

The effect of Y^{3+} and Eu^{3+} on properties of $Zn_3V_2O_8$ phosphor

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Abstract. In this paper, the $(Zn_{1-x}Y_x)_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphors were successfully prepared by high temperature solid state method. The effect of the doping amount of Y^{3+} and Eu^{3+} on the luminescent properties of phosphors was discussed. The phase, surface morphology and luminescent properties of the phosphors were characterized by X ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL). The results show that the phosphor is the target product, the sample of the composite particles is bulky, the excitation spectral range of $(Zn_{1-x}Y_x)_3V_2O_8$ phosphors is 300-400nm, the excitation peak is at 361nm, and $(Zn_{1-x}Y_x)_3V_2O_8$ phosphor emission spectra in the range of 420-690nm, the emission peak in 559nm. The results show that the crystal structure of $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ were the same, and the particle uniformity of $(Zn_{1-x}Eu_x)_3V_2O_8$ was better than $Zn_3V_2O_8$. The emission band $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ were present at the wave length of 420-690 nm, the luminescence property of $(Zn_{1-x}Eu_x)_3V_2O_8$ was enhance by Eu-doped.

1. Introduction

It is a hot spot for researchers to search for luminescent materials with high performance and high luminous efficiency. Choi^[1] et al synthesized successfully $Ca_3Sr_3(VO_4)_4:Eu^{3+}$ phosphors, the photoluminescence peak at 618 nm; Junjiao Kou^[2] spin crossover successfully synthesized metavanadic acid zinc ($Zn_2(OH)_3VO_3 \cdot Eu^{3+}$) and zinc pyrovanadate ($Zn_3(OH)_2V_2O_7 \cdot 2H_2O:Eu^{3+}$) and study its optical properties; Xiao Fen^[3] et al, with sol gel method, the Eu^{3+} activated $Ca_3(VO_4)_2$ red phosphors were successfully synthesized and their luminescent properties were studied; Shumei Lin^[4] et al were prepared by hydrothermal method with good crystallinity $(Zn_3(OH)_2V_2O_7 \cdot nH_2O)$ nanobelts, were obtained $(Zn_3(OH)_2V_2O_7 \cdot nH_2O)$ nanotubes by changing the reaction temperature; Donghua Chen, et al^[5] $Ca_3(VO_4)_4:Eu^{3+}, Sm^{3+}$ phosphors was synthesized successfully with high temperature solid phase method, and studied the related performance; Shibin Ni^[6], the $(Zn_3(OH)_2V_2O_7 \cdot nH_2O)$ nanobelts and nanosheets were prepared by hydrothermal method; Liu Hao et al^[7]. The green phosphor $Ca_5Mg_4(VO_4)_6$ was synthesized by solid state method, the effects of sintering temperature and heat treatment temperature on the luminescent properties of phosphors were also discussed; Shi^[8] also researched the preparation and property of nano materials of $Zn_3(OH)_2V_2O_7 \cdot 2H_2O$ deeply; The flower-type structure $Zn_3V_2O_8$ was obtained using the chemical bath deposition and the high-heat treatment without add any template agent and surfactant by Shi Rui^[9], Zhou^[10] et al $Ca_3(VO_4)_2:Eu^{3+}$ nanocrystals were synthesized at low temperature and their luminescence properties were analyzed; the $Zn_3V_2O_8$



nanosphere was obtained using the chemical bath deposition and the high-heat treatment with the base of amino acetic acid by Wang Miao^[11], Jiaolian Luo^[12] et al synthesized $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor successfully by using solid phase method. In this paper, V_2O_5 , Y_2O_3 , ZnO as raw materials, using high temperature solid state method, the $\text{Zn}_3\text{V}_2\text{O}_8:\text{Y}^{3+}$ phosphor was prepared successfully, the structure, surface morphology and luminescent properties of the synthesized phosphors were characterized by XRD, SEM and PL. And the effects of Y^{3+} concentration on the properties of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors were analyzed.

