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ARTICLE

Tunable Luminescence Properties and Elucidating the Electronic Structures of Single-Phase Spherical BaWO₄: Dy³⁺, Tm³⁺, Eu³⁺ Phosphors for Warm-White-Lighting

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ABSTRACT

A series of uniform single-phase spherical BaWO₄: Dy³⁺, Tm³⁺, Eu³⁺ phosphors were prepared via a microwave hydrothermal method by using trisodium citrate dehydrate as surfactant. The phase structure, morphology and photoluminescence properties were measured by powder X-ray diffraction, scanning electron microscope and fluorescence spectrometer, respectively. The results show that uniform spherical microcrystals with diameters in the range of 2–4 µm are obtained. And the phase and morphology of samples are not significantly changed by doping rare earth (RE³⁺) ions. Under the excitation wavelength of 356 and 365 nm, the samples BaWO₄: $0.03Dy^{3+}$, yTm^{3+} can emit cold white light. In order to lower the correlated color temperature (CCT) to get a warm white light, the Eu³⁺ ions were doped into BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$. Especially, under the excitation of 365 nm, BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$, $0.03Eu^{3+}$ phosphor shew a bright warm white light with color coordinate of (0.4013, 0.3629) and CCT of 3288 K. Moreover, in the BaWO₄: Dy^{3+} , Tm^{3+} , Eu³⁺ phosphors, the energy transfer mechanism among Dy^{3+} , Tm^{3+} and Eu^{3+} ions have been discussed and the change of electron structures have been calculated by first-principles calculations. The results shew that the uniform single-phase spherical BaWO₄: Dy^{3+} , Tm^{3+} , Eu^{3+} phosphors could be favorable candidates in warm white LEDs.

KEYWORDS

Barium tungstate; microwave hydrothermal method; spherical; warm white lighting; electron structures

1 Introduction

Solid-state white lighting equipment based on semiconductors chips and inorganic phosphors have become an excellent choice for providing ambient lighting because of the advantages of long service life, energy efficiency and environmental friendliness [1–3]. White light-emitting diodes (LEDs) have already replaced incandescent and fluorescent lamps as a new generation of lighting source [4]. There are a number of different strategies to realize a white LED. The most common one is InGaN blue chips combined with YAG: Ce³⁺ yellow phosphors, which shows high correlated color temperature (CCT > 4500 K) because of the deficiency of red component [5–8]. Another method is combined red, green and



blue (RGB) phosphors with ultraviolet (UV) or near-ultraviolet (NUV) chips, which still has a problem that phosphors may have different degradation rates and the final color of light will change over time [9–12]. A more attractive approach is using a UV chip in conjunction with a single-phase phosphor that has multiple emitting centers to get warm-white light [13–15].

Alkaline earth tungstate AWO₄ (A = Ca, Sr or Ba) include a wide range of applications materials such as scintillators, luminescent materials, electro-optical devices, and catalysts [16–18]. Barium Tungstate (BaWO₄) is considered an prominent matrix material for photoluminescence materials due to the charge transfer (CT) from oxygen to the tungsten under the UV light [19]. Rare earth (RE) ions have a large number of energy levels in which electrons can jump when excited by UV light. One of the RE ions Dy³⁺ has a great potential in the preparation of white phosphors because of the emission light of Dy³⁺ contain blue (470–500 nm) and yellow (570–600 nm) composition under UV excitation [20]. Thulium Tm³⁺ can be used as a sensitizer to promote the emission of Dy³⁺ ions due to the energy transfer between Tm³⁺ and Dy³⁺ [21]. Europium Eu³⁺ ions are wide used in phosphors due to the red emission upon UV excitation [22–24]. Among Dy³⁺, Tm³⁺ and Eu³⁺ ions in the host of BaWO₄, Tm³⁺ ions are activators. Therefore, in the present work, Dy³⁺, Tm³⁺, and Eu³⁺ ions were co-doped into a BaWO₄ matrix to obtain a single-phase warm-white phosphor with improved luminescence properties.

