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[Jiaolian Luo* 4(12): December, 2017] ISSN 2349-4506
Impact Factor: 2.785

Global Journal of Engineering Science and Research Management

THE EFFECT OF LUMINESCENT PROPERTIES OF $ZN_3V_2O_8$ PHOSPHOR WITH CALCINATION TEMPERATURE AND FIRST-PRINCIPLES CALCULATION

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DOI: 10.5281/zenodo.1134065

KEYWORDS: $Zn_3V_2O_8$ phosphor, Combustion synthesis method, First-principles.

ABSTRACT

$Zn_3V_2O_8$ phosphors were synthesized by combustion with (NH_4VO_3), $C_6H_8O_7 \cdot H_2O$ and $Zn(NO_3)_2$ as raw materials. The crystal structure and optical properties of the films were characterized by X-ray diffraction (XRD) and emission spectra. And based on the first-principles of density functional theory (DFT) The α-$Zn_3V_2O_8$ crystal model was established under zero pressure, and the dielectric and optical properties of the model were calculated. The experimental results show that the crystal structure of $Zn_3V_2O_8$ has no effect on the crystal structure of $Zn_3V_2O_8$. The emission intensity of the sample at 600℃ is the weakest, the light intensity of the sample is the strongest at 700℃, and the optical properties is changed with calcination temperature changed of $Zn_3V_2O_8$. The excitation spectrum of the phosphor is between 300nm and 420nm and the peak at 360nm, The emission spectrum of the range between 420-690nm, the peak at 550nm. The absorption coefficient of α-$Zn_3V_2O_8$ appears at 5.44 eV, the reflection peak is at 6.28 eV.

INTRODUCTION

Face to energy shortage and environmental pollution, the study of energy saving and environmental protection lighting technology and green energy materials has become one of the hot spots. White LED has been obtained by near-ultraviolet excitation single-chip substrate technology, which has a light color stability, high color rendering, low cost of production advantages, will become the future development trend of LED light source[1]. $Zn_3V_2O_8$ phosphor is a kind of material with better luminous performance, and the effective sensitized self-excited luminescence characteristic between VO_4^{3-} and rare earth exists in the electronic structure of $Zn_3V_2O_8$ phosphor. Theoretical analysis and experimental results show that $Zn_3V_2O_8$ phosphor has a wide emission spectrum [2]. (Y, Gd, Lu) VO_4, $ScVO_4$ and (K, Rb, Cs) VO_3 phosphors have been improved by the recent studies of red YVO_4 phosphors doped with rare earth Eu^{3+} phosphors have been successfully synthesized, and the compounds of VO_4^{3-} have been synthesized by Ishchenko A.V[3], Kuang S[4] and T. Nakajima[5] The tetrahedral structure of the luminescence process. Shahas S.Pitale[6] synthesized $Zn_3(VO_4)_2$ phosphors by hydrothermal synthesis and citric acid gel combustion; Dhobale.AR[7] synthesized $Mg_2V_3O_{12}$: Dy, Sm phosphors and studied Sm and Dy-doped luminescence process; Li T[8] studied the effect of calcined environment on the performance of $Zn_3V_2O_8$ phosphors; Luo J [9] and others solid phase synthesis of $Zn_3V_2O_8$ and $(Zn_{1-x}Eu_x)_3V_2O_8$ phosphor. In this paper, we use combustion method to synthesize $Zn_3V_2O_8$ to improve the luminescence properties of $Zn_3V_2O_8$ phosphor.

