

The effect in the production and Luminescence property of $Zn_3V_2O_8$ with Eu-doping

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Abstract. The $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ have been production by Solid phase method. The crystal structure, the crystal morphology and the luminescence property of $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ have been studied. 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.

Introduction

Zinc vitriol acid compounds ($Zn_3V_2O_8$) is a kind of excellent luminescent materials with the features of high luminous efficiency, environment-friendly and energy-saving, good luminous stability, high chemical resistance, life grow high luminous efficiency and so on^[1-3]. $Zn_3V_2O_8$ integrated of the unique structure of nanomaterials, so it used for the luminescent material base, the battery of poles materials, photocatalytic materials and energy storage and so on. Since the YVO_4 red phosphor have activation using Eu^{3+} was reported by Levine and Palill^[4], represented by the vanadate rare earth luminescent material of $Zn_3V_2O_8$ receives much concern, and becomes the studied focus. Recently, sol-gel, co-precipitation, chemical bath deposition, combustion method and microwave method are the common methods to prepare $Zn_3V_2O_8$ ^[5]. While, there are many V-O acid radical in the $Zn_3V_2O_8$ compounds, and form VO_4 , VO_5 and VO_6 coordination structures. This acid radical were coordinated with Zn and formed M_3VO_4 , $M_4V_2O_7$ and MVO_3 compounds^[6-7]. The existence of these compounds lead to the performance of $Zn_3V_2O_8$ was difference^[8]. So the studied of the excellent design and controllable synthesis of $Zn_3V_2O_8$ preparation methods and properties are become the focus of attention. Such as, 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^[9]. 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^[10]. The vanadate phosphors was prepared by high temperature solid phase method, a new yellow $Zn_2V_2O_7$ phosphor from activation have prepared in the calcine temperature of 600°C, another $M_2V_2O_7$ (M= Ba, Sr, Ca) phosphor from activation have prepared in the calcine temperature of 750°C. From the related literature review we found the luminescent properties of the vanadate that the cationic in the A family of the periodic table was increased, and the photoluminescence was moved to the direction of "blue shift". The YAG: Ce^{3+} phosphor was obtained base on the $Y(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, γ -AlOOH in deionized water to a scale, on this basis use blue chips and add the right amount of Eu^{3+} , Tb^{3+} and Gd^{3+} . While, the while LED phosphor was obtained and it luminescence property was increased by add the right amount of rare earth elements^[11]. But the rare earth element doped

technology is very important, the effect of luminescence property with the rare earth element and doping ratio. Such as, the phosphor $\text{CaCO}_3:\text{Eu}^{3+}$ was obtained using chemical bath deposition by Pan yue xiao, but the luminescence property was decreased it attributed to the Ca^{2+} and Eu^{3+} not match lead to the charge does not match. So in order to obtain the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor which have better morphology and high luminous efficiency. In this paper we studied the crystal phase and luminescence property of $\text{Zn}_3\text{V}_2\text{O}_8$ with Eu-doping in order to improved the luminescence property.

Experiment

The $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor sample was prepared using muffle furnace (SX2-4-4TP). Firstly, the ZnO (purity 99.99%), V_2O_5 (purity 99.99%) and Eu_2O_3 (purity 99.99%) were mixed according to the stoichiometric ratio in clean agate mortar, and fully grinding 50min. Second, the sample was placed in muffle furnace (the calcinations temperature was 600 °C, the calcinations time was 4h). The temperature of muffle furnace was set reduced to 30 °C from the calcinations temperature, in 120 min, after the completion of the wait for the response. The flow diagram of muffle furnace temperature was shown in figure 1.

