



# Tunable multicolor and white luminescence in Tb<sup>3+</sup>/Dy<sup>3+</sup>/Mn<sup>2+</sup> doped CePO<sub>4</sub> via energy transfer



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## ABSTRACT

In this paper, a series of Tb<sup>3+</sup>/Dy<sup>3+</sup>/Mn<sup>2+</sup> doped CePO<sub>4</sub> downconversion nanophosphors (DCNPs) were prepared by a one-pot hydrothermal process. The obtained DCNPs presented monoclinic and hexagonal phase structure with wire-like shape. The photoluminescence (PL) properties and the energy transfer (ET) mechanism of these DCNPs were investigated in detail. The ET mechanism of Ce<sup>3+</sup>/Tb<sup>3+</sup> in CePO<sub>4</sub> host was calculated by means of concentration quenching and spectral overlapping, and calculation results revealed that dipole–dipole interactions should be more responsible. The maximum value of ET efficiency was measured to 87.4% for Tb<sup>3+</sup> doped CePO<sub>4</sub> system. In addition, owing to the efficient ET between Ce<sup>3+</sup> and Tb<sup>3+</sup>/Dy<sup>3+</sup>/Mn<sup>2+</sup>, these as-prepared DCNPs exhibit tunable multi-color output under ultra-violet (UV) light excitation. More importantly, the intense cold and warm white emissions can be realized by singly doping 2%Dy<sup>3+</sup> and 20%Mn<sup>2+</sup> in CePO<sub>4</sub> host under UV irradiation, respectively. The corresponding CIE 1931 coordinates were calculated to be (0.30, 0.30) and (0.30, 0.32), respectively, which are closed to the standard white emission (0.33, 0.33). These findings demonstrate the efficient white light emission by singly doped Dy<sup>3+</sup> or Mn<sup>2+</sup> in CePO<sub>4</sub> system for the first time, which is different from commonly used co-doped or tri-doped system. The multicolor tuning and white emission make these Tb<sup>3+</sup>/Dy<sup>3+</sup>/Mn<sup>2+</sup> doped CePO<sub>4</sub> DCNPs potential phosphors in the fields of displays, lighting, and field-emission devices.

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## 1. Introduction

Recently, rare-earth based nanophosphors have attracted a fast-growing interest owing to their outstanding PL properties and promising applications in the fields such as displays, lighting, bioimaging [1–8]. According to different luminescence mechanisms, these emission processes can be classified into two broad categories: upconversion and downconversion. Due to the high efficiency and widespread application of DCNPs, more and more efforts have been devoted to investigating downconversion luminescent phosphors [9–15]. However, a mature and universal route should be selected for the preparation of DCNPs. The strategies used to prepare these luminescent nanomaterials mainly include thermal decomposition [16], hydro/solvothermal [17], Pechini-type sol–gel [18], co-precipitation [19], and others [20]. Among these methods, hydrothermal process is the most mild

and user friendly. Moreover, the phase, shape, and size can be easily controlled in the hydrothermal process, which are significant to the luminescent capabilities of the as-obtained products.

Furthermore, the host matrix is another important factor for PL properties. Apart from the well-established DCNPs based on fluorides [21–23], phosphates have gradually attracted plenty of attentions because of their high temperature stability and special fluorescence properties [24–31]. For instance, YPO<sub>4</sub> [24], LaPO<sub>4</sub> [25], GdPO<sub>4</sub> [26,27], and LuPO<sub>4</sub> [28] have been widely used as DCNPs by doping Eu<sup>3+</sup>, Ce<sup>3+</sup>, Dy<sup>3+</sup>, Tb<sup>3+</sup>, and so on. As shown in our previous work [27], Ce<sup>3+</sup>/Tb<sup>3+</sup> co-doped GdPO<sub>4</sub> was successfully fabricated for *in vivo* luminescent bioimaging owing to the intense green emission via ET between Ce<sup>3+</sup> and Tb<sup>3+</sup> under the UV irradiation. Not only Ce<sup>3+</sup>/Tb<sup>3+</sup> co-doping but also Ce<sup>3+</sup>/Dy<sup>3+</sup> and Ce<sup>3+</sup>/Mn<sup>2+</sup> show efficient ET, multicolor emission, and even white light in many phosphors systems [10–12,32–37]. These phenomena inspire us to pursue tunable emission and white light output utilizing ET between Ce<sup>3+</sup> and Tb<sup>3+</sup>/Dy<sup>3+</sup>/Mn<sup>2+</sup>. Nevertheless, the absence of Ce<sup>3+</sup> in host matrix indicates that at least two doped

