

# Tuning of photoluminescence by co-doping $\text{Eu}^{2+}$ , $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ in $\text{Ca}_9\text{NaZn}(\text{PO}_4)_7$ phosphor

Zhan-Chao Wu<sup>a</sup>, Fang-Fang Wang<sup>a</sup>, Kun Zhang<sup>a</sup>, Shi-Cheng Xu<sup>a</sup>, Jie Liu<sup>a,\*</sup>, Zhiguo Xia<sup>b,\*\*</sup>, Ming-Mei Wu<sup>c</sup>

<sup>a</sup> State Key Laboratory Base of Eco-chemical Engineering, Laboratory of Inorganic Synthesis and Applied Chemistry, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

<sup>b</sup> Beijing Municipal Key Lab for Advanced Energy Materials and Technologies, School of Materials Sciences and Engineering, University of Science and Technology Beijing, Beijing 100083, China

<sup>c</sup> School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

## ARTICLE INFO

### Keywords:

Phosphor  
Spectral tuning  
Reduction reaction mechanism  
Photoluminescence  
Thermal stability

## ABSTRACT

A series of  $\text{Ca}_9\text{NaZn}(\text{PO}_4)_7$ :  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  (CNZP:  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ) phosphors were synthesized by the solid-state reaction method. The results of structure refinement indicate that the chemical formula of CNZP can be written as  $\text{Ca}_{9.12(5)}\text{Zn}_{0.88(5)}\text{Na}_{1.0(2)}(\text{PO}_4)_7$ .  $\text{Ca}^{2+}$  ions fully occupy M1 site and partly occupy M2, M3 and M5 sites. The M4 sites are 100% occupied by  $\text{Na}^+$  ions and  $\text{Na}^+$  ions didn't participate in other sites.  $\text{Zn}^{2+}$  ions partly occupy M2, M3 and M5 sites and the biggest occupation 81(2)% of  $\text{Zn}^{2+}$  was observed for M5 sites. There are both 6-coordinated and 8-coordinated  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  in CNZP matrix. According to Davolo's theory, we speculated that  $\text{Eu}^{3+}$  ions could substitute both  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  ions in CNZP matrix, while  $\text{Eu}^{2+}$  ions could only replace  $\text{Ca}^{2+}$  ions but not  $\text{Zn}^{2+}$  ions in CNZP host.  $\text{Eu}^{3+}$  ions doped in CNZP matrix only partly were reduced to  $\text{Eu}^{2+}$  state under the preparation conditions. The reaction mechanism was proposed. The emission color of the as-prepared phosphor were tuned from blush-violet to warm-white and yellowish-green by energy transfer of  $\text{Eu}^{2+} \rightarrow \text{Tb}^{3+}$  and  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  in CNZP:  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  phosphor. The samples showed good thermal stability. All the results imply that CNZP:  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  phosphor is a potential color-tunable phosphor candidate for n-UV LEDs.

## 1. Introduction

In recent years, phosphor-converted white light-emitting-diodes (pc-WLEDs) have been attracting much attention due to their high luminous efficiency, good light stability, long lifetime and environmental protection [1–6]. Current commercial WLEDs are assembled via blue-emitting InGaN chips and yellow-emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}$ :  $\text{Ce}^{3+}$  (YAG:  $\text{Ce}^{3+}$ ) phosphor [7–13]. However, the WLEDs based on YAG:  $\text{Ce}^{3+}$  phosphor exhibits poor color rendering index ( $R_a < 80$ ) and high correlated color temperature ( $T_c > 4500$  K) because the emission spectrum lacks a red component [14–16]. In order to overcome the disadvantage, one important approach is to use near-ultraviolet (n-UV, 350–420 nm) chip with a mixture of blue, green, and red tricolor phosphors or single-component white-emitting phosphors to match n-UV chips [17–24].

