

# Effect of annealing temperature and doping concentrations on structure and optical properties of $\text{Eu}^{3+}$ -doped $\text{TiO}_2$ nanomaterials

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## **Abstract:**

In this study, we successfully synthesized europium-doped  $\text{TiO}_2$  ( $\text{TiO}_2:\text{Eu}^{3+}$ ) nanomaterials (NMs) with crystalline sizes ranging from 6.5 to 71.7 nm through a sol-gel method. Analysis of X-ray diffraction (XRD) patterns and ultraviolet-visible (UV-Vis) spectra indicates that the substitution of smaller-sized  $\text{Ti}^{4+}$  ions (0.745 Å) by larger-sized  $\text{Eu}^{3+}$  ions (0.947 Å) was more efficient at higher doping concentrations and annealing temperatures. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the synthesized  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs exhibit a strong red emission band peaking at 613 nm and remarkable absorption in the blue light region centered at 463 nm, making them suitable for use in white light-emitting diode (WLED) applications. Our findings reveal that both annealing temperature and doping concentration significantly influence the structure and properties of these materials. Besides, the research team has seen, under the experimental conditions, the  $\text{TiO}_2:7\%\text{Eu}^{3+}$  sample annealed at 800°C exhibits the highest PL intensity. These results underscore the potential of the synthesized  $\text{TiO}_2:\text{Eu}^{3+}$  NMs as red-emitting materials for WLED applications.

**Keywords:**  $\text{Eu}^{3+}$  doped  $\text{TiO}_2$ , nanomaterials (NMs), photoluminescence, sol-gel method,  $\text{TiO}_2$ .

**Classification numbers:** 2.1, 2.3

## **1. Introduction**

In the present era, the realization of WLEDs can be achieved through three distinct techniques, namely: i) the combination of red, green, and blue LED chips; ii) the utilization of near-ultraviolet (NUV) LED chips in conjunction with tricolor phosphors (blue, green, and red phosphors); iii) the employment of a yellow-emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  phosphor with a blue LED chip [1]. Nonetheless, current commercial WLEDs frequently suffer from a deficiency in the red light spectrum, resulting in a low color rendering index (CRI<80) [2]. Consequently, the incorporation of a red light emission

component into WLEDs becomes imperative for achieving high CRI values. To address this challenge, the development of red-emitting phosphors that can be efficiently excited by blue or near-NUV light has become a pressing need [1-3]. Unfortunately, existing red-emitting nitride or sulfide-based materials, which are excitable by blue or NUV light, are marred by chemical instability and environmental hazards [4, 5]. Recent research efforts have thus focused on red-emitting  $\text{Eu}^{3+}$ -doped oxide phosphors that can be excited by NUV light, such as  $\text{Y}_2\text{O}_3$ ,  $\text{CaMoO}_4$  [6, 7]. Amongst semiconductor oxides, anatase-phase titanium dioxide ( $\text{TiO}_2$ ) emerges

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as a promising host lattice due to its attributes of a high band gap (3.2 eV), chemical stability, facile synthesis, affordability, non-toxicity, and non-hygroscopic behavior [2]. Recent studies have demonstrated that  $\text{Eu}^{3+}$ -doped  $\text{TiO}_2$  can be effectively excited by blue light and exhibit a red emission band spanning from 540 to 740 nm, attributed to the  ${}^5\text{D}_0$ - ${}^7\text{F}_j$  ( $j=1-4$ ) transitions of  $\text{Eu}^{3+}$  ions [1, 8]. However, optimizing the procedure for synthesizing  $\text{Eu}^{3+}$ -doped  $\text{TiO}_2$  phosphors remains challenging owing to the significant differences in ionic radius and charge imbalance [2].

This study presents successful doping of  $\text{Eu}^{3+}$  ions into the  $\text{TiO}_2$  host lattice using a sol-gel method. It comprehensively investigates and discusses the impact of annealing temperature and doping concentration on the structure and optical properties of  $\text{Eu}^{3+}$ -doped  $\text{TiO}_2$  NMs.