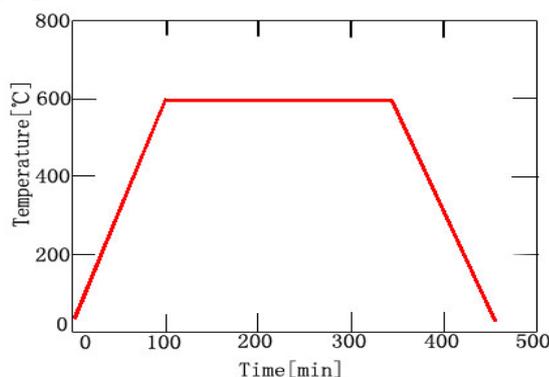


Figure 1 the flow diagram of muffle furnace temperature

The experimental results and discussion

The XRD 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 lattice parameter, phase structure and the status of Eu-doping of the sample $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ 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 $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphor under the resultant temperature of 600°C. The XRD of $\text{Zn}_3\text{V}_2\text{O}_8$ shows that the largest emission peak was appeared at the diffraction angle of 35° , and the largest emission peak was 5000. The XRD of $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ shows that the crystal structure of $\text{Zn}_3\text{V}_2\text{O}_8$ wasn't changed, the intensity of diffraction, fluorescence properties and color rendering index of $\text{Zn}_3\text{V}_2\text{O}_8$ was increased by Eu-doped.

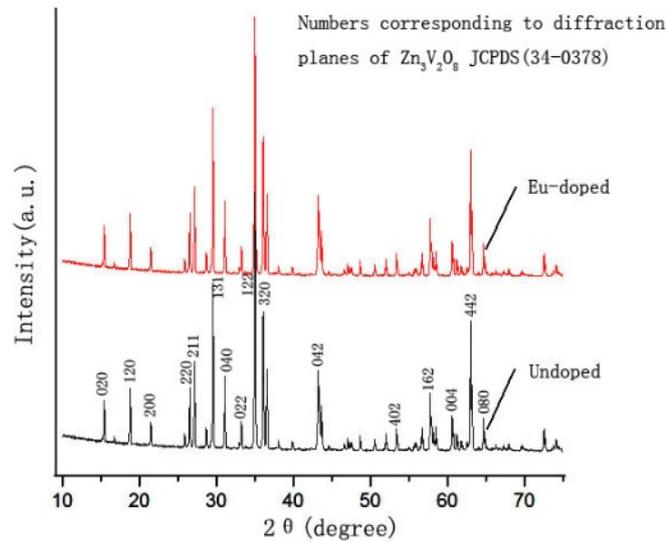


Figure 2 the XRD of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor under the resultant temperature of $600^\circ C$

The SEM analysis results of the sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$.

Figure 3 is the SEM analysis results of the sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$. The figure 3 shows that the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor have the rules morphology structure, uniform particles rod structure, and haven't reunion phenomenon. The SEM of $Zn_3V_2O_8$ phosphor was amplified with 200 times, the SEM of $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor was amplified with 500 times, this results were correspond with XRD standard drawing. At the same time, the SEM of $(Zn_{1-x}Eu_x)_3V_2O_8$ show that the phosphor surface was rough, the uniformity of particles is better, so the $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor is more suitable for the requirements of the powder in practical application.

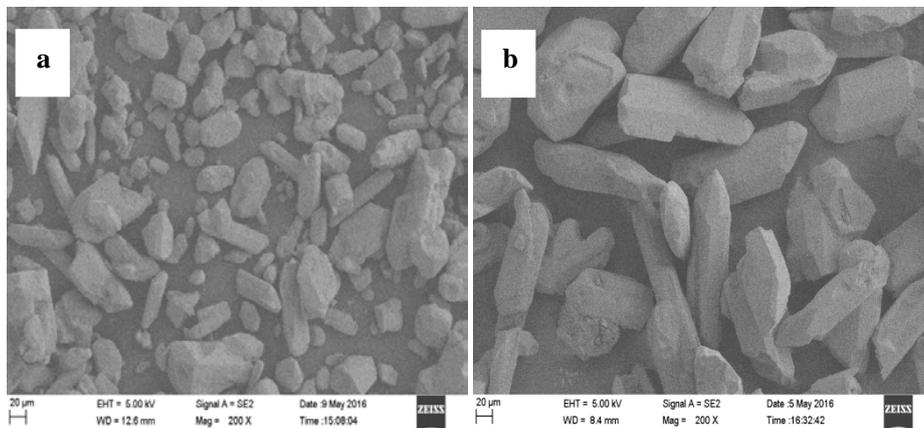


Figure 3 the SEM analysis results of the sample $Zn_3V_2O_8$ (a), $(Zn_{1-x}Eu_x)_3V_2O_8$ (b)

