The effect in the production and Luminescence property of $Zn_3V_2O_8$ with fluxing

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Abstract. The sample of $Zn_3V_2O_8$ has been preparation by high temperature solid phase method with fluxing, and studied the effect of preparation condition and the luminescence property with fluxing. The results of phase studied show that the crystal morphology was improved, the reunite of grain crystal was decreased, and the effect of crystal structure was none by fluxed. The results of luminescence property shows that the emission peak was appeared at the wave-length of 400—700 nm, and the highest peak appeared at the wave-length of 550nm under the near ultraviolet excitation light of 360nm, the results shows that the luminescence property was improved by flux of NH_4Cl, NH_4F and H_3BO_3.

Keywords: $Zn_3V_2O_8$; High temperature solid phase synthesis technique; Photo-luminescence; Flux; Crystal structure.

1. 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]. $Zn3V_2O_8$ 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[4-6]. Since the YVO_4 red phosphor have activation using Eu^{3+} was reported by Levine and Palill, represented by the vanadate rare earth luminescent material of $Zn_3V_2O_8$ receives much concern, and becomes the studied focus[7]. Recently, sol-gel, co-precipitation, chemical bath deposition, combustion method and microwave method are the common methods to prepare $Zn_3V_2O_8$ [8]. 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 [9-11]. This acid radical were coordinated with Zn and formed M_3VO_4, $M_4V_2O_7$ and MVO_3 compounds. The existence of these compounds lead to the performance of $Zn_3V_2O_8$ was difference. 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 $Zn_3V_2O_8$ nano-sphere was obtained using the chemical bath deposition and the high-heat treatment with the base of amino acetic acid by Wang Miao [12]. The flower-type structure $Zn_3V_2O_8$ was obtained using the chemical bath deposition and the high-heat treatment without add any template fluxing and surfactant by Shi Rui. High temperature solid phase method is a kind of good temperature of prepare $Zn_3V_2O_8$ phosphor, it have good control, simple preparation and low calcinations temperature (generally in 600 ℃) characteristic compared with other preparation technology. The $Zn_3V_2O_8$ phosphor appeared agglutination phenomenon when the calcinations temperature arrive 600 ℃, and it lead the photoluminescence decreased. In this paper we are adding the fluxing in order to decrease the agglutination phenomenon; improve the crystal structure of $Zn_3V_2O_8$ phosphor.

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2. Experiment

The $Zn_3V_2O_8$ phosphor sample was prepared using muffle furnace (SX2-4-4TP).Firstly, the ZnO (purity 99.99%) and V_2O_5 (purity 99.99%) were mixed according to the stoichiometric ratio 3:1. Second, add the fluxing (the purity of H_3BO_3, NH_4Cl and NH_4F are exceed analytically pure), and fully grinding 0.5h. Thirdly, the sample was placed in muffle furnace (the calcinations temperature was 600 ℃, the calcinations time was 4h). The sample was removed from the muffle furnace, after the completion of the wait for response and the calcinations temperature down to room temperature. Fourthly, the coarse sample was secondary grinding, the final sample was through choose, washing, baking post-processing.

Chemical equation: $3ZnO(s) + V_2O_5(s) \rightarrow Zn_3V_2O_8(s)$

Table 1 experiment sample

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 experimental results and discussion

3.1 The XRD analysis results of the sample $Zn_3V_2O_8$

$Zn_3V_2O_8$ sample is orthorhombic crystal, the space groups is *Abam*, the lattice constant a=8.2990, b=11.5284, c=6.1116, α=β=γ=90. Figure 1 is the XRD of sample $Zn_3V_2O_8$ and the sample adding fluxing (H_3BO_3, NH_4Cl and NH_4F), the XRD of sample shows that the crystal structure of $Zn_3V_2O_8$ wasn't changed using high temperature solid phase method with fluxing (H_3BO_3, NH_4Cl and NH_4F). The impurity $Zn_2V_2O_7$ is appeared in the sample $Zn_3V_2O_8$. From figure 2 we known the maximum diffraction peak of the sample $Zn_3V_2O_8$ and the impurity $Zn_2V_2O_7$ appeared at the (122) crystallographic plane, simultaneously. This results show that the content of impurities in the (122) crystallographic plane is maximum. The $Zn_3V_2O_8$ higher diffraction peaks of the high purity appeared in the (442), (131), (320) and (151) crystallographic plane. The impurity $Zn_2V_2O_7$ higher diffraction peaks appeared in (122) crystallographic plane, other impurity diffraction peaks are lower with adding NH_4Cl fluxing. It turned out that the less impurity content of $Zn_2V_2O_7$ in the sample, so the purity of $Zn_3V_2O_8$ is improved by adding NH_4Cl fluxing in the process of preparation.