## 2. Materials and methods

### 2.1. Synthesis of $\text{Eu}^{3+}$ doped $\text{TiO}_2$ NMs

$\text{Eu}^{3+}$ -doped  $\text{TiO}_2$  ( $\text{TiO}_2\cdot x\%\text{Eu}^{3+}$ ,  $x=1-10$ ) NMs were synthesized via a sol-gel method. Initially, a mixture of  $\text{Eu}(\text{NO}_3)_3$  and 20 ml of ethanol was stirred for 30 minutes. Subsequently, 5 ml of titanium butoxide ( $\text{Ti}(\text{OBU})_4$ ) and 0.85 ml of acetic acid ( $\text{CH}_3\text{COOH}$ ) were added and stirred continuously for 10 minutes. Nitric acid ( $\text{HNO}_3$ ) was gradually introduced to maintain a pH of 2 in the solution. It is worth noting that the calculated mole ratio of  $\text{Eu}^{3+}$  ions in  $\text{TiO}_2$  ranged from 1 to 10 mol%. In the subsequent step, the solution was further stirred for 2 hours and then air-dried at room temperature for 24 hours to yield a dry gel product. Finally, this dry gel was subjected to annealing at  $100^\circ\text{C}$  for 12 hours, followed by a second annealing process in air, ranging from 200 to  $1000^\circ\text{C}$  for 2 hours, to obtain the  $\text{TiO}_2\cdot\text{Eu}^{3+}$  NMs.

### 2.2. Characterisation

The surface morphology and crystallite structure of  $\text{TiO}_2\cdot\text{Eu}^{3+}$  NMs were analyzed using a field emission scanning electron microscope (FESEM-JEOL JSM-7600F) and XRD, D8 Advanced). The band gap energy was determined through UV-Vis absorption spectra, employing the JASCO V-750 Spectrophotometer. PL and PLE spectra were recorded using a Nanolog spectrophotometer, excited by a 450 W Xenon lamp, at room temperature.

## 3. Results and discussion

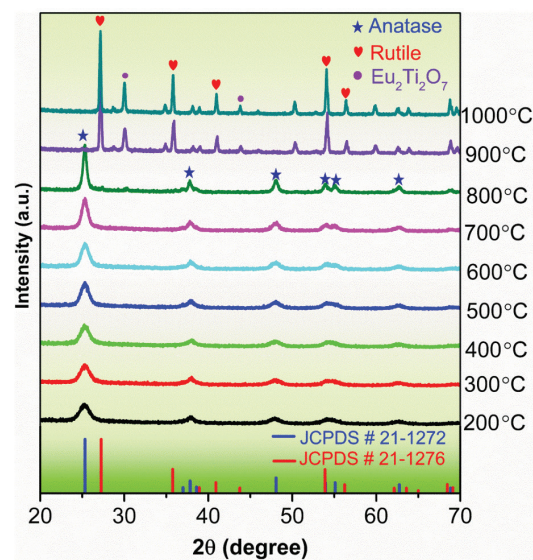


Fig. 1. XRD patterns of as-synthesized  $\text{TiO}_2\cdot 7\%\text{Eu}^{3+}$  NMs annealed in air at different temperatures of  $200$ - $1000^\circ\text{C}$  for 2 hours.

The XRD patterns of the as-synthesized  $\text{TiO}_2\cdot 7\%\text{Eu}^{3+}$  NMs, annealed in air in the range of  $200$ - $1000^\circ\text{C}$  for 2 hours, are presented in Fig. 1. At the lower temperature of  $700^\circ\text{C}$ , distinct diffraction peaks are observed at  $2\theta=25.28$ ,  $37.88$ ,  $48.09^\circ$ ,  $53.98$ ,  $55.20$ , and  $62.69^\circ$ , corresponding to the (101), (004), (200), (105), (211), and (204) planes of the  $\text{TiO}_2$  anatase phase (JCPDS # 21-1272), without any evidence of impurity phases [1]. When the temperature [8] is raised to  $800^\circ\text{C}$ , in addition to the anatase phase, new diffraction peaks attributed to rutile (JCPDS # 21-1276) [9] and  $\text{Eu}_2\text{Ti}_7\text{O}_7$  (JCPDS 01-087-1852) phases emerge in the XRD pattern. These peaks become prominent in samples annealed at higher temperatures ( $900$  and  $1000^\circ\text{C}$ ), indicating a phase transition from anatase to  $\text{TiO}_2$  rutile and  $\text{Eu}_2\text{Ti}_7\text{O}_7$  at  $800^\circ\text{C}$ .

