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Fluorescence Properties of LED Phosphoric Acid Rare Earth Phosphor

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As a new type of light source in twenty-first Century, energy saving and environmental protection, long use time, and high luminous efficiency are the advantages of white LED compared with the traditional incandescent lamp and fluorescent lamp. Through the combination of UV / near UV LED chip and three colour phosphors (blue, green and red) is the main way to realize white light LED. Therefore, all parts of the world study and breakthrough related technologies. In this paper, by high temperature solid phase reaction method, several white LEDphosphors that can be excited by UVare prepared, and the luminescence properties, thermal stability, concentration quenching and the mechanism are profoundlystudied. The main results are as follows:Na3YSi2O7: Sm3+ fluorescent powder for white light LED is prepared by high temperature solid phase method. Carry out X- ray diffraction analysis and UV Vis diffuse reflex spectra, excitation spectra, emission spectra, temperature dependent fluorescence spectroscopy and so on characteristics. Under the near ultraviolet (404 nm) excitation, Na3YSi2O7: Sm3+ emits orange light. In the emission spectrum, it presents the characteristic peak of Sm3+, namely4G5/2-6H5/2 (564 nm), 4G5/2-6H7/2 (583 nm), 4G5/2-6H7/2 (609 nm) and 4G5/2 -6H9/2 (651 nm). In Na3YSi2O7 matrix, the critical quenching concentration of Sm3+ is 3 mol%, and the concentration quenching mechanism is the electric dipole-electric dipole interaction function. The CIE coordinates of Na3YSi2O7: Sm3+ phosphor are calculated, (0.5449, 0.4472), and the activation energy of thermal quenching is 0.22 e V. The results show that Na3YSi2O7: Sm3+ phosphor can be used for white LED.

1. Introduction

As the main source of solid state lighting, LED has long service life, energy saving and environmental protection, high safety and other advantages, which is the biggest highlight of the lighting field development in recent years, being attached great importance to by the international community of science and technology industry. China is a big country of lighting. From 2003, in the ongoing support of Ministry of Science and Technology, Development and Reform Commission and other relevant departments, LED technology and industry development is updating each passing day, with the world's best scale. In this context, China's universities and research institutions carry out the relevant research work of LED.
In this paper, a series of white light luminescent materials doped with rare earth is synthesized by using high temperature solid state method and Na3YSi2O7 as matrix compound, and the luminescent properties, thermal stability properties, the quenching concentration and its mechanism are carefully researched. The research contents are as follows: new white LED using Na3YSi2O7: phosphor is synthesized by high temperature solid phase method. Make use of X- ray diffraction (XRD) and fluorescence spectroscopy and fluorescence spectroscopy at different temperatures to characterize the phosphor and luminescence properties.

2. Mechanism and optical properties of rare earth materials

The process of rare earth luminescence can be explained by the Theory of Energy Band.
Due to different electronic conditions in the band, if the electronic is full, it is called valence or filled with air; it is empty, it is called the conduction band, what between the two is forbidden band. The process of light absorption is to use the external light to stimulate emitting material, then the electronic will transit to the conduction band due to the excitation (de Sousa Filho, et al., 2015); light emission process refers to that the electrons reached the conduction band due to excitation transit to the ground state to achieve the balance,

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thus reflecting light emission phenomena. Luminescent materials generate the ground state energy level in the luminescence centre in the forbidden band and transit to the electrons of the excited state energy level.When reply, it will generate "fluorescent"; when it transits to electrons in the conduction band and obtains a certain energy, it will be re-captured and producelong-time light. In the study of rare earth luminescent materials, the optical properties of luminescent materials are characterized, so there are some basic optical properties, mainly including the following aspects:

1) Absorption spectrum: the study on the absorption spectra of the luminescent materials is about one of the important indexes for the study of its performance. Its light absorption equation is shown in Eq (1):

$$I(\lambda) = I_0(\lambda)_e^{-K_\lambda^x} \tag{1}$$

2) Excitation spectra: in the characterization of the luminescent materials, this test is to determine, when the luminescent materials produce light excitation,the optimal excitation wavelength for the wavelength of the excitation light and the emission intensity reaching the maximum.

3) Emission spectra: the linear of the emission spectra can be characterized by Gauss's function, as Eq (2):

$$E(v) = E(v_0)\exp[-\alpha(v - v_0)^2] \tag{2}$$

In the equation, vis the frequency,v_0 is the peak frequency, and E is the light intensity or the energy.

4) Diffuse reflex spectra: theatlas changes with the incident wavelength, the ratio of the total reflected light to the total amount of the incident light is known as diffuse reflex.Diffuse reflex spectroscopy can be carried out by UV - VIS spectrophotometer (Innocenzi, et al., 2016), and it needs to use the equipment of diffuse reflection integral sphere, powder box and so on.