The doping of RE ions will have an impact on the electronic structures of materials. The type and amount of doping elements can adjust the band gap and electronic state density distribution of materials, which will affect the practical application of materials [25,26]. Carvalho et al. employed the Density Functional Theory (DFT) to calculate band gap, electron density of states and optical properties of the AWO₄ (A = Ca, Sr or Ba) with scheelite-type structure [27]. But the change of the electronic structures when RE doped BaWO₄ were not discussed enough. Considering the influence of particle size and morphology on the fluorescence performance, uniform and spherical microcrystals is advantageous of fluorescence performance due to the high bulk densities and low light scattering. Therefore, in this works, a series of single phase BaWO₄: RE³⁺ (Dy³⁺, Tm³⁺ and Eu³⁺) were synthesized by a microwave hydrothermal method to explore the variations of electronic structures and test the photoluminescence properties of this samples. Based on the experimental results and theoretical calculations, the tunable color and single phase BaWO₄: RE³⁺ (Dy³⁺, Tm³⁺ and Eu³⁺) could be favorable candidates in warm white LEDs.

2 Experimental

2.1 Materials and Preparation

A series of samples of BaWO₄: xDy^{3+} , BaWO₄: xDy^{3+} , yTm^{3+} , BaWO₄: xDy^{3+} , yTm^{3+} , zEu^{3+} were prepared by the microwave hydrothermal method. The raw materials used were Ba(NO₃)₂(A.R.), Na₂WO₄•2H₂O(A.R.), Tm(NO₃)₃•6H₂O(A.R.), Dy₂O₃(99.9%) and Eu₂O₃(99.9%). Dy(NO₃)₃ and Eu (NO₃)₃ solution were obtained by dissolving the Dy₂O₃(99.9%) and Eu₂O₃(99.9%) in nitric acid solution under stirring. In a typical experiment, the Ba(NO₃)₂ (0.1 mol/L), Dy(NO₃)₃ (0.1 mol/L), Tm(NO₃)₃ (0.1 mol/L) solutions were mixed with the designed stoichiometric ratio. Then trisodium citrate dehydrate (C₆H₅Na₃O₇) (0.2 mol/L) as a surfactant were added with stirring for 10 min. After that, Na₂WO₄ (0.15 mol/L) were injected into the hybrid solution and the pH of mixture was adjusted to 8 by the sodium hydroxide solution. After stirring for 15 min, the mixture solution was transferred and sealed into a glass tube and heated by microwave (CEM-discovery, CEM, USA) with T = 160°C and t = 1 h. After naturally cooling to room temperature, the products were separated by centrifugation (5000 r/min, 10 min) and rinsed several times with water and alcohol, which were further dried at 80°C for 8 h.

2.2 Characterization

The crystal structure and phase composition of the samples were determined by the X-ray diffraction (XRD) analysis (SmartLab X-ray Diffractometer) with Cu K α radiation ($\lambda = 0.15405$ Å) at a scanning speed of 10°/min from 10° to 80°. The morphology and energy dispersive X-ray (EDX) spectrum were inspected by a scanning electron microscope (SEM, JSM-6510, JEOL Ltd., Japan). The fluorescence properties of prepared samples were carried out by a FL3-221 fluorescence spectrometer (HORIBA, France) using a Xe lamp as an excitation source. The TU-1810 UV-Vis spectrophotometer produced by Beijing Purse General Instrument Co., Ltd. China, is used to measure the UV absorption spectra of the materials.

2.3 Calculation Method

According to Cavalcante et al. report, scheelite-type structure BaWO₄ with lattice parameters (a = b = 5.6054 Å, c = 12.7041 Å) was chosen for the structural optimization and calculation [28]. The optimizations and calculations were performed by the DFT based on the software package CASTEP in Materials Studio. The exchange correlation interactions was described by generalized gradient approximation (GGA) with the Predew-Burke-Ernzerhof (PBE) scheme [28]. Throughout the calculation, the Vanderbilt ultrasoft pseudopotential with a cutoff energy of 571.4 eV was carried out and the Brillouin zone of samples were sampled using $3 \times 3 \times 1$ mesh of the Monkhorst–Pack scheme. The convergence tolerance for geometry optimization was $1.0 \times 10^{-6} \text{ eV}/\text{atom}$ and the maximal force on each atom was less than 0.01 eV/Å.