Figure 2 presents the focused XRD patterns within the  $2\theta$  range of  $20$  to  $45^\circ$ , revealing an increase in peak intensity and a reduction in the full width at half maximum (FWHM) with increasing temperature. This observation confirms the formation of a more well-defined crystalline structure with higher annealing temperatures. Furthermore, a slight shift in the peak position towards a larger angle at higher temperatures is noted. This shift can be attributed to the enhanced substitution of smaller-sized  $\text{Ti}^{4+}$  ions ( $0.745 \text{ \AA}$ ) by larger-sized  $\text{Eu}^{3+}$  ions ( $0.947 \text{ \AA}$ ) within the  $\text{TiO}_2$  host lattice [10, 11].

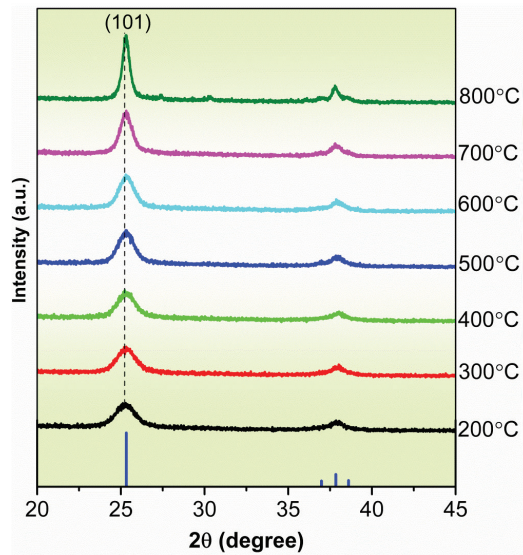


Fig. 2. XRD patterns focused in 2θ range from 20 to 45° of as-synthesized TiO<sub>2</sub>:7%Eu<sup>3+</sup> NMs annealed in air in the range of 200-800°C for 2 hours.

Moreover, the average crystallite size of all samples was determined using Debye-Scherrer’s Eq. (1) based on the FWHM of the (101) peak [12]:

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ (nm)} \quad (1)$$

where  $\lambda=1.54 \text{ \AA}$ ,  $\beta$ ,  $\theta$  and  $K=0.9$  are the X-ray wavelength, full width at half maximum of a diffraction peak, diffraction angle, and Scherrer constant, respectively. The calculated results are listed in Table 1, indicating a gradual increase in average crystallite size ranging from 6.5 Å to 71.7 Å with an increase in annealing temperature from 200 to 1000°C. A similar trend has also been reported in a previous study [12].

Table 1. An average crystallite size of TiO<sub>2</sub>:7%Eu<sup>3+</sup> NMs calculated at the (101) plane.

Temperature (°C)	$\beta$ (degree)	2θ (degree)	~D (nm)
As-synthesize TiO <sub>2</sub> :7%Eu <sup>3+</sup>	1.22	25.3	6.5
200	1.22	25.3	6.5
300	1.19	25.3	6.7
400	1.17	25.3	6.8
500	1.03	25.3	7.7
600	0.93	25.3	8.6
700	0.80	25.4	10.0
800	0.43	25.4	18.5
900	0.30	27.2	51.3
1000	0.21	27.2	71.7

Figure 3 illustrates XRD patterns of TiO<sub>2</sub>:x%Eu<sup>3+</sup> (x=0-10) NMs annealed in air at 800°C for 2 hours. Notably, only diffraction peaks corresponding to the TiO<sub>2</sub> anatase phase (JCPDS # 21-1272) were detected [1]. Additionally, the XRD patterns reveal a decrease in peak intensity with an increase in the concentration of doped Eu<sup>3+</sup> ions, suggesting that higher doping concentrations result in reduced crystallinity of TiO<sub>2</sub>. This phenomenon can be attributed to the presence of Eu<sup>3+</sup> ions, which may impede the phase transition process in TiO<sub>2</sub> materials. Furthermore, the peak position exhibits a slight shift towards larger angles with higher doping concentrations, which can be attributed to the enhanced substitution of smaller-sized Ti<sup>4+</sup> ions (0.745 Å) by larger-sized Eu<sup>3+</sup> ions (0.947 Å) within the TiO<sub>2</sub> lattice [2].

