Synthesis, characterization and photoluminescence properties of Tm^{3+} -doped Ca_2YTao_6 blue-emitting phosphors

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Abstract. A series of $\text{Ca}_2\text{YTao}_6: \text{Tm}^{3+}$ blue-emitting phosphors were firstly prepared by the solid-state method. The phase formations and purity of $\text{Ca}_2\text{YTao}_6: x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) were verified by X-ray powder diffraction. The morphological characteristics of $\text{Ca}_2\text{YTao}_6: 0.005\text{Tm}^{3+}$ were detected by scanning electron microscopy (SEM). Photoluminescence properties were discussed by emission ($\lambda_{\text{em}} = 460 \text{ nm}$) and excitation ($\lambda_{\text{ex}} = 359 \text{ nm}$) spectra. The critical doping concentration of the products was 0.005 mol. The proposed concentration quenching mechanism in Ca_2YTao_6 materials was the electric multipole interaction. Besides, the color coordinates (0.1408, 0.0891) of $\text{Ca}_2\text{YTao}_6: 0.005\text{Tm}^{3+}$ were located in blue region. The results suggested the $\text{Ca}_2\text{YTao}_6: \text{Tm}^{3+}$ phosphors can be promising blue-emitting components for the WLED applications.

1 Introduction

Attaching great importance of energy-saving and environment protection, the traditional fluorescent lamps and incandescent lamps in daily lighting were fade away. White light-emitting diodes (WLEDs) are getting growing attention for the merits of energy-saving, improving efficiency, etc.[1-7]. Nowadays, two common methods of WLED fabrication were widely used. (1) Combining the blue LED chips with Ce^{3+} doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ phosphors. However, the great limitations of the method are low color rendering index (CRI) and high correlated color temperature. And the low CRI was due to the lack of red composition [8-10]. Method (2) was mixing the tricolor (RGB) emission phosphors with a near-UV chip [11-13]. The quest for blue-emitting phosphors for lighting is an important and urgent challenge for investigators.

Tantalates enjoy the merits of excellent chemical and physical stability, which have drawn widespread attention in the synthesis of phosphors. Recently, Eu^{3+} , Sm^{3+} , Dy^{3+} , and Mn^{4+} doped Ca_2YTao_6 phosphors were proved to be well applied in the WLED applications [14, 15]. However, Tm^{3+} doped Ca_2YTao_6 phosphors were still unreported. Tm^{3+} is a good blue-emitting center. Many published works reported Tm^{3+} doped phosphors for the WLED applications, such as $\text{Y}_2\text{Mg}_2\text{Al}_2\text{Si}_2\text{O}_{12}: \text{Eu}^{2+}$, Ce^{3+} , $\text{NaY}_9\text{Si}_6\text{O}_{26}: \text{Ce}^{3+}$, Eu^{3+} , $\text{NaSrPO}_4: \text{Tm}^{3+}$, and $\text{Li}_3\text{Gd}_3\text{Te}_2\text{O}_{12}: \text{Tm}^{3+}$ [16-19]. In this work, $\text{Ca}_2\text{YTao}_6: \text{Tm}^{3+}$ phosphors were firstly synthesized through solid-state reaction (at 1550 °C, in air condition). The XRD data of the products were collected and

discussed. At the same time, the morphology, the concentration quenching mechanism, photoluminescence (PL) properties, and CIE color coordinates were investigated in detail.

2 Experimental

2.1 Synthesis method

The $\text{Ca}_2\text{YTao}_6: x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) phosphors were obtained by solid-state reaction. Starting materials CaCO_3 (99.99%), Y_2O_3 (99.99%), Ta_2O_5 (99.5%), and Tm_2O_3 (99.99%) were weighed according to the stoichiometric ratio. Following the general process, the mixed powder was ground for 15 minutes and was transferred into crucibles. Then, the reaction system was calcined at 1550°C for 3 hours in the muffle furnace. After the calcination was finished, hard white phosphors were obtained and reground for the subsequent luminescence characterizations.