$\beta\text{-Ca}_3(\text{PO}_4)_2$  is iso-structural to the nature mineral whitlockite, which crystallized in the space group  $R3c$  [25]. There are six metal sites (M1–6) in  $\beta\text{-Ca}_3(\text{PO}_4)_2$ -type compounds. Most of the six metal sites are

completely filled by  $\text{Ca}^{2+}$  ions except M4 and M6 sites. The M4 site is half occupied by  $\text{Ca}^{2+}$  ions and the M6 site is vacant. The coordination numbers (CN) of  $\text{Ca}^{2+}$  in M1–M5 sites are 8, 8, 8, 6 and 9, respectively. Ca1, Ca2 and Ca3 occupy in the general 18b sites with the average Ca–O distance of 2.54, 2.53 and 2.57 Å, respectively, while Ca5 occupies in the 6a sites with an average Ca–O bond length of 2.16 Å. Owing to their specific crystal structure, compounds with  $\beta\text{-Ca}_3(\text{PO}_4)_2$  structure show preminent thermal stability and high tolerance to doping with rare-earth and transition-metal ions [26–30]. The photoluminescence tuning based on the crystal structure of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  mainly include ion substitution for the modification of the host composition and energy transfer among the doped ions. For example, partial substitution of  $\text{Ca}^{2+}$  by  $\text{Sr}^{2+}$  in the  $\beta\text{-Ca}_3(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$  induced a phase transition and a red shift of the emission peak [28–30]. The  $\text{Ba}^{2+}$  ion substitution for  $\text{Ca}^{2+}$  ion in the  $\beta\text{-Ca}_3(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$  resulted in a shift of the emission color from blue to yellow with the increase of  $\text{Ba}^{2+}$  substitution [31]. The photoluminescence tuning through energy transfer in  $\text{Ca}_3(\text{PO}_4)_2$ :

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zsulijie@163.com](mailto:zsulijie@163.com) (J. Liu), [xiazg@ustb.edu.cn](mailto:xiazg@ustb.edu.cn) (Z. Xia).

$\text{Eu}^{2+}$ ,  $\text{Tb}^{3+}$  [32],  $\text{Ca}_3(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  [33],  $\text{Ca}_3(\text{PO}_4)_2$ :  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  [34],  $\text{Ca}_3(\text{PO}_4)_2$ :  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  [35] were also investigated.

The  $\text{Ca}_9\text{M}'\text{M}''(\text{PO}_4)_7$  ( $\text{M}' = \text{Ca}, \text{Mg}; \text{M}'' = \text{Li}, \text{Na}, \text{K}$ ) compounds also have a whitlockite-type structure like that of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  [36,37]. In the natural whitlockite type minerals, the monovalent alkali metal ions preferred to occupy the M4 sites (CN = 3) while  $\text{Mg}^{2+}$  ions have been well established to occupy the M5 sites (CN = 6), as it was obtained for  $\text{Ca}_9\text{MgM}(\text{PO}_4)_7$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) [38–40]. Among them,  $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$  has attracted more attention as the matrix for phosphors. Hou reported the color-tunable phosphors of  $\text{Ca}_9\text{MgM}'(\text{PO}_4)_7$ :  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  ( $\text{M}' = \text{Li}, \text{Na}, \text{K}$ ) [41]. Lin's group investigated trichromatic white-emitting  $\text{Ca}_9\text{MgNa}(\text{PO}_4)_7$ :  $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$  phosphor for FEDs [42]. Xia et al. deeply studied the crystallographic sites and luminescence properties of  $\text{Eu}^{2+}$  in  $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$  matrix [43]. Similarly,  $\text{Ca}_9\text{NaZn}(\text{PO}_4)_7$  (CNZP) also has a whitlockite-type structure. However, as far as we know, there was no research concentrating on this compound as a phosphor host. In this work,  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  co-doped CNZP phosphor were prepared by high-temperature solid state reaction. Unlike the previously reported  $\text{Eu}^{2+}$  in  $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ :  $\text{Eu}^{2+}$  phosphor [43], only a part of  $\text{Eu}^{3+}$  ions in CNZP phosphor can be reduced to  $\text{Eu}^{2+}$  ions. The reaction mechanism is conjectured. However, the coexistence of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in CNZP phosphor is just right for the necessary emission of blue and red light from the phosphor. This coincidence provides a possibility for white light emission by further co-doping with  $\text{Tb}^{3+}$  ions. The crystal structure, luminescence properties, concentration quenching, thermal stability of the as-prepared phosphors were studied comprehensively.