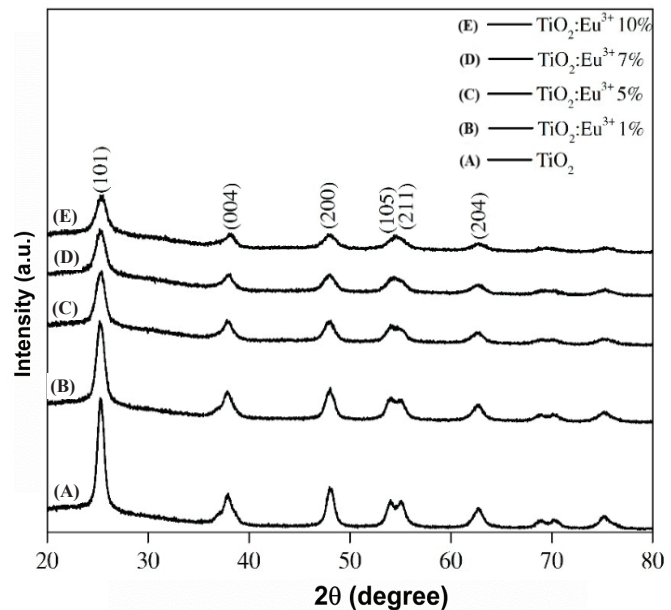


Fig. 3. XRD patterns of TiO<sub>2</sub>:x%Eu<sup>3+</sup> (x=0-10) NMs annealed in air at 800°C for 2 hours.

Figure 4 presents field emission scanning electron microscope (FESEM) images of TiO<sub>2</sub>:7%Eu<sup>3+</sup> NMs annealed in air at different temperatures ranging from 200 to 1000°C for 2 hours. The observations indicate a gradual increase in particle size with rising annealing temperature. This phenomenon is likely caused by the agglomeration of small clusters, resulting in the formation of larger particles at elevated temperatures [13]. The largest particle size from 200 nm at 200°C to 1 μm was obtained at 1000°C.



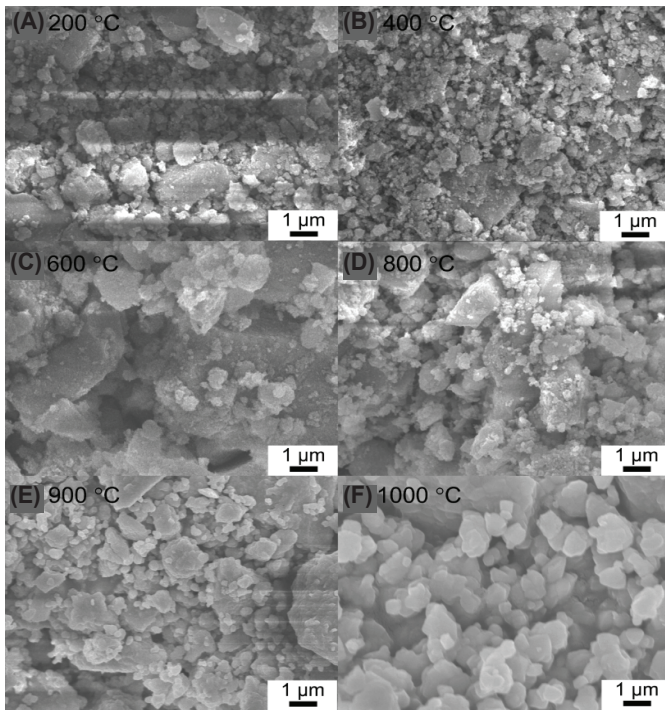


Fig. 4. FESEM images of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at different temperatures ranging from 200-1000°C for 2 hours (A-F).