2.2 Characterization method

The phase purity of phosphor was detected by the XRD through a Bruker D2 PHASER X-ray diffractometer with $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15405 \text{ nm}$), and the result was presented in 2θ range between 10° and 70° . The morphology was measured by a scanning electron microscope (JEOL JSM-6490). The PL spectra were

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achieved by Edinburgh FLS 980 spectrometer.

3 Results and discussion

Figure 1. XRD patterns of the $\text{Ca}_2\text{YTaO}_6:x\text{Tm}^{3+}$ phosphors ($x = 0.3\%-5\%$ mol).

The XRD patterns of $\text{Ca}_2\text{YTaO}_6:x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) phosphors were presented in Figure 1. A comparison of the patterns revealed that the diffraction peaks of the products match well with the simulated card of Ca_2YTaO_6 , indicating that the as-prepared products have a high phase purity, and the $\text{Ca}_2\text{YTaO}_6:\text{Tm}^{3+}$ phosphors were successfully synthesized. For the composition of

$\text{Ca}_2\text{YTaO}_6:0.005\text{Tm}^{3+}$, the cell parameters are $a = 5.814 \text{ \AA}$, $b = 8.050 \text{ \AA}$, $c = 5.578 \text{ \AA}$, $V = 261.07 \text{ \AA}^3$, respectively. As the ionic radii of the Y^{3+} ($0.90 \text{ \AA}$) are approximate to that of Tm^{3+} ions ($1.052 \text{ \AA}$), while the coordination number equals 6 [20], suggesting Tm^{3+} ions can take place of Bi^{3+} ions in relatively low concentration in the Ca_2YTaO_6 compound.

Figure 2. SEM micrograph of $\text{Ca}_2\text{YTaO}_6:0.005\text{Tm}^{3+}$ product.

The surface morphology and particle sizes of phosphors are important for WLED applications. The SEM micrograph of the typical $\text{Ca}_2\text{YTaO}_6:0.005\text{Tm}^{3+}$ product is shown in Figure 2. At $10000\times$ and $5000\times$ magnification, the particle sizes are distributed in the

range of a few microns to dozens of microns. The products have an irregular surface morphology with uneven size distribution among the pieces, which was the result of high-temperature annealing.

Figure 3(a). PLE ($\lambda_{\text{em}} = 460$ nm) and PL spectrum ($\lambda_{\text{ex}} = 359$ nm) of $\text{Ca}_2\text{YTaO}_6:0.005\text{Tm}^{3+}$ phosphor. **(b)** The energy level diagram of Tm^{3+} .

Figure 3(a) shows the intrinsic emission of $\text{Ca}_2\text{YTaO}_6:0.005\text{Tm}^{3+}$ under the excitation of 359 nm, which has a maximum wavelength at 460 nm. In the pink curve, a broadband (200-250 nm) is corresponding to $\text{O}^{2-} \rightarrow \text{Tm}^{3+}$ charge transfer band [21, 22]. And another strong peak at 359 nm is attributed to the characteristic $4f-4f$ transition of $^3\text{H}_6 \rightarrow ^1\text{D}_2$ of Tm^{3+} . In the blue curve, the single emission band at 460 nm is attributed to the electronic dipole transition of $^1\text{G}_4 \rightarrow ^3\text{H}_6$ of Tm^{3+} [23]. The energy level

diagram of Tm^{3+} illustrates the corresponding radiative process in the host. Under 359 nm excitation, the electrons in Tm^{3+} transitioned from the $^3\text{H}_6$ level of the ground state to the $^1\text{D}_2$ level of the excited state. Subsequently, the electrons of Tm^{3+} relaxed to $^1\text{G}_4$ level and returned to the $^3\text{H}_6$ level via radiative transitions and emitted blue light. The typical blue emission peaks of $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ suggest its potential applications as blue-emitting phosphors.

Figure 4(a). PL spectra ($\lambda_{\text{ex}} = 359$ nm) of $\text{Ca}_2\text{YTaO}_6: x\text{Tm}^{3+}$ ($x=0.3\%-5\%$ mol) phosphors. **(b)** The effect of doping Tm^{3+} concentrations.