5) Flux: it refers to, in a certain period of time, the visible energy radiated by a light in a certain area, represented by the symbol Φ, the units for lumens lm.

6) Luminescence intensity: luminescence intensity, abbreviated for light intensity.

7) Brightness: brightness formula: $B_\theta = d\phi/(d\sigma\cos\theta d\Omega)$.

8) Color index: when the object is illuminated by a light source, it can cause the color effect, which is color reflecting. But since that people's subjectivity is different, the qualitative color will be different. Then, compare the sensation of color and color effect generated by light radiation, and generally use CIE, namely color index to measure color. Different color indexes should be used in different places.

9) Lumen efficiency (ηL): it indicates the ratio of totalradiation luminous flux to power consumption, which can be used to characterize the luminescent powder light efficiency.

10) CIE coordinate: the luminous color of color material is characterized by the color coordinates. All colors can be quantitatively expressed through the blue (xo), green (yo) and red (zo) as the basic color: Ho = xxo + yyo + zzo, which is the principle of three primary colors (Kim, et al., 2016). And through the coordinate conversion, generally use x and y two values to characterize the color coordinates, and thus avoid three-dimensional but only using two-dimensional color map to show the color of the light. As shown in Figure 1, it is now the most commonly used color map, that is, 1931 CIE color chart.

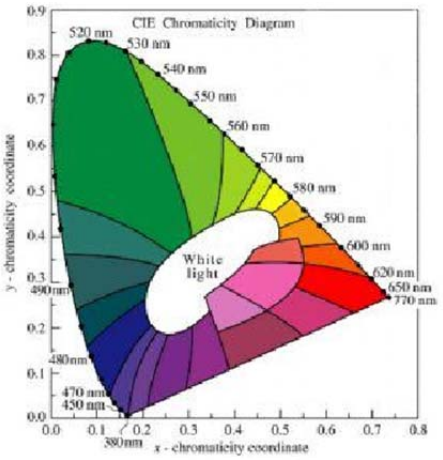

Figure 1: 1931 CIE chromaticity diagram

11) Quantum efficiency: quantum efficiency formula: η amount= N light / N absorption. Quantum efficiency and energy efficiency can be expressed by the Eq (3):

$$\eta_{energy} = \frac{E_{lighting}}{E_{absorbing}} = \frac{hv_{lighting}N_{lighting}}{hv_{absorbing}N_{absorbing}} = \frac{\eta_{amount}v_{lighting}}{v_{absorbing}} = \frac{\eta_{amount}\lambda_{absorbing}}{\lambda_{lighting}} \quad (3)$$

In the equation, λ absorption is the maximum value of the absorption band, and λ lighting is the maximum value of the wavelength in the luminescence band. The energy efficiency of the luminescent material is lower than that of the quantum efficiency because λ absorption is less than λ lighting.
12) Luminous efficiency: η_{energy}= $E_{lighting}$ / $E_{absorbing}$, also known as power efficiency or energy efficiency η_{energy}. The luminous efficiency energy efficiency can express the improvement of the excitation energy into the luminous energy (Tan et al., 2015).

3. Synthesis and luminescence properties of Na3YSi2O7: Sm3+ phosphor

3.1 Experimental reagents and instruments

Table 1: Experimental reagents and their manufacturers

Reagent name	Molecular formula	Specification	Manufacturer
Samarium oxide	Sm2O3	99.99%	Shanghai Chemical Reagent Packing Factory
Sodium carbonate	NaCO3	Analytical reagent	Beijing Chemical Plant
Yttrium oxide	Y2O3	Analytical reagent	Beijing Chemical Plant
Silicon dioxide	SiO2	Analytical reagent	Beijing Chemical Plant

Instrument: electronic balance, agate mortar, corundum crucible, muffle furnace, key, beaker.

3.2 Synthesis and performance test of Na3YSi2O7: Sm3+ phosphor

3.2.1 Material synthesis

A series of Na3YSi2O7: x Sm3+(x=0.01, 0.03, 0.05, 0.07, 0.09) are prepared by high temperature solid state method. According to the stoichiometric ratio, respectively weight certain quality raw material Na2CO3 (analytical reagent), Y2O3 (analytical reagent), Si O2 (analytical reagent), and Sm2O3 (99.99%). First of all, the raw material is placed in agate mortar, and after evenly mixed, fully grind for 30 minutes and the powder material has fine grinding evenly are all transferred to the corundum crucible (Tunsu, et al., 2014). Then, put in the muffle furnace, set the temperature of 1300 DEG C, and roast for 3 hours; finally, until the natural cooling to room temperature, take the sample placed in agate mortar, fully grind again into fine powder, thus obtaining the luminous material samples.

