Photoluminescence and Photocatalytic Activity in Ca\textsuperscript{2+} and Dy\textsuperscript{3+} Co-doped ZnWO\textsubscript{4} System

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Abstract. Ca\textsuperscript{2+} and Dy\textsuperscript{3+} co-doped ZnWO\textsubscript{4} system was synthesized successfully via high temperature solid-state reaction. The photoluminescent, X-ray diffraction (XRD), and photocatalytic properties of the phosphors had been studied systematically. The results indicated that Ca\textsuperscript{2+} and Dy\textsuperscript{3+} co-doped ZnWO\textsubscript{4} phosphors have lower luminescent intensity than that of ZnWO\textsubscript{4}: Dy\textsuperscript{3+} phosphors. The result of UV-Vis diffuse reflectance spectra demonstrated that Ca\textsuperscript{2+} and Dy\textsuperscript{3+} co-doped ZnWO\textsubscript{4} phosphors show higher UV absorption efficiency. In addition, photocatalytic activities of the Ca\textsuperscript{2+} and Dy\textsuperscript{3+} co-doped ZnWO\textsubscript{4} phosphors were evaluated by photo-degradation of RhB under ultraviolet irradiation. The result shows that Ca\textsuperscript{2+} and Dy\textsuperscript{3+} co-doped ZnWO\textsubscript{4} phosphors can exhibit higher photocatalytic activity than pure ZnWO\textsubscript{4}:Dy\textsuperscript{3+}, which could be ascribed to more electron-hole pairs generated and the combination of electrons and holes decreased in the co-doped phosphors. Thus, resulting in the increase of photocatalytic activity.

Introduction

Nowadays, the problem of global environmental pollution has received extensive attention, and water pollution is one of the most serious pollution problems. How to solve the problem of water pollution is one of the main tasks for every research worker. In recent years, photocatalytic degradation of organic pollutants by semiconductor photocatalysts has the potential to be a beneficial technology for environmental purification [1-2]. It has been regarded as a green low cost technology for degrading of organic pollutants under UV light irradiation [3].

ZnWO\textsubscript{4} as a widely functional material is an important photocatalytic material. Firstly, ZnWO\textsubscript{4} has been applied in LEDs due to its good luminescent properties [4]. It has also been investigated to generate white light as a kind of significant luminescent materials. The properties of ZnWO\textsubscript{4} with doped or co-doped rare earth ions still cannot meet the requirements of some applications. Rare earth ions-doped luminescent materials have been studied for a long time. As we all know, the luminescent materials consist of activator (rare earth ions) and matrixes (host materials) [5]. The lattice sites can be occupied by activators in different matrixes, causing a variety of local environmental symmetry. This is why the luminescent properties vary considerably [6]. The Dy\textsuperscript{3+} ion has abundant energy levels due to the inner 4f\textsuperscript{9} configuration. Moreover, The Dy\textsuperscript{3+} ion has two dominant emission bands, in which blue emission line (~490nm) corresponds to the \textsuperscript{4}F\textsubscript{9/2}–\textsuperscript{6}H\textsubscript{13/2} magnetic dipole transition and yellow emission line (~579nm) corresponds to the \textsuperscript{4}F\textsubscript{9/2}–\textsuperscript{6}H\textsubscript{13/2} electric dipole transition [7]. According to some reports, a large number of matrix materials can be doped with dysprosium ions, such as tungstates, vanadates, silicates, aluminates and molybdates, etc [8]. Among all the matrix materials, ZnWO\textsubscript{4} is a kind of self-activating phosphor and has stable chemical property and high light yield. Another virtue is the ability to show a broad blue-green
emission band excited by UV light. So when zinc tungstate is doped with dysprosium ions, because WO$_4^{2-}$ is kind of self-activating ions, it can emit bright blue light under ultraviolet excitation, and the excited WO$_4^{2-}$ can efficiently transfer energy to rare earths ions [9]. Second, it has also been applied for photocatalytic hydrogen production from water and mineralization of organic pollutants under UV light irradiation [10]. However, further research on the ZnWO$_4$ photocatalytic activities is still indispensable. There are many ways to improve the photocatalytic activity of ZnWO$_4$, such as doping ions and coupling with other semiconductors (WO$_3$- ZnWO$_4$, ZnO- ZnWO$_4$, TiO$_2$- ZnWO$_4$), but in general, photocatalytic activity depends strongly on the separation efficiency of photo-generated electron-hole pairs [11]. Over the years, a great amount of work has been made to facilitate the electron-hole separation and enhance the photocatalytic activity of ZnWO$_4$ [12]. However, ZnWO$_4$ has a large energy gap and only responds to ultraviolet irradiation, so this will limit its application in the high-energy solar radiation range. Up to date, great efforts had been made to prevent the recombination of charge carriers in the semiconductor by coupling with other semiconductors. As we all know, efficient charge separation and suppression of recombination between photogenerated electrons and holes are important factors for efficient photocatalytic degradation [13]. The doping of semiconductors with foreign ions has been proposed as an effective way to improve the recombination of electron-hole pairs [14]. For example, it has been reported that the optical absorption of TiO$_2$ can be modified as the result of electronic transitions from the dopant 2p or 3p orbitals to the Ti 3d orbitals. In addition, the doping with Eu$^{3+}$, Er$^{3+}$, or Ce$^{4+}$ could improve the photocatalytic activity of TiO$_2$, and doping with Dy$^{3+}$ could enhance the photocatalytic activity of ZnWO$_4$ [15-17]. Although there are many articles about Dy ions-doped ZnWO$_4$ and even though Dy$^{3+}$ could improve photocatalytic activity of ZnWO$_4$, the photocatalytic activity and luminescent properties of Dy$^{3+}$ and Ca$^{2+}$ co-doped ZnWO$_4$ phosphors have never been discussed. These ions reacted with the photogenerated holes, forming hydroxyl radicals in the reaction media that interact with Rhodamine B, leading to enhanced photocatalytic performance.