The PL spectra of $\text{Ca}_2\text{YTaO}_6: x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) are shown in Figure 4(a). All the emission curves have the same peak shapes while the doping concentration of Tm^{3+} is different. In Figure 4(b), when the doping concentration of Tm^{3+} reached 0.5% mol in the Ca_2YTaO_6 host, the

emission intensity of the $\text{Ca}_2\text{YTaO}_6: 0.005\text{Tm}^{3+}$ reached its maximum. Whereafter, the intensity gradually decreased with further increasing Tm^{3+} doping concentration, which is caused by concentration quenching.

The energy transfer mechanism in the $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ system is discussed in terms of critical energy transfer distance (R_c), which can be estimated by the equation (1) [24-28]:

$$R_c \approx 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (1)$$

Here X_c (0.005) represents the critical doping concentration. In the unit cell, V ($261.07 \text{ \AA}^3$) refers to the volume, and N (4) is the number of substitutable cations. According to equation (1), R_c was calculated to be $29 \text{ \AA}$, more than that of exchange interaction distance ($5.0 \text{ \AA}$). Thus, the electric multipole interactions between Tm^{3+} ions are proposed for the concentration quenching mechanism.

Besides, the specific type of the energy transfer

mechanism among Tm^{3+} in Ca_2YTaO_6 host is discussed according to Dexter's theory [29]:

$$\frac{I}{x} = K \left[1 + \beta (x)^{Q/3} \right]^{-1} \quad (2)$$

Where Q is a certain constant, representing types of energy transfer interaction, which are the nearest-neighbor ions ($Q=3$), electric dipole-dipole ($Q=6$), dipole-quadrupole ($Q=8$), and quadrupole-quadrupole ($Q=10$) interactions, respectively. x is the Tm^{3+} doping concentration, K and β are constants. The experimental data of the relationship between $\lg(I/x)$ and $\lg x$ (Figure 5) can be fitted by a linear relationship. The slope ($-Q/3$) of the line is well fitted to be -1.11 . Thus Q value is expected to be 3, suggesting the nearest neighbor ions interaction is the main mechanism for the concentration quenching in $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ compounds.

CIE chromaticity coordinates are important parameters that should be characterized to determine the luminescent properties of materials. The color coordinates of $\text{Ca}_2\text{YTaO}_6: x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) are displayed in Figure 6 with the uniform locations in blue region. The color purity of the products can be estimated by equation (3) [30, 31]:

$$\text{Color purity} = \sqrt{\frac{(x-x_i)^2 + (y-y_i)^2}{(x_d-x_i)^2 + (y_d-y_i)^2}} \times 100 \quad (3)$$

Here (x, y) are the chromaticity coordinates of the phosphors; (x_i, y_i) are the chromaticity coordinates of the white light source, equal to (0.333, 0.333); and (x_d, y_d) are the chromaticity coordinates of the dominant wavelength points [32]. As shown in Figure 6, the color coordinates of the products were in the blue region. In the $\text{Ca}_2\text{YTaO}_6: 0.05\text{Tm}^{3+}$ compound, the color purity was calculated around 94.6%. When the $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ is excited by UV light, it can emit blue light effectively with a high color purity.

4 Conclusions

The $\text{Ca}_2\text{YTaO}_6: x\text{Tm}^{3+}$ ($x = 0.3\%-5\%$ mol) phosphors were firstly prepared through solid-state method. At 359 nm excitation wavelength, the $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ phosphors present strong emission peaks at 460 nm. The critical doping concentration of Tm^{3+} is 0.5% mol in $\text{Ca}_2\text{YTaO}_6: x\text{Tm}^{3+}$. The concentration quenching mechanism is proposed for the interaction of the nearest-neighbor ions, while the relevant critical distance is around 29 Å. The CIE color coordinates near the standard blue position. The results indicate that the $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ products have blue-emission ability with good color purity. As a result, the $\text{Ca}_2\text{YTaO}_6: \text{Tm}^{3+}$ phosphors are promising blue-emitting candidates for WLED applications.

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