2. Experiment

The raw materials are V_2O_5 , Y_2O_3 , Eu_2O_3 , ZnO , according to the stoichiometric ratio of the reactants, weighing in a mortar, and fully grinding 50min, the reaction to the crucible in the ground, and then transferred to the muffle furnace; to muffle furnace in 100min to set the calcination temperature of 600°C . At preset temperatures for 4h, and then set the muffle furnace is reduced from calcination temperature to room temperature in the range of 120min, last, take out of sample. The experimental procedure of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ is same to it, Set the calcination temperature as shown in table 1:

Table 1 The temperature of the muffle furnace process

Reaction	Temperature	Time
Warming up stage	RT - 600°C	80 min
calcination stage	600°C	240 min
cooling stage	600°C - RT	120 min

3. The experimental result and discussion

3.1. The XRD analysis result of sample $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$

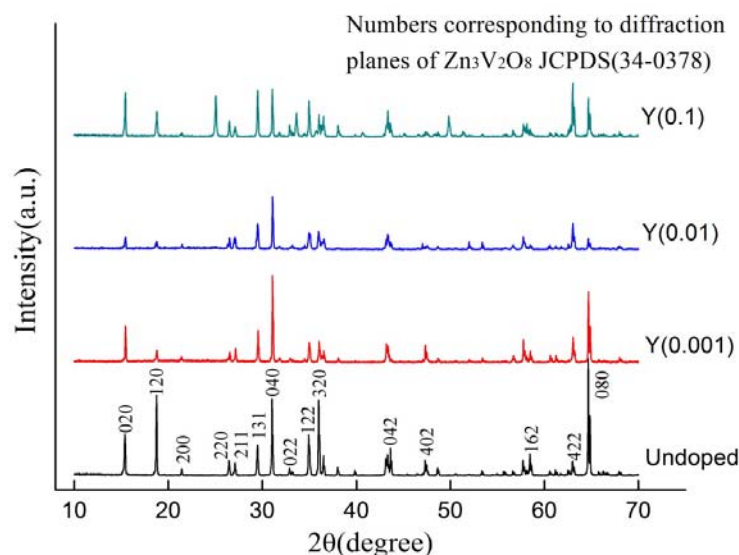


Figure 1. The XRD of the $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor under the resultant temperature of 600°C

Figure 1 is the XRD (DY1632) of the samples of $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphors calcined at a temperature of 600°C for 4h. It can be seen from the spectrogram that all the diffraction peaks are matched with the results of $\text{Zn}_3\text{V}_2\text{O}_8$ (JCPDS34-0378) standard card, which belongs to the orthorhombic system, in which the lattice constants $a=8.2290$, $b=11.5284$, $c=6.1116$, $Z=4$. Y^{3+} doped with a certain amount of $\text{Zn}_3\text{V}_2\text{O}_8$ fluorescent powder, controlling the molar amount, when the doping

amount of Y^{3+} is $x=0.001$, compared with the undoped, the characteristic peak of the product is no obvious change, no impurity peaks appeared in the crystal structure, and complete. The positions of the main peaks of the XRD spectra are in good agreement with each other, and the main diffraction peaks of the sample $(Zn_{1-x}Y_x)_3V_2O_8$ are basically matched with the results of the $Zn_3V_2O_8$ standard card.

3.2. The XRD analysis result of sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$.

Figure 2 is the XRD of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor under the resultant temperature of 600°C . The lattice parameter, phase structure and the status of Eu-doping of the sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ were analyzed by X-Ray diffraction (XRD) (DY1632). The operating voltage is 45 KV, the operating current is 40 mA, radiation source is Cu target, the scope of the scanning angle in the range of $10^\circ\sim 80^\circ$, the scanning time is 3 min. Figure 2 is the XRD of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor under the resultant temperature of 600°C . The XRD of $Zn_3V_2O_8$ shows that the largest emission peak was appeared at the diffraction angle of 35° , and the largest emission peak was 5000. The XRD of $(Zn_{1-x}Eu_x)_3V_2O_8$ shows that the crystal structure of $Zn_3V_2O_8$ wasn't changed, the intensity of diffraction, fluorescence properties and color rendering index of $Zn_3V_2O_8$ was increased by Eu-doped.