3. Results and Discussion

3.1 Structure and Morphology

The XRD patterns of BaWO₄: RE³⁺ (Dy³⁺, Tm³⁺ and Eu³⁺) samples synthesized by the microwave hydrothermal method with C₆H₅Na₃O₇ at 160°C for 1 h with pH = 8 were present in Fig. 1. All of the diffraction patterns detected can be assigned to the pure scheelite-type tetragonal crystal structures with the space group I41/*a* (88), which is in line with the PDF card (JCPDS 43-0646). The results indicate that the RE ions successfully introduced into the host and did not significantly change the BaWO₄ structure. But, with the concentration of the RE ions increased, the XRD diffraction peaks of the samples offset a little to the high angle region, because the radii of Dy³⁺ (0.912 Å), Tm³⁺ (0.880 Å) and Eu³⁺ (0.947 Å) are smaller than that of Ba²⁺ (1.350 Å). That further indicates that RE ions replace Ba²⁺ into the lattice. To balance the crystal charge, the vacancies of Ba (V_{Ba}) occurred, and the V_{Ba} increased with the increase of doping concentration, which will lead the diffraction peak intensities to be reduced and broad [29].



Figure 1: XRD patterns of BaWO₄: RE^{3+} samples prepared by the microwave hydrothermal method with $C_6H_5Na_3O_7$ at 160°C for 1 h

Fig. 2 shows the SEM images of the BaWO₄ and BaWO₄: RE^{3+} (Dy³⁺, Tm³⁺ and Eu³⁺) samples. It can be clearly seen that the BaWO₄ and BaWO₄: RE^{3+} samples are well-dispersed microspheres and the diameters are about 2–4 µm. As shown in Fig. 2, with the doping of RE^{3+} ions, the particle size of the sample decreased slightly and the particle surface becomes smooth. The reason for this phenomenon is that vacancy defects caused by unequal substitution between Ba²⁺ ions and RE^{3+} ions will restrict the growth of crystals and eventually lead to the reduction of particle size. Combining with XRD results, RE^{3+} ions doping into BaWO₄ host will not significantly change the crystal structure and morphology, which consistent with the previous reports [30]. As we know, spherical phosphor has a higher packing densities and lower light scattering characteristics, so a narrow particle size distribution and a spherical shape with an appropriate particle size are conducive to obtaining higher brightness [31].



Figure 2: SEM images of the synthesized samples (a) $BaWO_4$, (b) $BaWO_4$: $0.03Dy^{3+}$, (c) $BaWO_4$: $0.03Dy^{3+}$, $0.01Tm^{3+}$ and (d) $BaWO_4$: $0.03Dy^{3+}$, $0.01Tm^{3+}$, $0.03Eu^{3+}$

3.2 Electronic Structures

For purpose of exploring the electronic structure of BaWO₄, the band structures and density of states was calculated and shown in Fig. S1. The valence band (VB) maxima and conduction band (CB) minima are both located at the G point indicated that BaWO₄ is a direct gap material, which is keeping with other's experiment results. The band gap energy (E_g) of BaWO₄ is 4.666 eV, which is similar to the report [32]. Fig. 3 shew the band structures of BaWO₄: xDy^{3+} (x=0.01-0.05) calculated by the DFT calculations. With the doping of Dy^{3+} ions, comparing with pure BaWO₄, band gaps decreased linearly, which show in Fig. 3f. But the direct character of the band gap is not changed with the increased concentration of Dy^{3+} ions. As shown in Fig. S2 and Fig. 4, with the doping of Tm^{3+} and Eu^{3+} ions, the band gap still decreases linearly and keeps the direct character. By studying the change of partial density of states near the Fermi level of the BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$, zEu^{3+} , the *p* and *f* populations around the fermi level are shown in Fig. 4. The doping of RE³⁺ ions will affect both conduction band and valence band. And the effect on the valence band is more obvious The valence band rises while the conduction band falls, resulting in a decrease in the band gap, which consistent with the literature reported previously [33]. The reduction of the band gap helps the transition of electrons to improve the fluorescence performance. The experimental values obtained for the band gap of the BaWO₄ and

$$[F(R)hv] = (hv - E_g)^n \tag{1}$$

$$F(R) = \frac{(1-R)^2}{2R}$$
(2)

$$A = -\log R \tag{3}$$

where A was absorption constant, h was the Planck's constant, v was frequency of light, E_g was optical band gap and n takes the values n = 1/2 or 2, corresponding to the direct or indirect allowed transition. The E_g values are presented in Fig. S4, but the E_g values are larger than that of theoretical calculation. This is due to the defects of the GGA, which underestimates the correlation between the excited electrons and makes the calculated value lower than the experimental value [36]. The experiment band gaps shared a same trend with the theoretical calculations, RE³⁺ ions doping will reduce the band.