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ions containing  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  are needed to achieve ET mentioned above. Therefore, it is a good idea to take  $\text{Ce}^{3+}$  into the host ( $\text{CePO}_4$ ), which can make the experimental parameters more easily tunable. Meanwhile, high  $\text{Ce}^{3+}$  concentration can lead to more efficient ET ratio, which is ascribed to that  $\text{Ce}^{3+}$  serve as sensitizer ions in order to enhance the emission of other co-activators ( $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$  or  $\text{Mn}^{2+}$ ) by means of transmitting sectional excitation energy of itself to activators. Moreover, many previous literatures [25,29–31] have verified that  $\text{CePO}_4$  can actually emerge as an ideal DC host, while there is limited research on  $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  doped  $\text{CePO}_4$  DCNPs for color-tunable emission and white luminescence.

Herein, we report a simple hydrothermal process to synthesize  $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  doped  $\text{CePO}_4$  DCNPs. The phase and morphology were characterized by XRD and TEM, respectively. The optical properties containing excitation/emission spectra and decay time curve were investigated systematically. Besides, ET mechanism between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  in these as-prepared  $\text{CePO}_4$  DCNPs will be discussed in detail. The intense multicolor emission and white luminescence in  $\text{CePO}_4$  host will be demonstrated, indicating that the as-formed DCNPs have promising applications in multicolor three-dimensional display, lighting, and field-emission devices.

## 2. Experimental section

### 2.1. Chemicals and materials

The rare earth oxides ( $\text{Ce}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ , 99.99%) were bought from Sigma-Aldrich. Polyethylene glycol (PEG),  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{MnCl}_2$ , and other chemical reagents were of analytical purity and obtained from Sinopharm Chemical Reagent Co., China. All the reagents were used as received without further purification.  $\text{Ln}(\text{NO}_3)_3$  ( $\text{Ln} = \text{Ce}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Tb}^{3+}$ ) aqueous solutions with well-designed concentration were prepared via dissolving the corresponding oxides into dilute nitric acid.

### 2.2. Synthesis of $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$ doped $\text{CePO}_4$ DCNPs

$\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  doped  $\text{CePO}_4$  DCNPs were synthesized through a one-pot hydrothermal procedure using PEG as a surface modifier [39]. Take  $\text{CePO}_4:x\%\text{Tb}^{3+}$  ( $x = 0.5, 1.0, 2.0, 5.0, 10,$  and  $20$ ) DCNPs for example, 1.5 g of PEG was first dissolved in 20 mL of de-ionized water under vigorous stirring to form clear solution. And then, a total amount (1 mmol) of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Tb}(\text{NO}_3)_3$  with designed proportion were added into the mixture under agitation. After that, 1.5 mL of fresh-prepared

$\text{NH}_4\text{H}_2\text{PO}_4$  solution was slowly added in the mixture to form aqueous solution. The beakers were then sealed and stirred vigorously for about 30 min. The resulting mixture was transferred into a 50 mL stainless Teflon-lined autoclave and the system was maintained at  $190^\circ\text{C}$  for 24 h. After reaction, the system was cooled down to room temperature naturally and the obtained samples were aggregated in the bottom of a vessel. The final products were obtained after separating by centrifugation, washing with ethanol and de-ionized water in sequence, and drying at  $60^\circ\text{C}$  in air for several hours. For  $\text{CePO}_4:\text{Dy}^{3+}$  and  $\text{CePO}_4:\text{Mn}^{2+}$  DCNPs, similar procedures were conducted only by tuning the doping ions and concentrations.