The excitation spectrum and emission spectrum analysis of the sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$.

Figure 4 were the excitation spectrum and emission spectrum of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor under the resultant temperature of $600^\circ C$. The figure 4 shows that the excitation spectrum of $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor have the wavelength range of 300-400nm, the excitation spectrum of $Zn_3V_2O_8$ appeared at the wave length of 361 nm, was belong to the scope of ultraviolet light. The excitation spectrum of $(Zn_{1-x}Eu_x)_3V_2O_8$ was moving to the direction of the red shift, appeared at 380 nm, and was present between ultraviolet and near ultraviolet. The experimental results hews 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 $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor have the wavelength range of 420-690 nm, the emission spectrum of $Zn_3V_2O_8$ appeared at the

wave length of 560 nm, belong to the yellow green range of visible light. The emission spectrum of $(Zn_{1-x}Eu_x)_3V_2O_8$ 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.

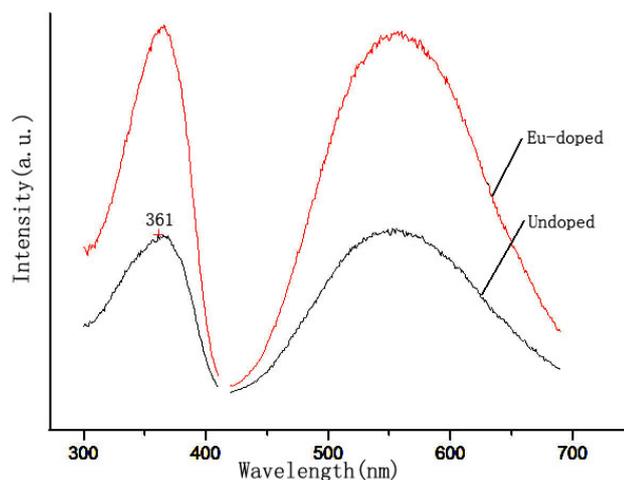


Fig 4 the luminescence property of the $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor

The light-emitting mechanism analysis results of the sample $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$.

The Zn vacancy and O vacancy are existed in the $Zn_3V_2O_8$ system, it lead to the V electron transited, independently. The Eu element was doped in the $Zn_3V_2O_8$ system and formed $(Zn_{1-x}Eu_x)_3V_2O_8$ compound, on account of the system have the rare earth ions Eu, enriched it energy level, and lead the atomic magnetic moment and 4f electronic without bonding increased. The d electronic and f electronic of rare earth ion Eu generated d-f chemical bond and form spin state transition, it lead to the characteristics of luminescence increased by rare earth Eu-doped.

Conclusions

The $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphors have been prepared by solid phase method under 600°C, and the crystal structure, crystal morphology and luminescence property have been studied. The XRD testing result shows that the diffraction peaks are close to the same. The SEM testing result shows that the particle distribution uniformity of $(Zn_{1-x}Eu_x)_3V_2O_8$ better than $Zn_3V_2O_8$, and the particles of $(Zn_{1-x}Eu_x)_3V_2O_8$ haven't reunion phenomenon, the crystal morphology was better, the diffraction peaks was stronger. The luminescence property analysis shows that the emission band of $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphors are wide, the excitation peaks were appeared at the wavelength of 560 nm and 570nm. The experimental results show that the luminescence property was increased by Eu-doped.

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