3.3 Luminescence Properties

The room temperature PLE and PL spectra of the BaWO₄: $xDy^{3+}(x=0.01-0.05)$ phosphors are shown in Fig. 5. The PLE spectrum monitored at 571 nm consists of a wide absorption band because of the $O^{2-} \rightarrow W^{6+}$ charge transfer band (CTB) and several bands located at 327, 351, 367, 389 and 427 nm, which are corresponded to the electronic transitions of Dy^{3+} from ${}^{6}H_{15/2}$ to ${}^{6}P_{3/2}$, ${}^{6}P_{7/2}$, ${}^{6}P_{5/2}$, ${}^{4}I_{13/2}$ and ${}^{4}G_{11/2}$, respectively [37]. Under the excitation at 351 nm, the characteristic emission peaks of the BaWO₄: $xDy^{3+}(x=0.01-0.05)$ phosphors are located at 482, 571 and 660 nm, which are ascribed to the transitions from the ${}^{4}F_{9/2}$ to the ${}^{6}H_{15/2}$, ${}^{6}H_{13/2}$ and ${}^{6}H_{11/2}$, respectively. The PL emission of Dy³⁺ are significantly influenced by the structural defects in the crystalline lattice, which will break the symmetry of the crystal structure and makes the electric dipole transition (yellow light) significantly stronger than the magnetic dipole transition (blue light). Fig. 4b shows the PL emission spectra of BaWO₄: $xDy^{3+}(x=0.01-0.05)$ phosphors upon 351 nm excitation. It can be seen that the emission intensity increased with the concentration of Dy³⁺ increasing to 0.03, and then declined due to the concentration quenching. The increase in emission intensity is mainly due to two reasons: on the one hand, the increase in the emission center, on the other hand, the reduction of the band gap enhance the charge transfer process between the WO₄ and REO₆, which corresponded with the literature reported previously [38]. The concentration quenching mainly arises from an increase in probability of non-radiative interaction with increasing distance between Dy^{3+} ions at higher concentrations. The critical distance R_c can be calculated by the following equation [39]:

$$R_C \approx 2 \left(\frac{3V}{4\pi x_c N}\right)^{\frac{1}{3}} \tag{4}$$

where V stands for the unit cell volume, x_c is the critical concentration, at which the emission intensity of Dy³⁺ reaches to maximum value, and N is the number of available sites for the dopant in the unit cell. For BaWO₄ host, V=399.17 Å³, N=4 and $x_c=0.03$. Hence, the $R_c=17.54$ Å. When the concentration of Dy³⁺ exceeded 0.03, the non-radiative transfer among Dy³⁺ ions giving rise to the decrease of fluorescence intensity.



Figure 3: Band structures of BaWO₄: xDy³⁺, (a) x = 0.01, (b) x = 0.02, (c) x = 0.03, (d) x = 0.04, (e) x = 0.05, and (f) the dependence of band gaps on x



Figure 4: Band structures of BaWO₄: 0.03Dy³⁺, 0.01Tm³⁺, zEu³⁺ (a) z = 0.01, (b) z = 0.02, (c) z = 0.03, (d) z = 0.04, (e) z = 0.05, and (f) the dependence of band gaps on z