## 2. Experimental section

### 2.1. Synthesis

CNZP:  $9x\text{Eu}^{3+}/\text{Eu}^{2+}$  ( $x = 0.000, 0.002, 0.004, 0.006, 0.008$  and  $0.010$ ) and CNZP:  $0.072\text{Eu}^{3+}/\text{Eu}^{2+}$ ,  $9y\text{Tb}^{3+}$  ( $y = 0.003, 0.006, 0.009, 0.012, 0.015$  and  $0.018$ ) were synthesized by high-temperature solid state reaction. The raw materials  $\text{CaCO}_3$  (A.R., Sinopharm Chemical Reagent Co., Ltd),  $\text{Na}_2\text{CO}_3$  (A.R., Tianjin Bodi Chemical Co., Ltd),  $\text{ZnO}$  (A.R., Sinopharm Chemical Reagent Co., Ltd),  $\text{NH}_4\text{H}_2\text{PO}_4$  (A.R., Sinopharm Chemical Reagent Co., Ltd),  $\text{Eu}_2\text{O}_3$  (99.99%, Ganzhou KMRing nonferrous metals materials Co. Ltd) and  $\text{Tb}_4\text{O}_7$  (99.99%, Ganzhou KMRing nonferrous metals materials Co. Ltd) were weighed according to the stoichiometric ratio and then ground in agate mortar thoroughly. Next, the powder mixtures were transferred to alumina crucible and sintered at  $1000^\circ\text{C}$  for 5 h in CO atmosphere. Finally, the synthesized samples were furnace-cooled to room temperature for measurement.

### 2.2. Measurements

The phase composition of as-prepared samples was identified by an X-ray diffraction analysis using DMAX2500/PC device (RIGAKKU Corporation, Tokyo, Japan) equipped with Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and operated at 40 kV and 20 mA. The powder diffraction data of  $\text{Ca}_9\text{ZnNa}(\text{PO}_4)_7$  for Rietveld analysis were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu- $\text{K}\alpha$  radiation) and linear VANTEC detector. The step size of  $2\theta$  was  $0.016^\circ$ , and the counting time was 1 s per step. The photoluminescence excitation (PLE) and emission (PL) spectra, temperature-dependent luminescence and luminescence decay curves were recorded using a fluorescence spectrophotometer (FLS920, Edinburgh Instruments, UK) equipped with a 450W Xe lamp and a 150 W nF900 flash lamp. In order to analyze the co-existence of the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in CNZP matrix, X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 xi) with Al  $\text{K}\alpha$  X-ray source has been applied. In the XPS measurements, high-resolution scans of elemental lines were recorded at 50 eV pass energy of the analyzer. All the binding energies (BEs) were calibrated using the C 1s peak (at 284.8 eV) of the adventitious carbon as an

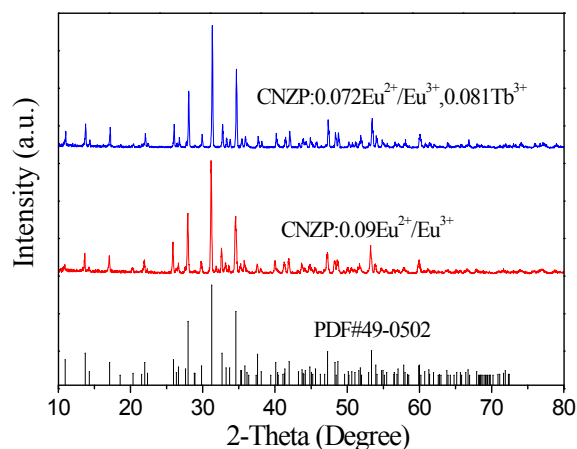


Fig. 1. XRD patterns for the as-prepared samples of CNZP:  $0.09\text{Eu}^{2+}/\text{Eu}^{3+}$  and CNZP:  $0.072\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $0.081\text{Tb}^{3+}$ .

internal standard.