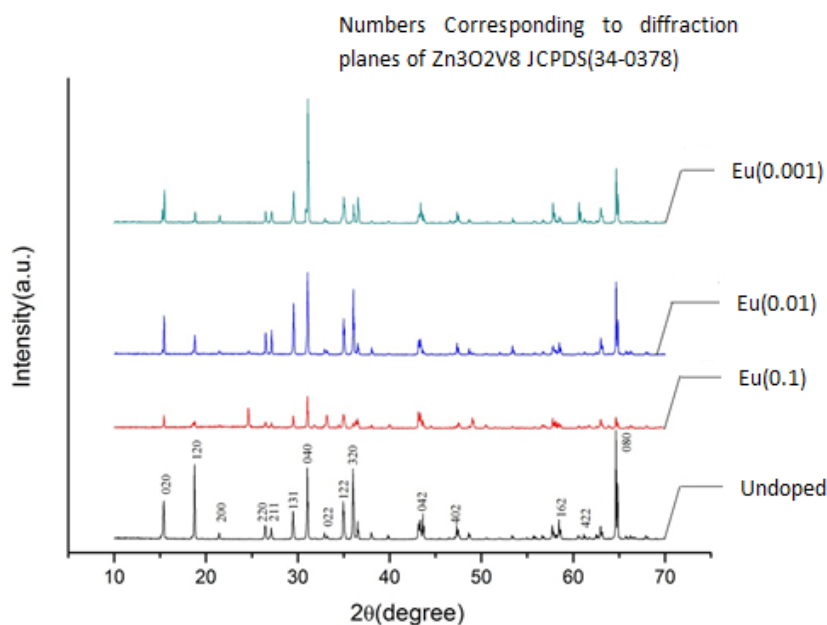


Figure 2. The XRD of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor under the resultant temperature of 600

3.3. The SEM analysis result of sample $Zn_3V_2O_8$ and $(Zn_{1-x}Y_x)_3V_2O_8$

Figure 3 is the SEM of $(Zn_{1-x}Y_x)_3V_2O_8$ phosphor powder calcined at a temperature of 600°C and the $Zn_3V_2O_8$ (EVO18) spectrum of the samples after isothermal 4h. It can be concluded from the figure that the sample size is large, and there is no agglomeration. The SEM diagram of $Zn_3V_2O_8$ phosphor is magnified 300 times, and the particle size is about $30\mu\text{m}$. And the scan of $(Zn_{1-x}Y_x)_3V_2O_8$ phosphor powder is magnified 300 times, 600 times, 1000 times, the particle size of $32\text{--}35\mu\text{m}$, which is consistent with the results of the spectrogram and XRD spectra of the same. It can be seen from the SEM spectra of rare earth doped fluorescent powder surface is rough, the two phosphor particles of $Zn_3V_2O_8$ and $(Zn_{1-x}Y_x)_3V_2O_8$ are same, they are suitable for practical application. However, the rare earth doped fluorescent powder particles is greater.