EXPERİMENT

$Zn_3V_2O_8$ phosphor samples were prepared using a muffle furnace (SX2-4-4TP). First, $Zn(NO_3)_2$, NH_4VO_3 and $C_6H_8O_7 \cdot H_2O$ were mixed according to the stoichiometric ratio, and an appropriate amount of deionized water was added to dissolve it. Then, the beaker was placed in a magnetic stirrer at 80°C and heated and stirred to form a colloid. Finally, the colloids were heated at 100℃ and the colloids were milled in the muffle furnace. The calcination temperature was 600℃, 650℃, 700℃, 750℃, the calcination time was 100min, the temperature was kept for 4h and cooled for 2h. The muffle furnace temperature flow chart is shown in Figure 1. The α-$Zn_3V_2O_8$ crystal model was established at zero pressure based on the first-principles planar wave super-soft pseudopotential method of density functional theory (DFT) is shown in Figure 2. Crystal of each α-$Zn_3V_2O_8$ cell contains four $Zn_3V_2O_8$ units with a total of 52 atoms, and V is coordinated with its surrounding O atom, and the α-$Zn_3V_2O_8$ crystal of the Cmca (No.64) space group is used to construct the calculated supercell into a tetrahedral structure,

Zn and its surrounding O atoms to form two octahedral structure. Due to the strong Coulomb interaction between electrons in the 3d orbit, a Hubbard energy term U correction was used(U = 2.5 eV). The dielectric function and optical properties of the model were calculated.

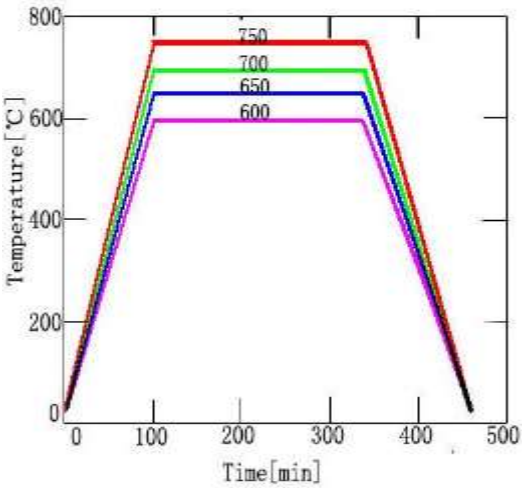

Figure 1 The flow diagram of muffle furnace temperature

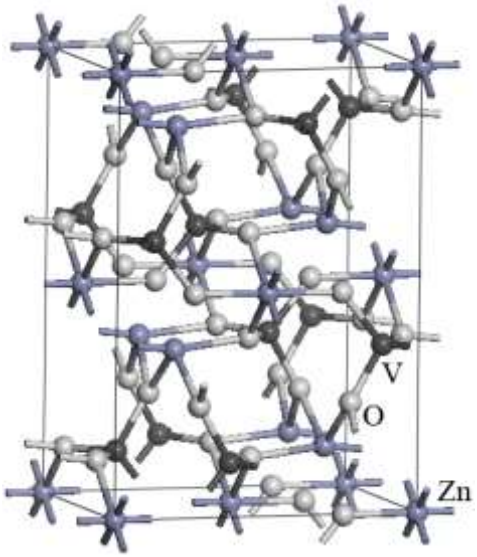

Figure 2 The supercell structures of α-$Zn_3V_2O_8$

THE EXPERİMENTAL RESULTS AND DİSCUSSİON

The XRD analysis results of the sample $Zn_3V_2O_8$

Figure 3 shows the XRD pattern of the sample $Zn_3V_2O_8$. The curve shows the peak value of the sample. The calcination temperature is 600℃, 650℃, 700℃, 750℃ and the calcination time is 4h. The results show that all the diffraction peaks match the results of the standard card of $Zn_3V_2O_8$ (JCPDS34-0378). The crystal structure shows that the $Zn_3V_2O_8$ sample is an orthorhombic structure with a lattice constant a = 8.299Å, b = 11.528Å, c = 6.1116 Å, [Z = 4] (JCPDS 00-034-0378). The second stage is $Zn_3V_2O_7$. When the calcination temperature is 700℃, the crystal structure of the sample is complete and no impurity peaks appear. The diffraction value of $Zn_3V_2O_8$ reaches the maximum value.