As shown in Fig. 6a, the PLE spectra of BaWO₄: 0.03Tm^{3+} and BaWO₄: 0.03Dy^{3+} phosphors are monitored at 451 and 571 nm, respectively. The BaWO₄: 0.03Tm^{3+} shows blue emission at 451 nm, which was ascribed to the ${}^{1}\text{D}_{2} \rightarrow {}^{3}\text{F}_{4}$ transition (451 nm) of the Tm³⁺ ions upon excitation at 360 nm [40]. There is an obvious overlap part between the excitation peak of Dy³⁺ peaking at 454 nm (${}^{6}\text{H}_{15/2} \rightarrow {}^{4}\text{I}_{15/2}$) and the emission peak of Tm³⁺ peaking at 451 nm (${}^{1}\text{D}_{2} \rightarrow {}^{3}\text{F}_{4}$), indicating Tm³⁺ ions can be employed as efficient sensitizers for Dy³⁺ emission. And it also indicating that the light of the overlap can excite Dy³⁺ and Tm³⁺ in BaWO₄: Dy³⁺, Tm³⁺ phosphor concurrently. So we selected 356 and 365 nm which are corresponding to the intersection point of the PLE curves of BaWO₄: 0.03Tm^{3+} and BaWO₄: 0.03Dy^{3+} , 0.01Tm^{3+} phosphors excited by 351, 356, 360 and 365 nm, respectively. The excitation peaks at 351 and 360 nm are attributed to the transition ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{P}_{7/2}$ of Dy³⁺ and the transition ${}^{3}\text{H}_{6} \rightarrow {}^{1}\text{D}_{2}$ of Tm³⁺, separately. With a change of the lights, the emission intensity at 451 nm of Tm³⁺ is too weak to change the color of light. And the luminescence intensity of Dy³⁺ at 360 nm is much lower than that at 351 nm. So, we selected 356 and 365 nm excited Dy³⁺ and Tm³⁺ co-doped phosphors.



Figure 5: (a) The excitation spectra of BaWO₄: $xDy^{3+}(x=0.01-0.05)$, (b) the emission spectra of BaWO₄: $xDy^{3+}(x=0.01-0.05)$

For purpose of tuning the color of the emitted light, a series of BaWO₄: 0.03Dy^{3+} , $y\text{Tm}^{3+}$ (y = 0, 0.005, 0.01, 0.02, 0.03 and 0.04) were synthesized in this work. As shown in Fig. 7, under 356 nm light excitation, the emission peaks at 451 nm correspond to the transitions of Tm³⁺ and the emission peaks at 481 and 571 nm are attributed to the transitions of Dy³⁺. Fig. 7 inset showed the change of emission intensities peaking at 451, 481 and 571 nm on Tm³⁺ concentration. With the concentration of Tm³⁺ increasing, the emission intensities peaking at 451, 481 and 571 nm on Tm³⁺ concentration. With the concentration of Tm³⁺ increasing, the emission intensity of Tm³⁺ centered at 451 nm are gradual increasing, whereas that of Dy³⁺ first increase and then decrease. This phenomenon shows that there is an energy transfer between Dy³⁺ and Tm³⁺ in them co-doped phosphors. As shown in Fig. S4., under 365 nm light excitation, the same phenomenon happened with exciting at 356 nm. Tab. 1 shows the Commission International de I'Eclairage (CIE) chromaticity of BaWO₄: 0.03Dy³⁺, $y\text{Tm}^{3+}$ and the CIE diagrams are shown in Figs. 11a and 11b. Because of the enhancing emission of Tm³⁺ and the weakening emission of Dy³⁺, the CIE coordinates moved to the blue

region except the BaWO₄: 0.03Dy³⁺, 0.005Tm³⁺ sample. When the doping concentration of Tm³⁺ is 0.005, the emission of Dy³⁺ enhanced and CIE coordinates shifted toward the yellow region. The CCT values can be calculated by the equation [41]:

$$CCT = -449n^3 + 3525n^2 - 6823.3n + 5520.33 \tag{5}$$

where n = (x - 0.332)/(y - 0.186). And the results also shown in Tab. 1. It can be clearly seen that the CCT are more than 4000 K and belongs to the cold white light.



Figure 6: (a) The PL and PLE spectra of BaWO₄: Tm³⁺ (blue) and PLE spectrum of BaWO₄: Dy³⁺ (green), (b) the PL spectra of BaWO₄: 0.03Dy³⁺, 0.01Tm³⁺ under different excitation light



Figure 7: PL spectra of BaWO₄: 0.03Dy³⁺, yTm³⁺ with different Tm³⁺ doping concentrations excited at 356 nm. Inset shows dependence of emission intensity peaking at 451, 481 and 571 nm

In order to get warm white light, the Eu³⁺ ion which can supplement red light ingredients is introduced into BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$ phosphors. Fig. 8 depicts the PL spectrum of BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$ samples excited by 365 nm. And the PLE spectrum of BaWO₄: $0.03Eu^{3+}$ sample monitored by 612 nm. Some main excitation band located at 363, 395, 466 and 536 nm are ascribed to the transitions of Eu³⁺ from ⁷F₀ to⁵D₄, ⁵L₆, ⁵D₂ and ⁵D₁, respectively [42]. It can be distinctly seen that two overlap parts located in the range of 455–480 nm and 550–580 nm. This phenomenon shows that energy transfers among Tm³⁺, Dy³⁺ and Eu³⁺ ions are existed in BaWO₄: Dy³⁺, Tm³⁺, Eu³⁺ phosphors.