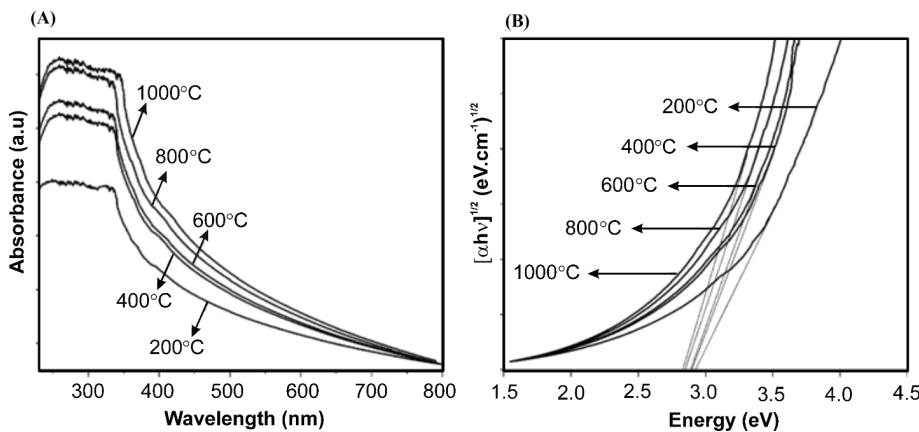


Fig. 5. UV-Vis absorption spectra of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed at 200, 400, 600, 800, and 1000°C (A), relationship between  $h\nu$  and  $(\alpha h\nu)^2$  (B).

Figure 5A displays the UV-Vis spectra of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at various temperatures within the range of 200 to 1000°C for 2 hours. It is evident that  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs exhibit strong absorption in the ultraviolet region (200-350 nm) and a weaker absorbance band in the NUV to visible range (350-500 nm). The former is attributed to the near band-edge absorption of  $\text{TiO}_2$ , while the latter is likely associated with the presence of  $\text{Eu}^{3+}$  ions doped into the  $\text{TiO}_2$  lattice [3]. Furthermore, an increase in absorption intensity with rising annealing temperature can be attributed to the substitution of larger-

sized  $\text{Eu}^{3+}$  ions for smaller  $\text{Ti}^{4+}$  ions. This phenomenon is also supported by the XRD pattern analysis presented in Fig. 2. The bandgap energy ( $E_g$ ) of  $\text{TiO}_2:\text{Eu}^{3+}$  NMs can be estimated from the absorption spectra in Fig. 5A using the Tauc Eq. (2) [1-3]:

$$(\alpha h\nu)^{1/n} = K(h\nu - E_g) \quad (2)$$

where  $\alpha$ ,  $h\nu$ ,  $K$  are the absorption coefficient, photon energy and characteristic constant of the specific material, respectively. For an indirect semiconductor like  $\text{TiO}_2$ ,  $n=2$ . Utilising the Tauc Eq. (2), the  $E_g$  values for  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed at 200, 400, 600, 800, and 1000°C were calculated to be 2.94, 2.90, 2.89, 2.85, and 2.82 eV, respectively. These values indicate that the bandgap of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs is smaller than that of pure  $\text{TiO}_2$  ( $E_g=3.2$  eV) and gradually decreases with higher annealing temperatures [4, 5, 14]. This phenomenon can be attributed to the increased substitution of smaller-sized  $\text{Ti}^{4+}$  ions with larger-sized  $\text{Eu}^{3+}$  ions within the  $\text{TiO}_2$  lattice, consistent with findings reported in recent studies [1-3].

It has been reported that the incorporation of  $\text{Eu}^{3+}$  ions into the  $\text{TiO}_2$  lattice introduces intermediate energy levels located below the conduction band, resulting in the narrowing of the energy band gap of  $\text{TiO}_2$  [Ceramics International 43 (2017) 9838-9845]. Conversely, when  $\text{Eu}^{3+}$  is introduced into the host lattice of  $\text{TiO}_2$ , it can increase the density of absorption centers, subsequently leading to higher absorbance in the UV-Vis spectrum. Therefore, a higher substitution of larger-sized  $\text{Eu}^{3+}$  ions can increase the density of absorption centers, resulting in enhanced absorption.

