

Effect of Solvent on the Luminescence Properties of $\text{Zn}_3\text{V}_2\text{O}_8$ and the First Principle Calculation of α - $\text{Zn}_3\text{V}_2\text{O}_8$

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Abstract. In this paper, $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors were synthesized by high temperature solid method. The effect of flux on the luminescent properties was studied. And based on the first-principles planar wave super-soft pseudo potential method of density functional theory (DFT), the α - $\text{Zn}_3\text{V}_2\text{O}_8$ crystal model was used to calculate the electronic structure and optical properties of the model. The results show that the crystal morphology of the sample is improved, the grain agglomeration is reduced and the crystal structure isn't changed. The excitation spectrum ranges from 300-400nm, the excitation peak is at 360nm, and the emission spectrum is in the range of 420-690 nm, the peak at 550 nm. α - $\text{Zn}_3\text{V}_2\text{O}_8$ is an indirect band gap, α - $\text{Zn}_3\text{V}_2\text{O}_8$ has a band gap of 2.715eV, α - $\text{Zn}_3\text{V}_2\text{O}_8$ has a strong UV-near ultraviolet light absorption capacity.

1. Introduction

Because of the effective sensitization of VO_4^{3-} on rare earth ions and the VO_4^{3-} self-activated luminescent properties in the lattice of vanadate phosphor, it is a solid luminescent material with good luminescent properties and stable [1]. At the same time, the low temperature of the luminescent materials, the chemical stability and thermal stability of the phosphors are more and more concerned, so the vanadate luminescent materials are a kind of very promising luminescent materials. Shoreas S.Pitale [2] synthesized $\text{Zn}_3(\text{VO}_4)_2$ phosphors by hydrothermal synthesis and citric acid gel combustion method. Zhou et al [3] synthesized $\text{Ca}_3(\text{VO}_4)_2:\text{Eu}^{3+}$ nanocrystals in low temperature and analyzed their luminescent properties. A series of rare earth doped vanadate micro / nanospheres with hollow spherical structure were synthesized with hydrothermal method by Zan X R [4]. The effects of reaction conditions such as reaction temperature and reaction time on the luminescent properties were studied. Choi[5] successfully synthesized $\text{Ca}_3\text{Sr}_3(\text{VO}_4)_4:\text{Eu}^{3+}$ phosphor, the emission peak at 618nm; $\text{Zn}_3\text{V}_2\text{O}_8$ and $(\text{Zn}_{1-x}\text{Eu}_x)_3\text{V}_2\text{O}_8$ phosphors were successfully synthesized by solid phase method[6]. KN Shinde et al [7]. Ssuccessfully synthesized white phosphors $\text{Sr}_{3-3x/2}(\text{VO}_4)_2\text{xEu}$ ($0 \leq x \leq 0.3$) phosphors by solution solid phase method and studied the luminescent properties of phosphors. $(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ microspheres were prepared by glycine-assisted treatment, and 3D vanadate microspheres were obtained by 600 °C high temperature treatment. The photoluminescence properties were studied



[8]. In this paper, $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was prepared by solid phase method, flux was added to reduce agglomeration, and the crystal structure of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was improved and its luminescent properties were improved.

2. Experiment

$\text{Zn}_3\text{V}_2\text{O}_8$ phosphor were prepared using a muffle furnace (SX2-4-4TP). ZnO and V_2O_5 was carried out according to the stoichiometric ratio. The fluxes H_3BO_3 , NH_4Cl and NH_4F were added and completely ground for 0.5h. The samples were calcined in a muffle furnace (calcination temperature 600°C , calcination time 4h). After the end of the whole process, the calcination temperature is reduced to room temperature, the sample is taken out from the muffle furnace; the coarse sample is subjected to secondary grinding, and finally the sample is selected, washed and baked. The $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ crystal model was established at zero pressure based on the first-principles planar wave super-soft pseudopotential method of density functional theory (DFT). The electronic structure and optical properties of the model were calculated.