| Label | Samples | Excitation (nm) | CIE (x, y) | CCT (K) |
|-------|---|-----------------|------------------|---------|
| 1 | BaWO ₄ :0.03Dy ³⁺ | 356 | (0.3736, 0.4118) | 4381 |
| 2 | BaWO ₄ :0.03Dy ³⁺ , 0.005Tm ³⁺ | 356 | (0.3748, 0.4137) | 4360 |
| 3 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ | 356 | (0.3554, 0.3830) | 4762 |
| 4 | BaWO ₄ :0.03Dy ³⁺ , 0.02Tm ³⁺ | 356 | (0.3658, 0.3958) | 4511 |
| 5 | BaWO ₄ :0.03Dy ³⁺ , 0.03Tm ³⁺ | 356 | (0.3628, 0.3916) | 4577 |
| 6 | BaWO ₄ :0.03Dy ³⁺ , 0.04Tm ³⁺ | 356 | (0.3580, 0.3790) | 4662 |
| 7 | $BaWO_4:0.03Dy^{3+}$ | 365 | (0.3725, 0.4103) | 4402 |
| 8 | BaWO ₄ :0.03Dy ³⁺ , 0.005Tm ³⁺ | 365 | (0.3735, 0.4120) | 4385 |
| 9 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ | 365 | (0.3451, 0.3672) | 5049 |
| 10 | BaWO ₄ :0.03Dy ³⁺ , 0.02Tm ³⁺ | 365 | (0.3641, 0.3927) | 4544 |
| 11 | BaWO ₄ :0.03Dy ³⁺ , 0.03Tm ³⁺ | 365 | (0.3583, 0.3832) | 4672 |
| 12 | BaWO ₄ :0.03Dy ³⁺ , 0.04Tm ³⁺ | 365 | (0.3541, 0.3711) | 4752 |
| 13 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.01Eu ³⁺ | 356 | (0.3730, 0.3950) | 4306 |
| 14 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.02Eu ³⁺ | 356 | (0.3677, 0.3770) | 4351 |
| 15 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.03Eu ³⁺ | 356 | (0.3700, 0.3692) | 4229 |
| 16 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.04Eu ³⁺ | 356 | (0.3721, 0.3694) | 4166 |
| 17 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.05Eu ³⁺ | 356 | (0.3727, 0.3616) | 4089 |
| 18 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.01Eu ³⁺ | 365 | (0.3880, 0.3876) | 3855 |
| 19 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.02Eu ³⁺ | 365 | (0.3961, 0.3708) | 3501 |
| 20 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.03Eu ³⁺ | 365 | (0.4013, 0.3629) | 3288 |
| 21 | $BaWO_4:0.03Dy^{3+}, 0.01Tm^{3+}, 0.04Eu^{3+}$ | 365 | (0.4170, 0.3651) | 2945 |
| 22 | BaWO ₄ :0.03Dy ³⁺ , 0.01Tm ³⁺ , 0.05Eu ³⁺ | 365 | (0.4187, 0.3498) | 2721 |

