. Bull.*, 2017, **93**, 144.
- 30 S. Pattnaik and V. K. Rai, *Mater. Res. Bull.*, 2020, **125**, 110761.
- 31 M. Prasad and V. K. Rai, *J. Alloys Compd.*, 2020, **837**, 155289.
- 32 L. Budigi, M. R. Nasina, K. Shaik and S. Amaravadi, *J. Chem. Sci.*, 2015, **127**, 509.
- 33 I. M. Pinatti, P. F. S. Pereira, M. Assis, E. Longo, *et al.*, *J. Alloys Compd.*, 2019, **771**, 433.
- 34 L. Li, S. Gao, B. Li, Q. Zhou, *et al.*, *RSC Adv.*, 2017, **7**, 35477.
- 35 A. K. Soni, R. Dey and V. K. Rai, *RSC Adv.*, 2015, **5**, 34999.
- 36 S. Som, A. K. Kunti, V. Kumar, V. Kumar, *et al.*, *J. Appl. Phys.*, 2014, **115**, 193101.
- 37 G. K. Reddy, A. J. Reddy, R. H. Krishna, B. H. Nagabhushana and G. R. Gopal, *J. Asian Ceram. Soc.*, 2017, **5**, 350.
- 38 A. D. Prokhorov, M. T. Borowiec, M. C. Pujol, I. M. Krygin, *et al.*, *Eur. Phys. J. B*, 2007, **55**, 389.
- 39 N. Singh, G. Sivaramaiah, J. L. Rao, S. Watanabe, *et al.*, *J. Lumin.*, 2017, **188**, 423.



- 40 A. Abraham and B. Bleaney, *EPR of transition ions*, Clarendon Press, Oxford, 1970, p. 534.
- 41 A. L. Taylor, G. Filipovich and G. K. Lindeberg, *Solid State Commun.*, 1970, **8**, 1359.
- 42 A. J. Reddy, M. K. Kokila, H. Nagabhushana, J. L. Rao, *et al.*, *Spectrochim. Acta, Part A*, 2011, **81**, 59.
- 43 D. E. Motaung, P. R. Makqwane and S. S. Ray, *Mater. Lett.*, 2015, **139**, 475.
- 44 A. Kumari, A. K. Soni and V. K. Rai, *Infrared Phys. Technol.*, 2017, **18**, 313.
- 45 L. Li, W. Xiaochun, W. Xiantao and C. Yonghu, *Phys. B*, 2011, **406**, 609.
- 46 D. K. Mohanty, V. K. Rai and Y. Dwivedi, *Spectrochim. Acta, Part A*, 2012, **89**, 264.
- 47 R. S. Yadav, S. J. Dhoble and S. B. Rai, *Sens. Actuators, B*, 2018, **273**, 1425.
- 48 S. Sinha, M. K. Mahata and K. Kumar, *RSC Adv.*, 2016, **6**, 89642.