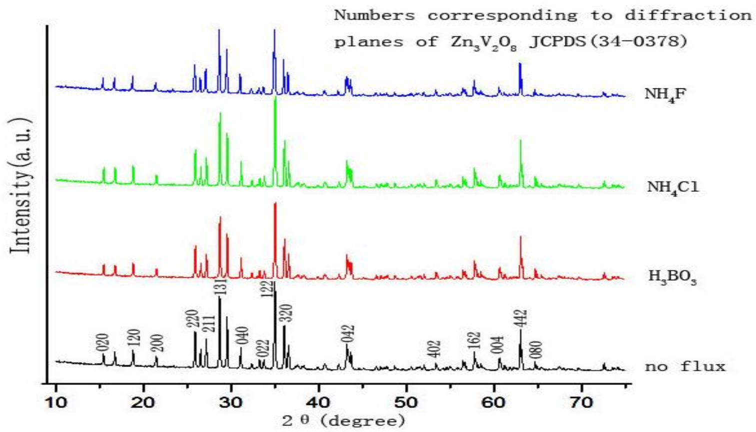

Fig 1 The XRD of the sample $Zn_3V_2O_8$ with the fluxing of NH_4Cl, NH_4F and H_3BO_3

3.2 The SEM analysis results of the sample $Zn_3V_2O_8$

Figure 2 is the SEM analysis result of the sample $Zn_3V_2O_8$, figure 3 is the SEM analysis results is the sample $Zn_3V_2O_8$ adding NH_4Cl fluxing. The figure 2 and figure 3 shows that in the aspect of crystal morphology the morphology of $Zn_3V_2O_8$ phosphor is long strips of particles, haven't sharp corners and edges, and the surface is rough. The morphology of $Zn_3V_2O_8$ phosphor adding NH_4Cl fluxing is the approximate spherical particles, the surface is smooth. In dimensionally, the grain diameter of $Zn_3V_2O_8$ phosphor in the range of 50~200 um. The grain diameter of $Zn_3V_2O_8$ phosphor adding NH_4Cl fluxing in the range of 3~7 um, the grain is relatively, the particle only slight reunion phenomenon.

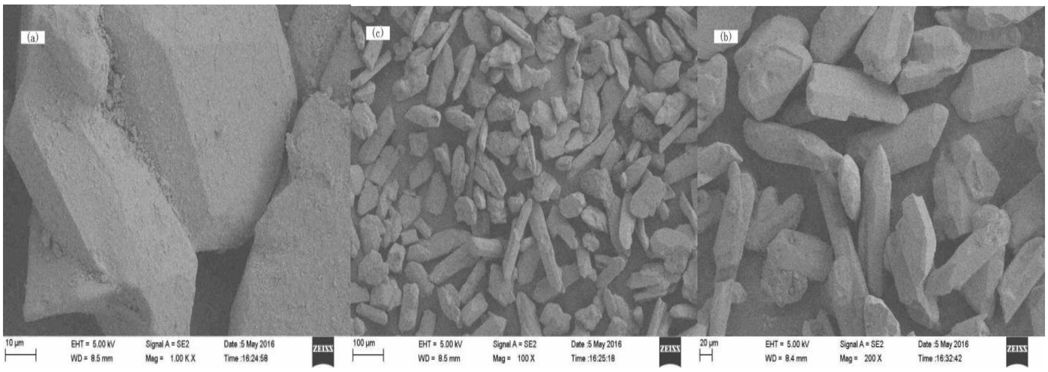

Fig 2 The SEM of the sample $Zn_3V_2O_8$

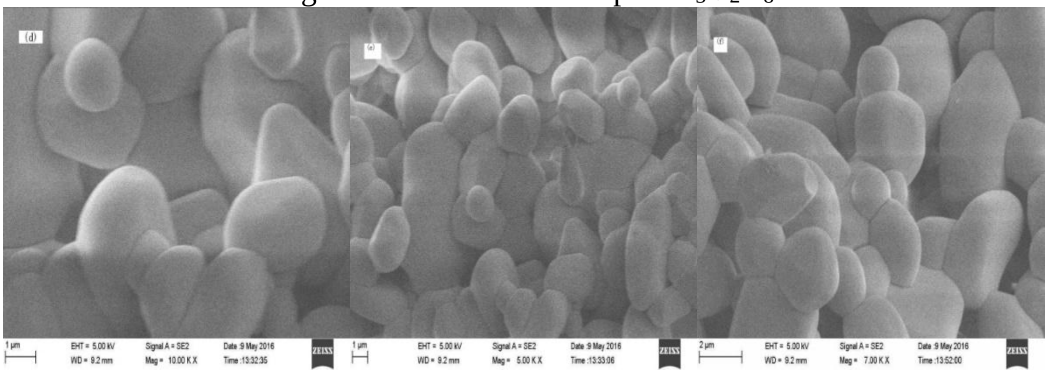

Fig 3 The SEM of the sample $Zn_3V_2O_8$ adding NH_4Cl

3.3 The excitation spectrum and emission spectrum analysis of the sample $Zn_3V_2O_8$

Figure 4 were the excitation spectrum and emission spectrum of the $Zn_3V_2O_8$ phosphor and the $Zn_3V_2O_8$ adding fluxing. The part of the wavelength less than 400nm is the excitation spectrum, the part of the wavelength more than 450nm is the emission spectrum. A wide excitation band appeared at the wavelength range of 300-400 nm, it indicated that $Zn_3V_2O_8$ apply to near ultraviolet LED chip excitation. The maximum excitation peak appeared at the wavelength of 360 nm, this is the electron transition from O^{2-} to V^{5+} in the VO_4 tetrahedron and throughout the entire excitation emission process, it ascribe to the primary cause of the fluorescence property. Under the near ultraviolet excitation, A wide emission band appeared at the wavelength range of 420~690 nm, the maximum emission peak appeared at the wavelength of 550 nm, this is the electron transition of V^{5+} in the d-d electronic energy levels.