Table 1: CIE chromaticity coordinates for BaWO₄: Dy³⁺, Tm³⁺, Eu³⁺ samples

The purpose of this work is to tunable color to get warm white light in a single phase host. To achieve this goal, a series of BaWO₄: 0.03Dy³⁺, Tm³⁺, zEu³⁺ (z = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) were synthesized in this work. Fig. 9 shows the PL spectra of BaWO₄: 0.03Dy³⁺, Tm³⁺, zEu³⁺ (z = 0.01, 0.02, 0.03, 0.04 and 0.05) phosphors excited at 356 and 365 nm, respectively. The emission peak at 612 nm is attributed to the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ of Eu³⁺ [43]. The emission intensities peak at 451 nm (Tm³⁺), 571 nm (Dy³⁺) and 612 nm (Eu³⁺) with change of the concentration of Eu³⁺ ions are shown in inset of Figs. 9a and 9b. With the increasing content of Eu³⁺ ions, the Eu³⁺ related red emission (peak at 612 nm) increases, however the intensity of characteristic emission peaks of Dy³⁺ and Tm³⁺ decreased because of the energy transfers among the Dy³⁺, Tm³⁺ and Eu³⁺ ions. Under 356 nm light exciting, only one emission of Eu³⁺ peaks at 612 nm due to the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ can be identified and that has a low emission intensity. This suggests that the light of 356 nm cannot effectively excite Eu^{3+} ions. Whereas, upon excitation at 365 nm, two characteristic peaks appeared: electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ peak at 612 nm and magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ peak at 588 nm. And electric dipole transition intensity is much stronger than magnetic dipole transition intensity, which means that Eu³⁺ ions occupied the non-inversion symmetry center in the matrix material lattice [44]. The CIE coordinates and CCT of this series of BaWO₄: 0.03Dy^{3+} , Tm^{3+} , $z\text{Eu}^{3+}$ phosphors are also calculated and shown in Tab. 1. Due to the red emission of Eu³⁺ ions, CIE coordinates shifted toward to the red region and the CCT have decreased.



Figure 8: The PL spectrum of $BaWO_4$: 0.03Dy³⁺, 0.01Tm³⁺ (blue) and the PLE spectrum of $BaWO_4$: 0.03Eu³⁺ (red)

For a better understand the energy transfer mechanism among Tm^{3+} , Dy^{3+} and Eu^{3+} ions, a possible schematic diagram is shown in Fig. 10. According to the results of the previous calculation, when the Tm^{3+} , Dy^{3+} and Eu^{3+} ions doping into the BaWO₄, the band gap is decreasing, which indicates that the 2 p electron of O^{2-} are more easily jumped to the 5 d orbit of W^{6+} in WO_4^{2-} under UV excitation and then a part of the energy is released in the form of light, and the other part is transferred to the RE ions. On the other hand, under UV excitation, for example ground state (${}^{3}\text{H}_{6}$) electrons of Tm^{3+} will absorb energy and jump to a higher energy state (${}^{1}\text{D}_2$). And then some excited electrons returned to the lower energy level (${}^{1}\text{D}_2 \rightarrow {}^{3}\text{F}_4$) and the excess energy was released as light. Some high energy states electrons returned to lower energy level (${}^{1}\text{D}_2 \rightarrow {}^{3}\text{F}_4$) by emitting light. As for Dy^{3+} and Eu^{3+} , ground state electrons first jumped to a higher energy states by NR, and finally fell to lower energy states by emitting different colors of light such as yellow light (${}^{4}\text{F}_{9/2} \rightarrow {}^{6}\text{H}_{13/2}$) of Dy^{3+} and red light (${}^{5}\text{D}_0 \rightarrow {}^{7}\text{F}_2$) of Eu³⁺ [45]. Moreover, combining with the Figs. 6a and 8, the blue emission (${}^{1}\text{D}_2 \rightarrow {}^{3}\text{F}_4$) of Tm³⁺ can excited the ground state (${}^{6}\text{H}_{15/2}$) electrons of Dy^{3+} to excitation state (${}^{4}\text{I}_{15/2}$) and then electrons fell back to lower energy states by NR and emitting light.



Figure 9: Continued



Figure 9: The PL spectra (a) $\lambda_{ex} = 356$ nm and (b) $\lambda_{ex} = 365$ nm of BaWO₄: Dy³⁺, Tm³⁺, zEu³⁺ (z = 0.01–0.05) phosphors. Inset shows dependence of emission intensity peaking at 451, 571 and 612 nm



Figure 10: A schematic energy level diagram indicating energy transfer progresses under UV excitation. NR and ET stand for non-radiation transition and energy transfer, respectively

For a better catching on the actual emission color of the phosphor, the CIE chromaticity coordinates and CCT for BaWO₄: xDy^{3+} , yTm^{3+} , zEu^{3+} phosphors are calculated by the emission spectra excited at different lights and the consequences are shown in Tab. 1 and Fig. 11. The doping concentration of Dy^{3+} is fixed at 0.03, with the doping of Tm^{3+} increasing, under 356 and 365 nm excitation, the emitting color of the phosphors are modulated from yellow to blue as shown in Fig. 11a (Points 1–6) and (b) (Points 7–12).