In this paper, Dy$^{3+}$ and Ca$^{2+}$ co-doped ZnWO$_4$ samples were prepared by the traditional high temperature solid-state method. We investigated the effects of Dy$^{3+}$ and Ca$^{2+}$ co-doping on the luminescent, UV-Vs diffuse reflectance spectra and photocatalytic properties of the samples. In addition, the mechanism of the photocatalytic process for Dy$^{3+}$ and Ca$^{2+}$ co-doped ZnWO$_4$ was also discussed in detail.

**Experiment**

The C$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ phosphors were prepared by the conventional solid-state reaction method. The reagents including ZnO (A.R.), CaCO$_3$ (A.R.), WO$_3$ (A.R.), and Dy$_2$O$_3$ (99.9%) were used as the raw materials without any further purification. Raw materials with stoichiometric ratio were weighed, sufficiently mixed and ground together in an agate mortar. The C$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ phosphors were denoted as S$_1$ and the Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphors were denoted as S$_2$. The Samples were annealed for 2 h at 500 °C and re-annealed at 1000 °C for 6 hours, and then were slowly cooled down to room temperature. As a result, white phosphor samples were produced.

The phase structure of the product was characterized by using XD-2 X-ray powder diffractometer (CuKα, 36 KV, 20 mA). A scan rate of 0.02°/s was applied to record the patterns in 20 range 10–70°. The photoluminescence spectra were recorded by a Hitachi FLS-980 Fluorescence Spectrophotometer with a Xe lamp excitation, and the scanning rate was 1200 nm per minute. The UV-Vis diffuse reflectance spectra (DRS) were performed on a Evaluation 220 UV-Vis spectrophotometer with an integrating BaSO$_4$ sphere.