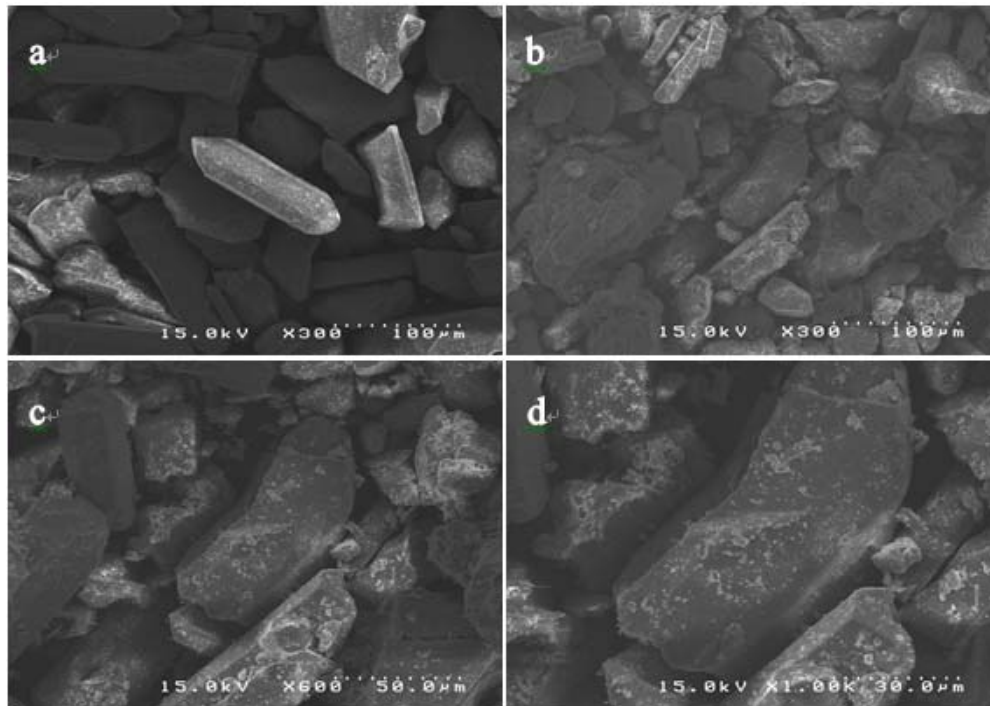


Figure 3. The SEM analysis result of sample $\text{Zn}_3\text{V}_2\text{O}_8$ (a) and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ (b, c, d)

3.4. The SEM analysis results of the sample $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$.

Figure 4 is the SEM analysis results of the sample $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$. The figure 4 shows that the $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor have the rules morphology structure, uniform particles rod structure, and haven't reunion phenomenon. The SEM of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was amplified with 200 times, the SEM of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor was amplified with 500 times, this results were correspond with XRD standard drawing. At the same time, the SEM of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ show that the phosphor surface was rough, the uniformity of particles is better, so the $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor is more suitable for the requirements of the powder in practical application.