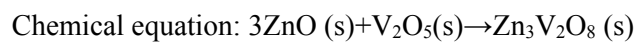


Table 1 The sample of experimental

Material (g)	ZnO	V_2O_5	Fluxing
Sample 1	1.2207g	0.9094g	0g
Sample 2	1.2210g	0.9095g	0.0423g
Sample 3	1.2208g	0.9095g	0.0428g
Sample 4	1.2209g	0.9094g	0.425g

3. The result and discussion of experiment

3.1. The XRD analysis of $\text{Zn}_3\text{V}_2\text{O}_8$ sample

Fig 1 shows the XRD diffraction pattern of $\text{Zn}_3\text{V}_2\text{O}_8$ and the addition of H_3BO_3 , NH_4Cl and NH_4F . It can be seen that the $\text{Zn}_3\text{V}_2\text{O}_8$ sample is orthorhombic crystal, the space group is Abam, the lattice constant $a = 8.2990$, The maximum diffraction peak of $\text{Zn}_3\text{V}_2\text{O}_8$ and $\text{Zn}_2\text{V}_2\text{O}_7$ in the sample $\text{Zn}_3\text{V}_2\text{O}_8$ appeared in the ($\text{Zn}_3\text{V}_2\text{O}_8$), and the maximum diffraction peak of $\text{Zn}_3\text{V}_2\text{O}_8$ and $\text{Zn}_2\text{V}_2\text{O}_7$ appeared in the ($\text{Zn}_3\text{V}_2\text{O}_8$) 122). The results show that the impurity content in the (122) crystal plane is the largest, and the high diffraction peak of $\text{Zn}_3\text{V}_2\text{O}_8$ appears in the crystal plane. The higher diffraction peaks of impurity $\text{Zn}_2\text{V}_2\text{O}_7$ appear on the (122) crystal face, and the other impurity diffraction peaks decrease with the addition of NH_4Cl . The results show that the content of $\text{Zn}_2\text{V}_2\text{O}_7$ in the sample is low, so adding NH_4Cl in the preparation can improve the purity of $\text{Zn}_3\text{V}_2\text{O}_8$.

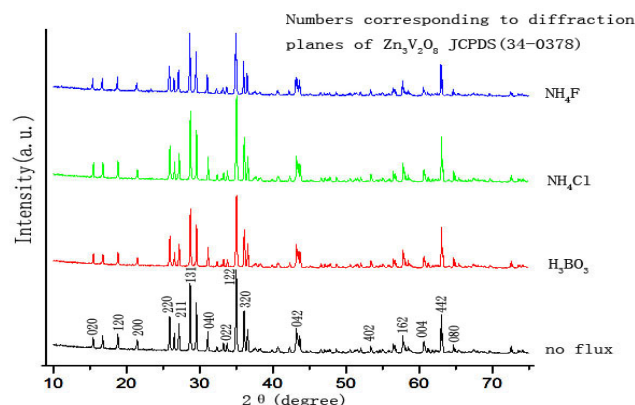


Figure 1 The XRD of the sample $\text{Zn}_3\text{V}_2\text{O}_8$ with the fluxing of NH_4Cl , NH_4F and H_3BO_3

3.2. The SEM analysis of $Zn_3V_2O_8$

Fig 2 is the SEM spectrum of the sample $Zn_3V_2O_8$, Fig 3 is the SEM spectrum of the sample $Zn_3V_2O_8$ added to the NH_4Cl . The results show that the morphology of $Zn_3V_2O_8$ phosphor is elongated particles with no sharp corners and edges, and the surface is rough. The $Zn_3V_2O_8$ phosphor with the addition of NH_4Cl is the size of the $Zn_3V_2O_8$ phosphor, and the grain size of the $Zn_3V_2O_8$ phosphor is $50 \sim 80 \mu m$. The grain size of the $Zn_3V_2O_8$ phosphor with the addition of NH_4Cl is $3 \sim 7 \mu m$, the particle size is relatively small, and the particles only a slight agglomeration phenomenon.