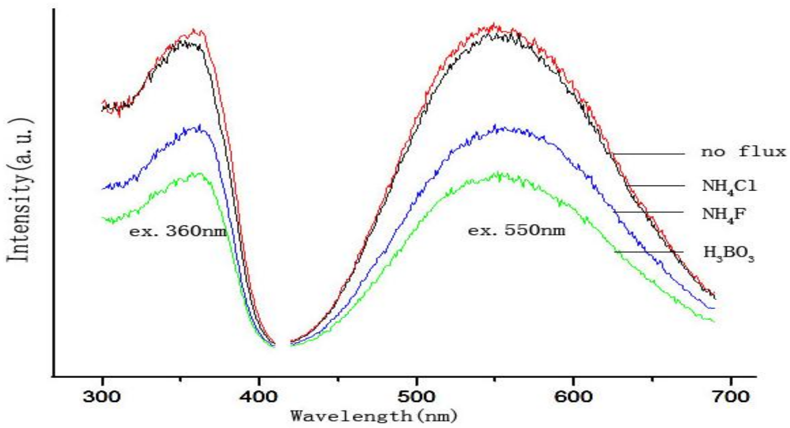

Fig 4 the excitation spectrum and emission spectrum of the sample $Zn_3V_2O_8$

4. Conclusion

The $Zn_3V_2O_8$ and the $Zn_3V_2O_8$ adding phosphors have been prepared by solid phase method under 600℃, the sintering time is 4h, and the crystal structure, crystal morphology and luminescence property have been studied. The XRD testing result shows that the crystal structure is not changed by adding fluxing; the microstructure of particles between the reunion phenomenon is reduced by adding fluxing. The luminescence property of $Zn_3V_2O_8$ results show that a wide excitation band of the $Zn_3V_2O_8$ phosphors appeared the wavelength range of 420~690 nm, under the irradiation of ultraviolet 360nm excitation light, the major excitation peak located at 550 nm. The studied results show that the appropriated fluxing also improves luminescence properties of phosphor.

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References

[1]. Meng Yan. The studied of the preparation and the luminescence property of vanadate phosphors [D]. Graduate school of Qingdao university of science and technology, 6 (2013) 28-31.

[2]. Wang Yong, Li Ping, Wang Jieqiang. The research progress of preparation of rare earth doped YAG phosphors [J].Shangdong Chemical indutry, 36 (2007) 22-27.

[3]. Wang Yi, Gao Yaoji, Huang Jingcheng. The research progress of white LED with phosphors [J].Guangdong chemicals, 42 (2014) 15-19.

[4]. Levine A K,Palilla F C.A new highly efficient red emitting cathodoluminescent phosphor-(YVO4:Eu) for color television[J]. Applied Physics. 06 (1964): 1130-1135.

[5]. Fu Xiaoyan, Niu Shuyun, Zhang Hongwu etal. Nanoscale alkaline earth metal vanadate luminescent material A3 (VO4) 2: Eu luminescence properties research [J].spectroscopy and spectral, 26 (2006) 27-29.

[6]. Sheng Leijun, Li Bo, Wang Zhongzhi etal. Rare earth luminescent material vanadate system is reviewed [J]. Rare earth, 36 (2015) 130-135.

[7]. Niu Shuyun, Han Yan, Fu Xiaoyan etal. Nano YVO4: Ln (Ln = Eu, Tm, Dy) the development of the luminescent powder and the corresponding block spectral contrast of luminous powder [J]. Rare earth, 26 (2005) 14-18.

[8]. Xie Yongping. The crystal materials and growth synthesis of calcium vanadate [J]. Journal of synthetic crystals, 33 (2004) 28-30.

[9]. Wang Guichao, Li Zhiguang. The influence of crystal structure particle morphology and luminescent properties of BaMgAl10O17: Eu2+ phosphor for different flux blue [J]. Chemial intermediate, 03 (2011) 40-42.

[10]. Tingting li, Jiaolian luo, zentaro Honda, Takeshi Fukuda. Norihiko kamata. Sintering Condition and Optical Properties of Zn3V2O8 Phosphor. Advances [J]. Materials physics and chemistry, 2 (2012)173-177.

[11]. Yang Xu, Geng Xiujuan, Li Xinyang etal. The impact of luminescence performance for Ca0.7 Sr0.3 MoO4: Eu3+ red phosphor with flux [J]. Electronic components and materials, 33 (20142) 46-48.

[12]. Liu Guanghua. Rare earth soild materials [M].Beijing: China Machine press, 1997: 180.