As for BaWO₄: 0.03Dy^{3+} , $y\text{Tm}^{3+}$ (y = 0, 0.005, 0.01, 0.02, 0.03 and 0.04) phosphors, all CIE coordinates locate in white light area. But the CCT of BaWO₄: 0.03Dy^{3+} , $y\text{Tm}^{3+}$ (y = 0, 0.005, 0.01, 0.02, 0.03 and 0.04) phosphors are more than 4000 K, which cannot be used as warm white light. Therefore, a series of BaWO₄: 0.03Dy^{3+} , 0.01Tm^{3+} , $z\text{Eu}^{3+}$ (z = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) phosphors were been synthesized. Under excitation at 356 and 365 nm, the CIE coordinates move to the red area by increasing of Eu³⁺ content and are shown in Fig. 11c (point 13–17) and (d) (Points 18–22). Especially, under excitation at 356 nm, the coordinate of BaWO₄: 0.03Dy^{3+} , 0.01Tm^{3+} , 0.03Eu^{3+} is (0.4013, 0.3629) and the CCT is 3288 K, which meets the requirements of warm white light. And the digital photographs of BaWO₄: 0.03Dy^{3+} , 0.01Tm^{3+} , 0.01Tm^{3+} , 0.02Eu^{3+} and BaWO₄: 0.03Dy^{3+} , 0.01Tm^{3+} , 0.03Eu^{3+} phosphors excited at 365 nm and shown in Fig. 11d.



Figure 11: CIE chromaticity diagram of BaWO₄: Dy³⁺, Tm³⁺, Eu³⁺ samples

4 Conclusion

In summary, a series of uniform single-phase color-tunable spherical BaWO₄: xDy^{3+} , yTm^{3+} , zEu^{3+} phosphors were synthesized by microwave hydrothermal method. The XRD patterns and SEM images illustrate that the doping of RE ions does not significantly change the crystal structure and morphology. According to the DFT calculations, the doping of RE ions will causes the bands gap to decrease due to both the VB maximum and CB minimum are both changed by the substitution of the RE³⁺ cation electronic states. The reduction of the band gap is conducive to electron transition and thus to increase the luminescence intensity. For the BaWO₄: xDy^{3+} phosphors, the quenching concentrations of Dy^{3+} were 0.03. With increasing Tm³⁺ concentration, emission colors of BaWO₄: $0.03Dy^{3+}$, yTm^{3+} phosphors were properly tuned from yellow to blue. By supplement red component of light, single-phased phosphors BaWO₄: Dy^{3+} , Tm^{3+} , Eu^{3+} with warm white light were prepared. Under 365 nm excitation, the CIE coordinate of BaWO₄: $0.03Dy^{3+}$, $0.01Tm^{3+}$, $0.03Eu^{3+}$ was (0.4013, 0.3629) and the CCT was 3288 K, which could be a favorable candidate in warm white LEDs.

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Supplementary Information

Figure S1: (a) The energy band structure around fermi energy level and (b) the representative orbital populations of $BaWO_4$. DFT calculations revealed that the $BaWO_4$ was a kind of direct bandgap (4.666 eV) materials



Figure S2: (Continued)



Figure S2: Band structures of BaWO₄: 0.03Dy³⁺, yTm³⁺, (a) y = 0.005, (b) y = 0.01, (c) y = 0.02, (d) y = 0.03, (e) y = 0.04, and (f) the dependence of band gaps on y



Figure S3: Respectively, (a) p and (b) f orbital populations around the fermi level in BaWO₄: 0.03Dy³⁺, 0.01Tm³⁺, zEu^{3+} (z = 0.01 – 0.05)



Figure S4: UV-visible absorption spectra for phosphors, (a) $BaWO_4$, (b) $BaWO_4$: $0.03Dy^{3+}$, (c) $BaWO_4$: $0.03Dy^{3+}$, $0.01Tm^{3+}$, (d) $BaWO_4$: $0.03Dy^{3+}$, $0.01Tm^{3+}$, $0.03Eu^{3+}$



Figure S5: PL spectra of BaWO₄: 0.03Dy³⁺, yTm³⁺ with different Tm³⁺ doping concentrations excited at 365 nm. Inset shows dependence of emission intensity peaking at 451, 481 and 571 nm