Figure 6 presents the PLE spectrum measured at 613 nm (A) and the PL spectrum excited at 463 nm (B) of the  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at 800°C for 2 hours. The PL spectrum exhibits a red emission band spanning from 540 to 740 nm, with peak wavelengths at 577, 594, 613, 655, and 703 nm. These peaks correspond to the  $^5\text{D}_0-^7\text{F}_0$ ,  $^5\text{D}_0-^7\text{F}_1$ ,  $^5\text{D}_0-^7\text{F}_2$ ,  $^5\text{D}_0-^7\text{F}_3$ , and  $^5\text{D}_0-^7\text{F}_4$  transitions of  $\text{Eu}^{3+}$  ions, respectively [2, 4, 15-17]. As depicted in Fig. 6B, the PLE spectrum displays notable absorption in the blue light region centred at 463 nm, which is well explained by a  $^7\text{F}_0-^5\text{D}_2$  transition of  $\text{Eu}^{3+}$  ions [2, 5].

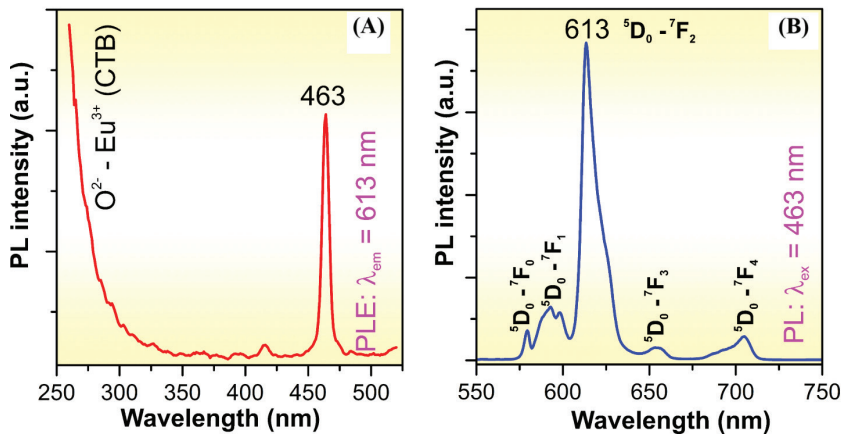


Fig. 6. PLE spectrum measured at 613 nm (A) and PL spectrum excited at 463 nm (B) of the  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at  $800^\circ\text{C}$  for 2 hours.

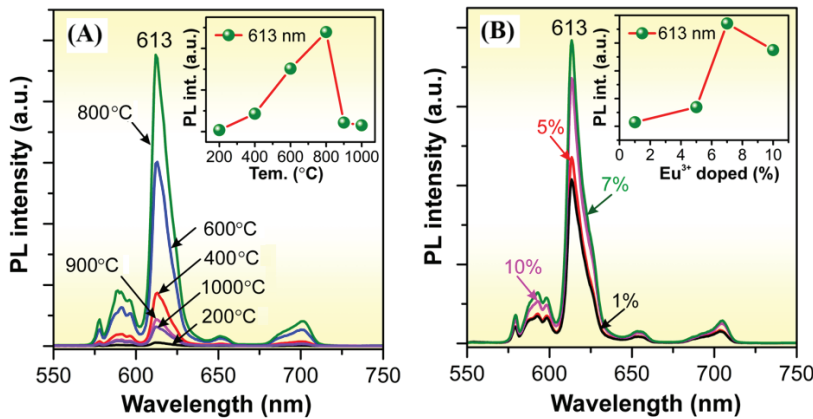


Fig. 7. PL spectra of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at different temperatures ranging from  $200\text{--}1000^\circ\text{C}$  for 2 hours (A) and  $\text{TiO}_2:x\%\text{Eu}^{3+}$  ( $x=0\text{--}10$ ) NMs annealed in air at  $800^\circ\text{C}$  for 2 hours (B).

Figure 7A presents the PL spectra excited at 463 nm of  $\text{TiO}_2:7\%\text{Eu}^{3+}$  NMs annealed in air at different temperatures within the range of 200 to  $1000^\circ\text{C}$  for 2 hours. All PL spectra exhibit a similar shape, but their intensities are significantly dependent on the annealing temperature. As the annealing temperature increases from 200 to  $800^\circ\text{C}$ , there is a gradual enhancement in PL intensity. This improvement can be attributed to the formation of a more well-defined crystalline structure or the substitution of larger-sized  $\text{Eu}^{3+}$  ions for smaller-sized  $\text{Ti}^{4+}$  ions within the  $\text{TiO}_2$  host lattice [13, 18, 19]. However, after reaching  $800^\circ\text{C}$ , there is a marked reduction in PL intensity, which can be attributed to the phase transition from anatase to rutile or the formation of the  $\text{Eu}_2\text{TiO}_7$  compound.