## 3. Results and discussion

### 3.1. Phase identification and crystal structure

The XRD patterns of the prepared CNZP:  $0.072\text{Eu}^{2+}/\text{Eu}^{3+}$  and CNZP:  $0.072\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $0.081\text{Tb}^{3+}$  phosphors are shown in Fig. 1 and the standard data for CNZP are also shown as a reference. It is apparent that all the diffraction peaks are well assigned to the pure phase of CNZP (PDF card no. 49–0502), which indicates that the as-prepared samples are in single phase state and the incorporations of  $\text{Eu}^{2+}/\text{Eu}^{3+}/\text{Tb}^{3+}$  don't generate impurity phases in CNZP matrix. To further study the structure of the obtained phosphors, Rietveld structure refinement of CNZP matrix was performed by using TOPAS 4.2 [44]. Fig. 2a depicts the results of Rietveld refinement pattern of the obtained sample. In this structure, almost all peaks were indexed by trigonal cell (R3c) with parameters close to  $\text{Ca}_9\text{Eu}(\text{PO}_4)_7$  [45]. Therefore, this crystal structure of was taken as starting model for Rietveld refinement. There are 5 Ca/Eu sites (M1, M2, M3, M4, M5) in  $\text{Ca}_9\text{Eu}(\text{PO}_4)_7$  structure (Fig. 2b). In our model, all these sites were occupied by Ca/Zn/Na ions and the occupations were refined in assumption that sum of all occupancies in each site is equal to 1. The refinement data  $\chi^2$  (Fitting factor) = 1.73,  $R_{\text{wp}}$  (weighted-profile R value) = 6.53%, and  $R_p$  (profile R value) = 4.94% indicate that all these factors satisfy the reflection condition. For CNZP sample, the cell parameters were determined to be  $a = b = 10.35492(8) \text{ \AA}$ ,  $c = 37.0664(3) \text{ \AA}$ ,  $V = 3441.95(6) \text{ \AA}^3$  and  $Z = 6$ . The refinement was stable and gives low R-factors (Table 1). The atom coordinates and main bond lengths are listed in Tables 1 and 2, respectively. It was found that  $\text{Ca}^{2+}$  ions 100% occupy M1 and partly occupy M2, M3 and M5 sites,  $\text{Na}^+$  ions 100% occupy M4 site and didn't penetrate any other sites,  $\text{Zn}^{2+}$  ions occupy M2, M3, M5 sites and the biggest occupation 81(2)% of  $\text{Zn}^{2+}$  was observed in M5 site. From the refinement, the chemical formula can be written as  $\text{Ca}_{9.12(5)}\text{Zn}_{0.88(5)}\text{Na}_{1.0(2)}(\text{PO}_4)_7$ . The results of structure refinement indicate that there are both 6-coordinated and 8-coordinated  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  in CNZP matrix.

There are two different kinds of bivalent cations ( $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$ ) in CNZP compound. In theory, both of them are likely to be replaced by luminescent center such as  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$ . But it is not so simple in fact. Several factors (such as ionic radii and coordination number) determine which lattice site could be entered by  $\text{Eu}^{3+}$  or  $\text{Eu}^{2+}$ . The cation radii for different coordination numbers (CN) are shown in Table 3. Davolos et al. reported that an acceptable percentage difference between doped and substituted ions do not exceed 30% [46,47]. The radius percentage difference between dopant ions ( $\text{Eu}^{3+}$  or  $\text{Eu}^{2+}$ ) and the

Download English Version:

<https://daneshyari.com/en/article/6599341>

Download Persian Version:

<https://daneshyari.com/article/6599341>

[Daneshyari.com](https://daneshyari.com)