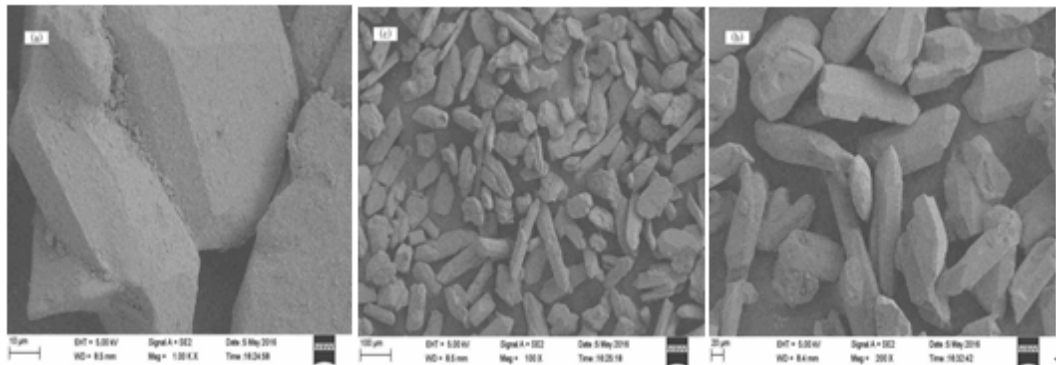


Figure 2 The SEM Spectrum of the sample $Zn_3V_2O_8$

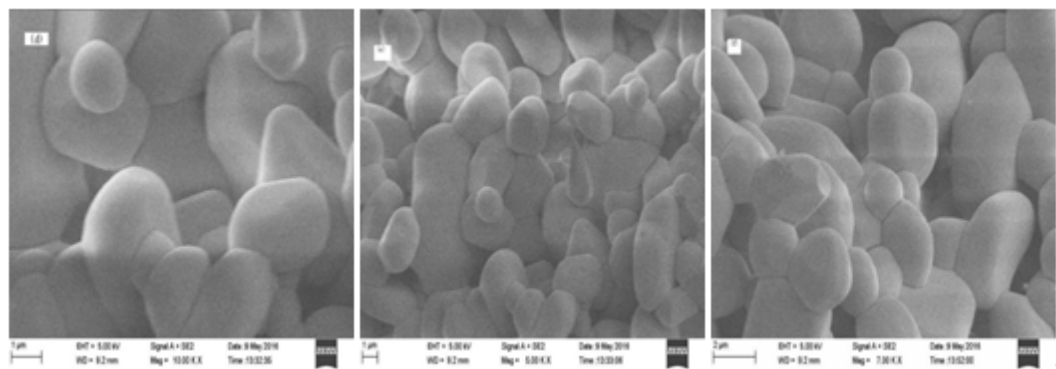


Figure 3 The SEM Spectrum of the sample $Zn_3V_2O_8$ added to the NH_4Cl

3.3. The excitation spectrum and emission spectrum of $Zn_3V_2O_8$

Fig 4 shows the excitation spectra and emission spectra of $Zn_3V_2O_8$ phosphors and $Zn_3V_2O_8$ with flux. A portion having a wavelength of less than 400 nm is an excitation spectrum, and a portion having a wavelength greater than 450 nm is an emission spectrum. It can be concluded that when the added solvent is NH_4Cl , its luminescent performance is the best, and when adding NH_4F and H_3BO_3 , its luminescent performance is lower than that when it is not added. Under the excitation of near ultraviolet light, The spectral range is between 300-400 nm and the excitation peak is at 360 nm, which is the electron transition from O_2 to V^{5+} in the VO_4 tetrahedron, and the emission spectrum is in the range of 420-690 nm, and the emission peak is at 550 nm range.

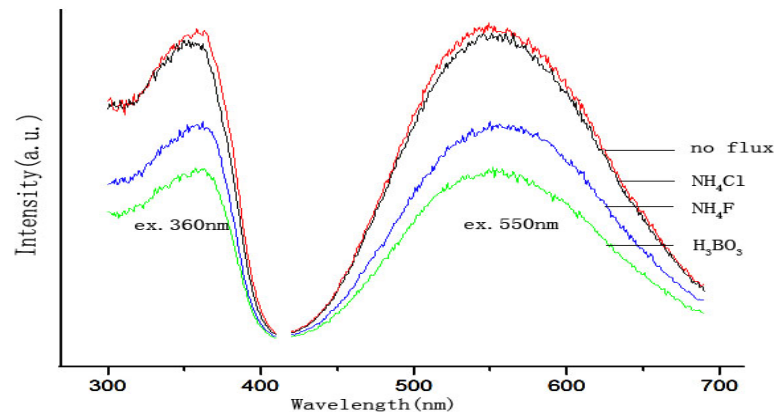


Figure 4 the excitation spectrum and emission spectrum of the sample $\text{Zn}_3\text{V}_2\text{O}_8$

3.4. The electronic structure of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$

The electronic structure of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ was simulated by plane wave ultrashort pseudopotential method based on density functional theory (DFT). The valence electrons of Zn, V and O were $3d^{10}4s^2$, $3d^34s^2$ and $2s^22p^4$, respectively. The calculated supercells were constructed with $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ crystals belonging to the group of D2h-18 point group and Cmca (No. 64) space. Each $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ unit cell contained four $\text{Zn}_3\text{V}_2\text{O}_8$ units with a total of 52 atoms, O atoms are coordinated into tetrahedral structures, and Zn forms two octahedral structures with the surrounding O atoms.

As shown in Fig 5, the valence band of pure $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ is located at the point G of the Brillouin zone. The bottom of the conduction band is located at the Q point between the SIG of the Brillouin zone, which is an indirect bandgap. 2.715eV; the conduction band bottom 2-4eV is mainly derived from the V 3d state and the O 2p state, and the valence band top -6.0eV is mainly due to the contribution of Zn 3d, O 2p and V 3d states. As an effective approximation method, can provide a theoretical basis for the experiment.