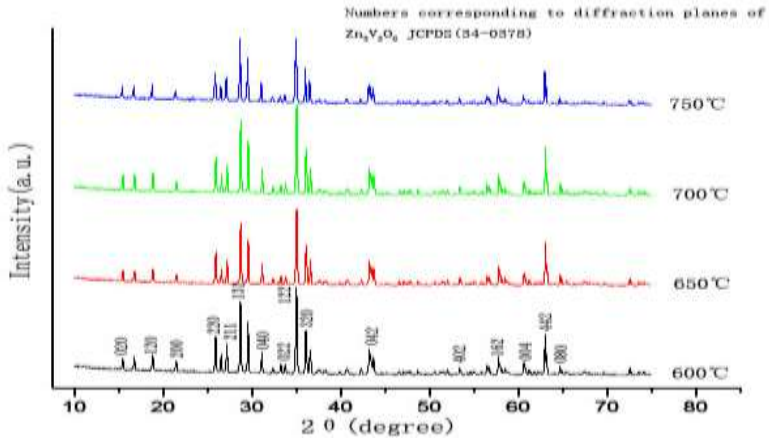

Figure 3 The XRD diffraction pattern of sample $Zn_3V_2O_8$

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

Figure 4 shows the excitation spectra and emission spectra of $Zn_3V_2O_8$ phosphors at temperatures of 600℃, 650℃, 700℃ and 750℃. The results show that the excitation spectrum of $Zn_3V_2O_8$ phosphor powder ranges from 300nm to 420nm, and its absorption band with wide wavelength range (1A1-1T2,1A1-1T1) has a peak at 360nm, which indicates that $Zn_3V_2O_8$ can be applied to near ultraviolet The emission wavelength range is between 420-690nm and the peak is at the wavelength of 550nm. The light emitting area covers the wavelength of visible light and can be used as white light. The light intensity at 600℃ is the weakest, 600℃ with $Zn_2V_2O_7$ impurities. The luminous intensity of the sample at 700℃ is the strongest, because the sample is pure $Zn_3V_2O_8$ phosphor at 700℃, no other impurities. The results show that the luminescent properties of $Zn_3V_2O_8$ vary with the calcination temperature.

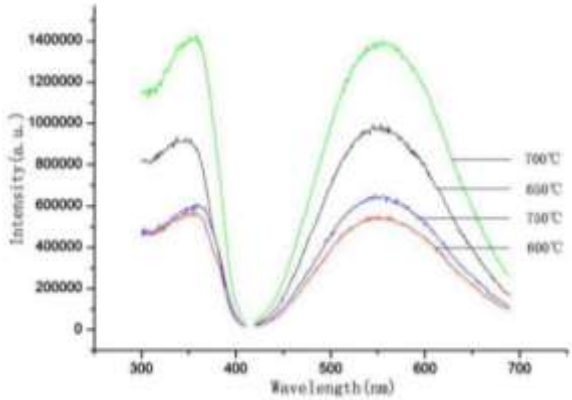

Figure 4 the spectrum analysis of the sample $Zn_3V_2O_8$

Dielectric function of α-$Zn_3V_2O_8$

Figure 5 shows the real and imaginary parts of the α-$Zn_3V_2O_8$ electrical function. The distribution of the dielectric peaks is related to the process of electrons traveling from the valence band to the conduction band, especially the imaginary part of the dielectric function. It is very important to reflect the solid band structure and other spectral information. in the energy range of 0-10eV, pure α-$Zn_3V_2O_8$ has a peak at 3.91 eV, it is caused by an optical transition between V-3d and O-2p states.Since the real part of the dielectric function is derived from the differentiation of the imaginary part and is integrated over a fairly wide interval, the real part appears maximally and minimally at the maximum slope of the ascent and descent of the imaginary part. Respectively. the real part of the dielectric function of $Zn_3V_2O_8$ reaches 2.4 when the energy is 0eV, and the surface has a certain dielectric property.