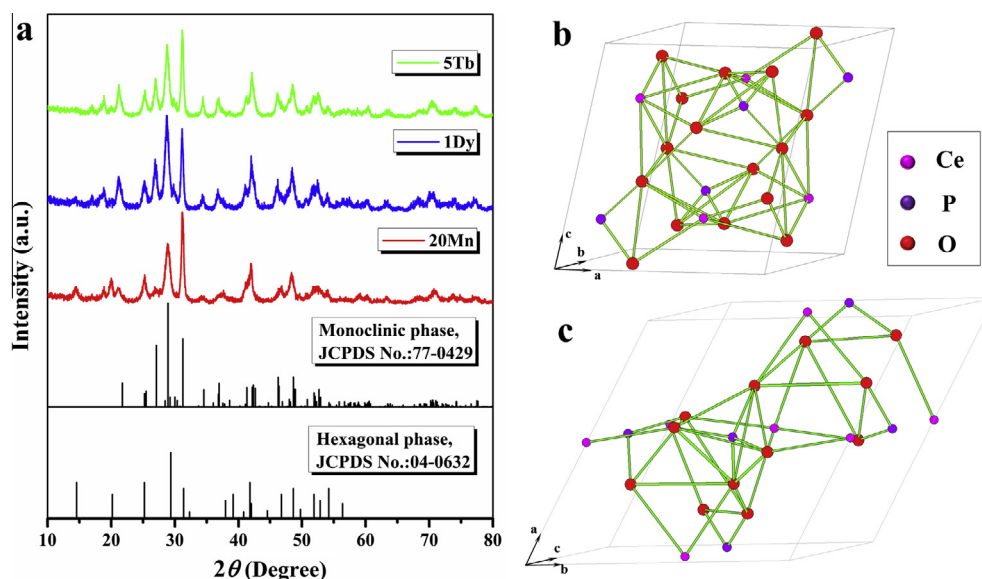
### 2.3. Characterizations

The crystal phase and phase compositions of the as-prepared  $\text{CePO}_4:5\text{Tb}^{3+}$ ,  $\text{CePO}_4:1\text{Dy}^{3+}$ , and  $\text{CePO}_4:20\text{Mn}^{2+}$  DCNPs were recorded by X-ray powder diffraction (XRD) utilizing a Rigaku 2500 X-ray diffractometer at 40 kV and 250 mA with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The data were collected while the 2-theta was changing from  $10^\circ$  to  $80^\circ$  at a speed of  $8^\circ$  per minute. The morphologies of these as-prepared samples were characterized by transmission electron microscopy (TEM), scanning TEM (STEM) with a JEOL-2100F TEM equipped with an energy-dispersive X-ray spectroscopy (EDS) system using an accelerating voltage at 200 kV. The DC luminescence excitation and emission spectra were recorded by a Zolix Analytical Instrument (fluoroSENS 9000A) equipped with a 150 W xenon lamp as light source. The decay time profile of these obtained samples was examined using an Edinburgh instrument (FLS980). The digital photographs of the as-synthesized powders were taken by a Canon digital camera under the excitation at the corresponding wavelength using a 150 W xenon lamp.

## 3. Results and discussion

### 3.1. Phase and microstructure study

The phase composition and purity of the as-synthesized DCNPs were examined by XRD. Fig. 1 presents the representative XRD patterns of the as-synthesized  $\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Mn}^{2+}$  doped DCNPs:  $\text{CePO}_4:5\text{Tb}^{3+}$ ,  $\text{CePO}_4:1\text{Dy}^{3+}$ , and  $\text{CePO}_4:20\text{Mn}^{2+}$ . The diffraction peaks of all these DCNPs can be exactly assigned to the monoclinic phase  $\text{CePO}_4$  (JCPDS file number: 77-0429) and hexagonal phase  $\text{CePO}_4$  (JCPDS file number: 04-0632). These results confirm that the doped ions were completely incorporated into the  $\text{CePO}_4$  host lattice at the current doping molar ratio. The quantified calculation of phase structure based on the structure refined XRD analysis reveals that the relative amount of the monoclinic and hexagonal phases  $\text{CePO}_4$  DCNPs are 94.96% and 5.04%, respectively. The crystal structures of monoclinic and hexagonal phase  $\text{CePO}_4$  with one unit cell were shown in Fig. 1 [40]. The monoclinic phase  $\text{CePO}_4$



**Fig. 1.** (a) XRD patterns of the as-prepared  $\text{CePO}_4:5\text{Tb}^{3+}$ ,  $\text{CePO}_4:1\text{Dy}^{3+}$ , and  $\text{CePO}_4:20\text{Mn}^{2+}$  DCNPs, and the standard monoclinic phase  $\text{CePO}_4$  (JCPDS file number: 77-0429) and hexagonal phase  $\text{CePO}_4$  (JCPDS file number: 04-0632). Schematic crystal structures of (b) monoclinic and (c) hexagonal phase  $\text{CePO}_4$  with one unit cell.

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