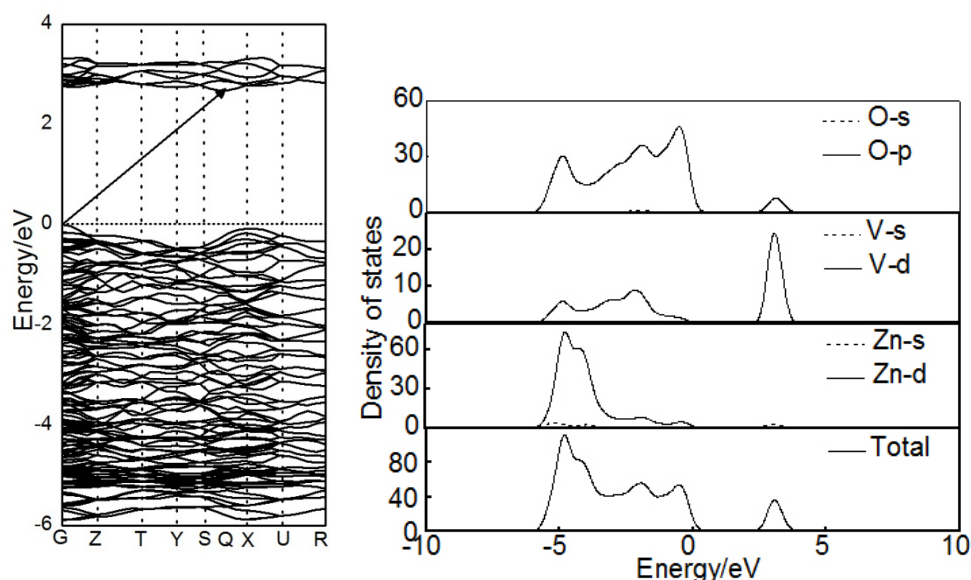


Figure 5 The Band structure and state density of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$

3.5. Optical Properties of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$

Fig 6 (a) is the absorption coefficient of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ in the range of 0-10eV, and (b) is the reflection spectrum of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ in the range of 0-10eV. It can be seen that the energy of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ is not

absorbed. When the energy is about 2eV, the absorption coefficient gradually absorbs the peak, which indicates that the absorption capacity of $\text{Zn}_3\text{V}_2\text{O}_8$ to visible light is relatively weak. The absorption coefficients of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ appeared at 5.44eV, respectively, which indicated that they had strong UV-near-ultraviolet absorption, which was in good agreement with the experiment. In the visible region, the absorption coefficient and reflectance of $\text{Zn}_3\text{V}_2\text{O}_8$ are very low, which indicates that this material has a high permeability, where the reflection peak of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ is at 6.28eV.

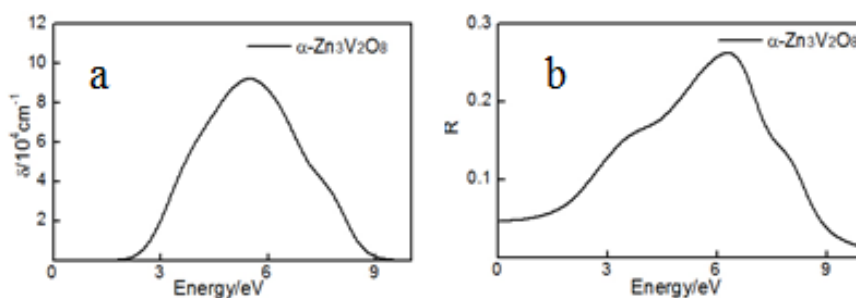


Figure 6 The absorption spectra and emission spectra of $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$

4. Conclusion

In this paper, the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was synthesized by high temperature solid phase method. The effect of the flux on the luminescent properties was studied. The crystal structure, morphology and fluorescence spectra of the synthesized phosphor were analyzed and the first principle was calculated. The experimental results show that the addition of flux can't change the crystal structure, but the agglomeration phenomenon is reduced. The surface of the additive is smooth and the particle size is single. Under the excitation of near ultraviolet light, the excitation spectrum ranges from 300-400nm, The peak is at 360nm, and the emission spectrum is in the range of 420 ~ 690nm. The peak of the emission spectrum belongs to the visible range at 550nm, and the addition of the appropriate flux can improve the luminescent performance of the phosphor. $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ is an indirect band gap, $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ has a band gap of 2.715eV, $\alpha\text{-Zn}_3\text{V}_2\text{O}_8$ has a strong UV-near ultraviolet light absorption capacity.

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