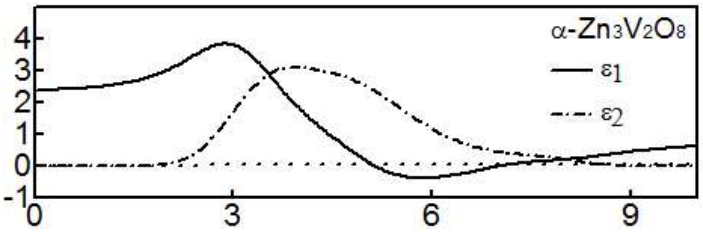

Figure 5 Real and imaginary parts of the dielectric function of α-$Zn_3V_2O_8$

Optical Properties of α-$Zn_3V_2O_8$

In the first principle calculations, the optical properties of materials are mainly studied by the dielectric function. The absorption coefficient (δ) and the emission spectrum(R) can be obtained by the dielectric function:

$$\delta(\omega) = \sqrt{2}\omega[\sqrt{\varepsilon_1^2(\omega) - \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)]^{1/2} \quad (1)$$

$$R(\omega) = \left| \frac{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} + 1} \right|^2 \quad (2)$$

Figure 6 (a) is the absorption coefficient of α-$Zn_3V_2O_8$ in the range of 0-10eV, and (b) is the reflection spectrum of α-$Zn_3V_2O_8$. It can be seen that the energy of α-$Zn_3V_2O_8$ is not absorbed in the energy range of 0-2eV. When the energy is about 2eV, the absorption coefficient gradually absorbs the peak, which indicates that the absorption capacity of $Zn_3V_2O_8$ to visible light is relatively weak. The absorption coefficients of α-$Zn_3V_2O_8$ appeared at 5.44eV. Corresponds to the orbital electron transition from V 3p to O 2p and at the same time indicates that $Zn_3V_2O_8$ has certain absorption selectivity for photons. In the experiment, it was also observed that $Zn_3V_2O_8$ emits in the white region, so the theoretical calculation is in good agreement with the experiment. 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 $Zn_3V_2O_8$ are very low, which indicates that this material has a high permeability, where the reflection peak of α-$Zn_3V_2O_8$ at 6.28eV.

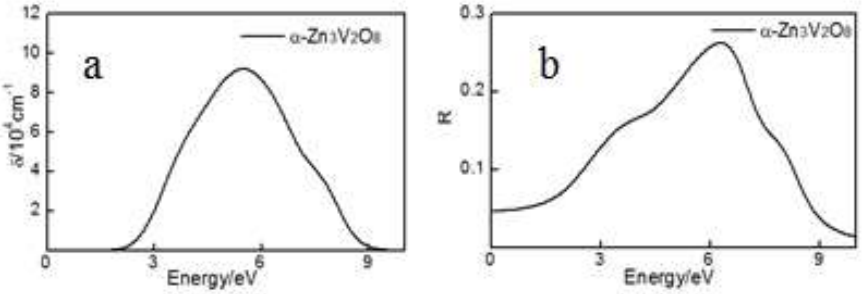

Figure 6 Absorption(a) and Reflection(b) spectrum curves of α-$Zn_3V_2O_8$

CONCLUSİON

$Zn_3V_2O_8$ phosphors were synthesized by using (NH_4VO_3), (Zn (NO_3) $_2$) and $C_6H_8O_7 \cdot H_2O$ as raw materials in this paper. The effects of calcination temperature on the properties were investigated. The crystal structure and luminescence performance was characterized. The results show that the crystal structure of $Zn_3V_2O_8$ has no effect on the crystal structure of $Zn_3V_2O_8$, and the emission intensity is the weakest at 600 ℃. There is a small amount of $Zn_2V_2O_7$ in $Zn_3V_2O_8$. For samples with sintering temperature of 700℃, the luminous intensity is the strongest. The emission band is caused by electron transfer between VO_4^{3-} 2p and V^{5+} 3d, forming a wide emission band. The emission spectrum of $Zn_3V_2O_8$ phosphor is in the range of 300nm-420nm, the peak at 360nm. The emission spectrum range between 420-690nm, the peak at 550nm wavelength, the light emitting area covering the wavelength of visible light can be used as white light. $Zn_3V_2O_8$ has a peak at 3.91eV in the energy range of 0-10eV, and the absorption coefficient of α-$Zn_3V_2O_8$ appears at 5.44eV,. The peak is at 6.28eV. From the dielectric

function of α-$Zn_3V_2O_8$, it can be seen that $Zn_3V_2O_8$ can lead to emission in the visible region, so that it can be used as a good luminescent material.

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