The photocatalytic degradation tests were carried out in photoreactor (BL-GHX-V) using 0.02g S$_1$ and S$_2$ powders dispersed in 45ml Rhodamine B aqueous solution ($4\times10^{-5}$ mol/L), respectively. Prior to the reaction, the mixture aqueous solution was put into a beaker with magnetic stirring for 0.5h. The light source was a 500W ultraviolet lamp and continuous magnetic stirring should be maintained the suspension of the powder in the Rhodamine B solution. Then 6ml of the suspension was gathered for every 20min and centrifuged to remove the photocatalytic powders. After these
suspensions were centrifuged at high speed for 5 minutes and measured via an Ultraviolet-visible Light Spectrometer by measuring its absorbance at a wavelength of 553 nm. The decolorization rate percentages of RhB were calculated by the following equation:

\[
\text{Decolorization \%} = \frac{(C_0 - C_t)}{C_0}
\] (1)

Where \(C_0\) is the initial concentration of RhB and \(C_t\) is the concentration of RhB measured every 20 min of UV irradiation.

**Results and Discussion**

![XRD patterns of the samples.](image)

The crystal structures of \(\text{Ca}_{0.1}\text{Zn}_{0.89}\text{WO}_4:0.01\text{Dy}^{3+}\) (S1) and \(\text{Zn}_{0.99}\text{WO}_4:0.01\text{Dy}^{3+}\) (S2) phosphors were characterized as shown in Fig. 1. The diffraction peaks of all samples in the patterns match well with the characteristic reflections of zinc tungstate (JCPDS No. 15-0774) when appropriately doped with \(\text{Dy}^{3+}\)[18]. No other diffraction peaks belonging to the impurity phase were observed, which indicated that the samples were pure phase. The peaks were indexed as the (010), (100), (011), (110), (111), (021), (200), and (121) crystal planes of \(\text{ZnWO}_4\). However, a few peaks of \(\text{WO}_3\) appeared when the \(\text{Zn}_{0.99}\text{WO}_4\) phosphors were doped with \(\text{Dy}^{3+}\) and \(\text{Ca}^{2+}\) (Fig 1). Except for this impure phase, all the diffraction peaks are in good agreement with the standard card of \(\text{ZnWO}_4\) (JCPDS No. 15-0774), indicating that the samples belong to monoclinic wolframite structure with space group P2/c. In addition, the results show that the \(\text{Ca}^{2+}\) and \(\text{Dy}^{3+}\) in these samples should have substituted the \(\text{Zn}^{2+}\) sites. According to the Bragg equation, \(2d \sin \theta = \lambda\) (here \(d\) is the interplanar distance of corresponding crystal plane, \(\theta\) is the diffraction angle and \(\lambda\) is the wavelength of employed X-ray), because the interplanar distance \(d\) decreases, the movement of 20 shift to higher diffraction angles. But did not move that way in this pattern. The reason is that the ionic radius of \(\text{Ca}^{2+}\) (99 pm) and \(\text{Dy}^{3+}\) (91 pm) is close to that of \(\text{Zn}^{2+}\) (74 pm), but are larger than the ionic radius of \(\text{W}^{6+}\) (60 pm). According to the charge balance condition and the ions radius similarity principle, calcium ions would enter the lattice of host and occupy the sites of zinc ions. So lead to the expansion of the lattice and the cell volume becomes larger. In the pattern, \(\text{Dy}^{3+}\) and \(\text{Ca}^{2+}\) have been doped into the \(\text{ZnWO}_4\) host and did not significantly affect the phase structure of the samples.
The photoluminescence (PL) spectra of samples Ca$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ (S$_1$) and Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ (S$_2$) are illustrated in Fig. 2. The photoluminescence emission is a useful technique for investigating the generation, transfer, and recombination of photogenerated charge carriers. Lower intensity peaks indicate a high separation efficiency of electron-hole pairs. Under the excitation wavelength of 310 nm, it can be found that there are two strong emissions centered at 488 nm and 575 nm and a weak emission at 667 nm, which are originated from the $^4F_{9/2} - ^6H_{15/2}$, $^4F_{9/2} - ^6H_{13/2}$ and $^4F_{9/2} - ^6H_{11/2}$ transition of Dy$^{3+}$, respectively. It not only includes a broad band in the range from 400 to 550 nm, but also includes two sharp peaks extending from 550 to 700 nm. The broad band is composed of two parts: left part of the broad band in the range from 400 to 550 nm belongs to the intrinsic emission of WO$_4^{2-}$, and the other part of broad band corresponds to the combination of intrinsic emission of WO$_4^{2-}$ and the $^4F_{9/2} - ^6H_{15/2}$ magnetic dipole transition of Dy$^{3+}$. It is also found that the broad band peak have much more overlap with the excitation peak of the Dy$^{3+}$ at 488 nm [20]. The other two sharp emission peaks are ascribed to the $^4F_{9/2} - ^6H_{13/2}$ and $^4F_{9/2} - ^6H_{11/2}$ electric dipole transition of Dy$^{3+}$ with its maximum at 575 nm and 667 nm, respectively. Generally speaking, the phosphor luminescence performance can be affected by the matrix structure. Under the excitation 310 nm, Ca$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ and Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ are both direct-gap materials, the band gap energy of these samples can be calculated by the formula: $(\alpha h\nu)^2 = A(h\nu- E_g)$, where $A$ is the characteristic constant of semiconductor, $h$ is Plank’s constant, $\nu$ is the light frequency, $E_g$ is the optical band-gap energy and $\alpha$ is absorption coefficient. In the formula, $(\alpha h\nu)^2$ has a linear relation with $h\nu$. As displayed in the Fig.3(b), the band gap of Ca$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ and Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ are approximately 3.56 and 4.22 eV, respectively. Due to the doping of calcium ions, $E_g$ of S$_1$ decreases, leading to a higher light harvest capability [21]. Thus, more photogenerated electron–hole pairs are provided, resulting in a higher photocatalytic activity. 