Figure 7B illustrates the PL spectra of  $\text{TiO}_2:x\%\text{Eu}^{3+}$  ( $x=0\text{--}10$ ) NMs annealed in air at  $800^\circ\text{C}$  for 2 hours.

While the shape of the spectra remains consistent, there is a significant variation in PL intensity with increasing  $\text{Eu}^{3+}$  ion concentration. The PL intensity gradually increases within the range of  $\text{Eu}^{3+}$  ion concentrations from 1 to 7%, and then decreases at a higher concentration of 10%. This phenomenon can be explained by PL quenching due to concentration effects [5, 15, 20]. At low doping concentrations, the  $\text{Eu}^{3+}$  ions are widely spaced apart, resulting in a low density of luminescent centres and, consequently, a low luminescent intensity. Conversely, at high concentrations, the proximity of  $\text{Eu}^{3+}$  ions reaches a threshold where energy transfer among the  $\text{Eu}^{3+}$  ions is facilitated, leading to a decrease in PL intensity (as seen in Fig. 7B). This is known as the PL quenching phenomenon. In this study, the PL quenching effect is observed at a higher  $\text{Eu}^{3+}$  doping concentration of 7%. Thus, the optimal concentration of  $\text{Eu}^{3+}$  ions to achieve the highest PL intensity is determined to be 7%.

#### 4. Conclusions

In summary, we have successfully synthesised red-emitting  $\text{Eu}^{3+}$ -doped  $\text{TiO}_2$  NMs (NMs) through a sol-gel method. Our study highlights the significant influence of annealing temperature and doping concentration on the crystalline structure and optical properties of  $\text{TiO}_2:\text{Eu}^{3+}$  NMs.

Notably, annealing at  $800^\circ\text{C}$  facilitated a phase transition from the anatase phase to a combination of  $\text{TiO}_2$  rutile and  $\text{Eu}_2\text{TiO}_7$  phases. Furthermore, a gradual increase in annealing temperature within the range of 200 to  $1000^\circ\text{C}$  led to a more pronounced substitution of smaller-sized  $\text{Ti}^{4+}$  ions ( $0.745 \text{ \AA}$ ) by larger-sized  $\text{Eu}^{3+}$  ions ( $0.947 \text{ \AA}$ ) within the  $\text{TiO}_2$  lattice. The PL spectra, excited at 463 nm, exhibited a substantial red emission band with peak wavelengths at 577, 594, 613, 655, and 703 nm, corresponding to the  $^5\text{D}_0\text{--}^7\text{F}_0$ ,  $^5\text{D}_0\text{--}^7\text{F}_1$ ,  $^5\text{D}_0\text{--}^7\text{F}_2$ ,  $^5\text{D}_0\text{--}^7\text{F}_3$ , and  $^5\text{D}_0\text{--}^7\text{F}_4$  transitions of  $\text{Eu}^{3+}$  ions, respectively. Remarkably, the  $\text{TiO}_2:7\%\text{Eu}^{3+}$  sample annealed at  $800^\circ\text{C}$  demonstrated the highest PL intensity, indicating the optimal conditions for emission enhancement. In conclusion, our study underscores the promising potential of  $\text{TiO}_2:\text{Eu}^{3+}$  NMs for applications in WLEDs, owing to their unique optical properties and tunability.

## CRedit author statement

Nguyen Tri Tuan: Reviewing, Methodology, Formal analysis, Writing, Editing; Tong Thi Hao Tam, Nguyen Tu, Do Quang Trung, Nguyen Van Du, Tran Minh Tien, Vu Thi Hang: Data analysis; Nguyen Trong Tuan, Nguyen Van Quang: Editing; Manh Trung Tran: Reviewing, Editing.

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## COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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