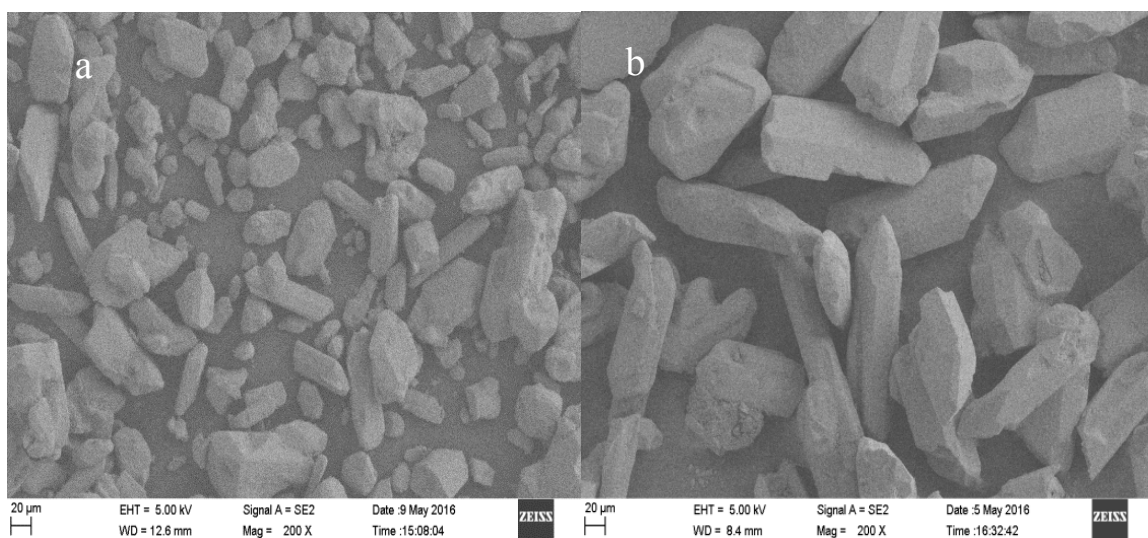


Figure 4. The SEM analysis results of the sample $\text{Zn}_3\text{V}_2\text{O}_8$ (a), $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ (b)

3.5. The excitation spectrum and emission spectrum analysis of the sample $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$

Figure 5 is the excitation spectra and emission spectra of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor powder at 600°C with 4h constant temperature, can be drawn from the figure, when the doping amount of rare earth Y^{3+} $x=0.001$, the luminescent properties of $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor is the best, when the doping amount Y^{3+} is $x=0.01$ and $x=0.1$ respectively, luminescence properties of $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphors were low compared to undoped Y^{3+} , $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphors have wide excitation spectrum between 300-400nm, $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors excitation peak at 361nm, which belongs to the near ultraviolet range, the excitation peak of $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor is in 361nm too. The results indicate that the two kinds of phosphor can be effectively excited by near UV, so the two kinds of fluorescent powder can be used as a near ultraviolet excitation chip LED phosphors. At the same time, the emission spectrum range of $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor is between 420-690nm, and the peak value of the emission spectrum is 559nm, which belongs to the range of visible yellow and green light. Compared with the two phosphors, the luminescent properties of rare earth doped Y^{3+} ($x=0.001$) phosphors were better. It is of great significance to the application of white LED.

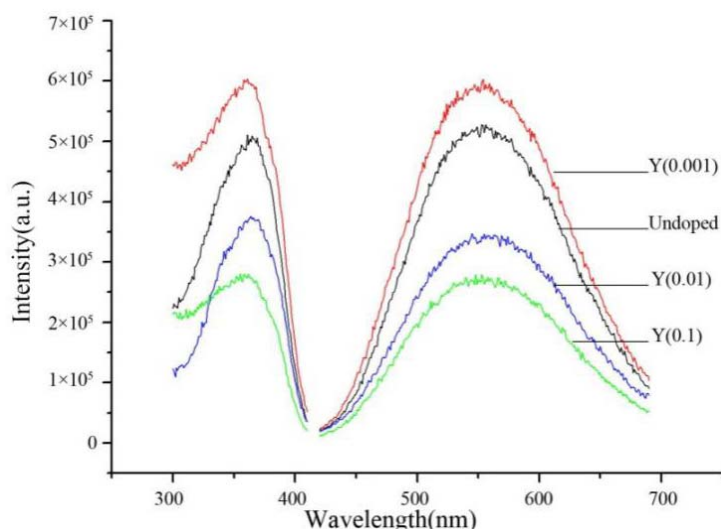


Figure 5. The luminescence property of the $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor

Figure 6 were the excitation spectrum and emission spectrum of the $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor under the resultant temperature of 600°C . The figure 4 shows that the excitation spectrum of $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor have the wavelength range of 300-400nm, the excitation spectrum of $\text{Zn}_3\text{V}_2\text{O}_8$ appeared at the wave length of 361 nm, was belong to the scope of ultraviolet light. The excitation spectrum of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ was moving to the direction of the red shift, appeared at 380 nm, and was present between ultraviolet and near ultraviolet. The experimental results shows that the excitation spectrum was not affected by Eu-doping, and existed the white LED that using the near ultraviolet excitation by rare earth elements. At the same time, the emission spectrum of $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor have the wavelength range of 420-690 nm, the emission spectrum of $\text{Zn}_3\text{V}_2\text{O}_8$ appeared at the wave length of 560 nm, belong to the yellow green range of visible light. The emission spectrum of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ was moving to the direction of the red shift, appeared at 570 nm, fall with the scope of visible light yellow green-yellow light. Comparing the experimental results we find the luminescence property was improved by Eu-doped. More important, the intensity of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ is more stonger than $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ when $x=0.001$.