3.2.2 Performance test

Use the German X-ray diffractometry (radiation source for the Cu target K^{α}, 30 k V, 20 m A, λ = 1.5406 Å) to test X- ray diffraction of sample powder. Set the starting angle =10o, end angle =80o. Adopt continuous scanning mode, and the scanning speed is 12o(2θ)/min. Determine excitation and emission spectra of the samples by using Japan Hitachi F-7000 fluorescence spectrometer, and 150W xenon lamp is used as excitation light source. The above tests are carried out under the condition of room temperature. The United States HORIBA JOBIN YVON Fluoro Log-3 fluorescence spectrometer and the United States TAP-02 temperature heating device are connected to determine the temperature dependent emission spectra of samples (Yang, et al., 2013), and the Japanese type photomultiplier tube is used for signal detection equipment.

4. Test results and discussion

4.1 Phase analysis of Na3YSi2O7: Sm3+ phosphor

Figure 2 shows the X- ray diffraction patterns and JCPDS standard card 72-2011 of Na3YSi2O7: x Sm3+ (x= 0.01, 0.03, 0.05, 0.07, 0.09) fluorescent powder. It can be seen from the figure that all the diffraction peaks of the sample are in line with the Na3YSi2O7 crystal standard card, and there is no impurity peak. The results show that Sm3+ doped into the Na3YSi2O7 matrix does not cause change in crystal structure and crystal phase formation matrix. As a result, we think that the synthesized samples are single phase.

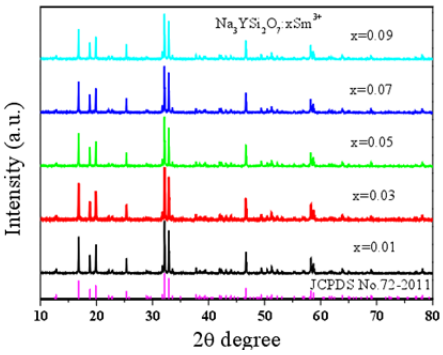

Figure 2: X-ray diffraction patterns of Na3YSi2O7: x Sm3+(x = 0.01, 0.03, 0.05, 0.07, 0.09) phosphors and JCPDS card no. 72-2011 as a reference

4.2 Luminescent properties

4.2.1 Excitation and emission spectra of Na3YSi2O7: Sm3+ phosphor

Figure 3 shows the excitation spectra and emission spectra of Na3YSi2O7: 0.03Sm3+ phosphor tested at room temperature. From the picture, we can easily see the excitation characteristics peak area in the wavelength range of 325 nm to 500 nm. The characteristic peaks are caused by the Sm3+ band gap transition, respectively correspond to: 6H5/2 - 4H9/2 (344 nm), 6H5/2 - 4D3/2 (359 nm), 6H5/2 - 6P7/2 (374 nm), 6H5/2 - 4F7/2 (404 nm), 6H5/2 - 4G9/2 (434nm), and 6H5/2 - 4I11/2 (473 nm). The transition intensity at 404 nm is higher than other locations seen from the excitation map. This result proves that the prepared phosphor can be effectively excited by near UV light, which further demonstrates the potential value of the application of the LED in the light conversion (Yang, et al., 2012). Under the excitation of 404 nm, a series of obvious emission peaks can be seen from the emission spectra map. Among them, 564 nm corresponds to the 4G5/2 to 6H5/2 transition, the 583 nm corresponds to the 4G5/2 to 6H7/2 transition, the 609 nm corresponds to the 4G5/2 to 6H7/2 transition, and the 651 nm corresponds to the 4G5/2 to 6H9/2 transition. In these transitions, 4G5/2 to 6H5/2 is mainly the magnetic dipole transition mode, the 4G5/2 - 6H7/2 transition includes both the magnetic dipole transition and the electric dipole transition, and the 4G5/2 - 6H9/2 transition is completely electric dipole. And the intensity of the emission peak at 609 nm is the largest, which indicates that the prepared phosphor has the value to be applied to the orange red luminescent material.