Figure 2. The PL spectra of samples with the excitation wavelength of 310 nm.
In order to investigate whether the ZnWO₄:0.01Dy³⁺ phosphors synthesized with Ca²⁺ can influence the photocatalytic activity under the UV irradiation [22], the photocatalytic activities of the Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺ and Zn₀.₉₉WO₄:0.₀₁Dy³⁺ were determined by comparing the degradation efficiency of RhB under UV light irradiation (Fig. 4). The decomposition rate for the Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺/Rhodamine B and Zn₀.₉₉WO₄:0.₀₁Dy³⁺/Rhodamine B composites reached 96% and 86% after 80min, respectively [23]. Fig. 5 showed the effect of degradation of Rhodamine B after 80 minutes for all samples. We found that Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺ and Zn₀.₉₉WO₄:0.₀₁Dy³⁺ exhibited high photocatalytic activities for the Rhodamine B decomposition reaction under the ultraviolet irradiation [24]. By comparison, Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺ had better photocatalytic activities than that of Zn₀.₉₉WO₄:0.₀₁Dy³⁺. As we all know, the photocatalytic activity depends on the numbers of photoinduced electron and holes, and the proper band positions [25]. When Ca²⁺ was introduced into the system, with the increasing of trap concentration in Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺, more carriers would be caught than that in Zn₀.₉₉WO₄:0.₀₁Dy³⁺, thereby avoiding the recombination of photogenared electron-hole pairs and increasing the separation of electrons and holes. That is the reason why Ca₀.₁Zn₀.₈₉WO₄:0.₀₁Dy³⁺ showed better photocatalytic activity than Zn₀.₉₉WO₄:0.₀₁Dy³⁺.
Conclusion

In summary, Ca$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ and Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphors were synthesized successfully by a high-temperature solid-state reaction in ambient air. The Ca$^{2+}$ caused the decrease of the photoluminescence intensity of Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphor, which could be ascribe to the formation of new traps by the Ca$^{2+}$ doping. Studies of photocatalytic activity of the Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphor have indicated that Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphor with Ca$^{2+}$ exhibited higher catalytic activities than Zn$_{0.99}$WO$_4$:0.01Dy$^{3+}$ phosphor for the degradation of Rhodamine B under ultraviolet irradiation. This is because the Ca$_{0.1}$Zn$_{0.89}$WO$_4$:0.01Dy$^{3+}$ phosphor owns more traps to storage the photoinduced carriers, and the traps can capture the photoinduced electrons and holes to reduce the carriers recombination. Our work may provide a plausible strategy to develop efficient photocatalysts for environmental remediation and it is worth to be extended to the preparation of other photocatalysts with high activity.

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References