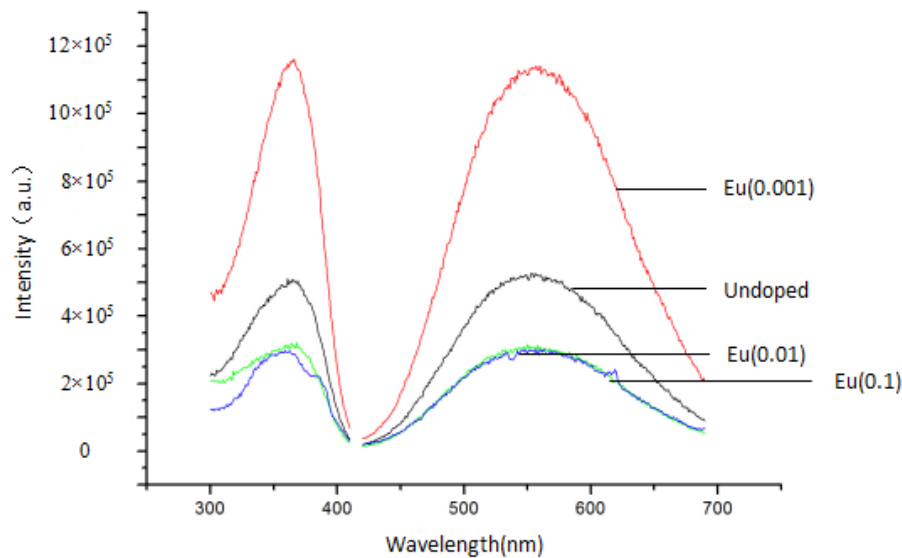


Figure 6. The luminescence property of the $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor

3.6. The effect of Y^{3+} and Eu^{3+} doping on Luminescence Properties

the Y^{3+} doped $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors with different concentrations of light intensity variation, rare earth ion as the luminescent center, the doping concentration has an important influence on the luminescence properties of rare earth ions by fluorescent powder preparation requirements to different doping concentration to obtain the best luminescent properties not, under normal circumstances, the higher the concentration was, the better the luminescent intensity. From Figure 1 and Figure 3 shows: with the increase of Y^{3+} concentration, due to the concentration quenching phenomenon, the diffraction peak intensity of the product gradually weakened, while the emission intensity between 420-690nm, $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ fluorescent powder is also gradually reduced. The effect of Eu^{3+} doping on luminescence properties is same as Y^{3+} .but when $x=0.001$, the the intensity of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ is more stronger than $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$.

4. Conclusion

In this paper, $\text{Zn}_3\text{V}_2\text{O}_8$: Y^{3+} phosphors were synthesized by high temperature solid phase method. The results show that when the amount of Y^{3+} doping is $x = 0.001$, the luminous intensity of the obtained phosphor is stronger than that of the undoped $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor, and the luminescence intensity of the phosphor is stronger than that of the undoped $\text{Zn}_3\text{V}_2\text{O}_8$. But the Y^{3+} concentration had no obvious effect on the lattice structure of the zinc vanadate phosphor. However, with the increase of Y^{3+} , As a result of the concentration quenching phenomenon, the product of the diffraction peak intensity gradually weakened, $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$ phosphor at 420-690nm, the emission peak intensity of the product is gradually decreasing. The effect of doped Eu^{3+} is same as Y^{3+} .And when $x=0.001$, the the intensity of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ is more stronger than $(\text{Zn}_{1-x}\text{Y}_x)_3\text{V}_2\text{O}_8$.

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