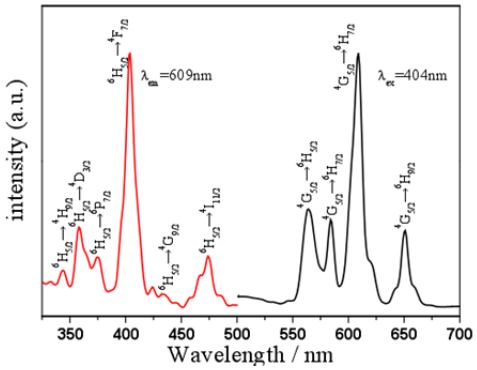

Figure 3: Excitation and emission spectra of typical Na3YSi2O7: 0.03Sm3+phosphor at room temperature

4.2.2 Variable concentration emission spectrum

To further study the effect of different Sm3+ doping concentration on the luminescence properties, we synthesize a series of Na3YSi2O7: x Sm3+ (x = 0.01, 0.03, 0.05, 0.07, 0.09) phosphor with different concentrations. And these samples are tested under the same conditions. Figure 4 shows the emission spectra of samples with different Sm3+ doping concentrations at 404 nm. It can be seen from the figure that, with the increase of Sm3+ concentration, the emission intensity firstly increases. When the Sm3+ concentration reaches 0.03, the emission intensity reaches the maximum value. Then, due to the concentration of Sm3+ produces too much concentration quenching, strength begins to decrease. The relative variation of the corresponding integral emission intensity can be seen from the illustration. In general, the concentration quenching of the luminescence is caused by two reasons. On the one hand, when the distance

between the ions is too close, it will cause the interaction between ions enhance and thus result in energy transfer; on the other hand, there will occur cross relaxation phenomenon and lead to decrease of luminous intensity between Sm3+ with 4G5/2+6H5/2 - 26F9/2 mode.

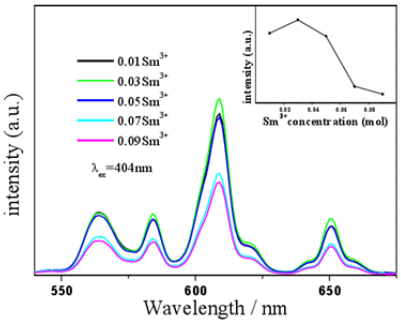

Figure 4: PL emission spectra of Na3YSi2O7: x Sm3+phosphors under 404 nm excitation, and the influence of the concentration on the emission intensity of Na3YSi2O7: x Sm3+(x = 0.01, 0.03, 0.05, 0.07, 0.09) phosphors

It is necessary to calculate the critical distance (Rc) between the donor and acceptor when the energy transfer mechanism of phosphor powder is used. According to the Blasses theory, the critical distance (Rc) can be calculated by the formula of the critical distance, as shown in Eq (4).

$$R_c = 2\left[\frac{3V}{4\pi\chi_c N}\right]^{1/3} \tag{4}$$

In Eq (4), V is the volume of the unit cell; xc is the critical concentration of the activator ion; N is the number of Sm3+ in each unit cell. For Na3YSi2O7 matrix, N=6, V=1.06018 nm3 xc = 0.03. In consequence, according to the Eq (4), we calculate the value of Rc of Sm3+, 2.2406 nm.

Generally speaking, the resonance energy transfer is divided into two modes: the electron cloud exchange interaction and the electric multiple-pole interaction (Zhu, et al., 2016). It has been proved that the electron cloud exchange effect is effective only when the critical distance of the active agent ion in the unit cell is less than 0.5 nm. This is much smaller than the Sm3+ in the Na3YSi2O7 matrix, so the energy transfer mode between Sm3+ in Na3YSi2O7: Sm3+ phosphor should be electric multiple level interaction. According to Dexter's theory, the multilevel effects are divided into three types: electric dipole - electric dipole interaction, electric dipole - electric quadrupole interaction, and electric quadrupole - electric quadrupole interaction. In order to further study and confirm, according to Van Uitert theory, the ionic strength (I) of each activator follows the Eq (5).

$$\frac{I}{x} = K\left[1+\beta(x)^{\theta/3}\right]^{-1} \tag{5}$$

In Eq (5), x is the activator concentration; the theta value of θ is 6, 8, 10 respectively corresponding to electric dipole - electric dipole interaction, electric dipole - electric quadrupole interaction, and electric quadrupole - electric quadrupole interaction; in the same excitation condition, for a given crystal, K and β are constants. Carry out logarithm of the Eq (5), to obtain the Eq (6):

$$\lg\left(\frac{I}{x}\right) = C - \frac{\theta}{3}\lg x \tag{6}$$

Select the Sm3+ concentration of 0.03, 0.05, 0.07, 0.09 and their corresponding emission intensities under 404 nm excitation. Draw the relationship curve of lg(I/x) to lgx, it is supposed to obtain a straight line with slope of -θ/3. As shown in Figure 5, the slope of lg(I/x) to lgx is -1.52, and θ value is 4.56, the closest to 6. Therefore, the concentration quenching mechanism of Na3YSi2O7:Sm3+ is electric dipole - electric dipole interaction.

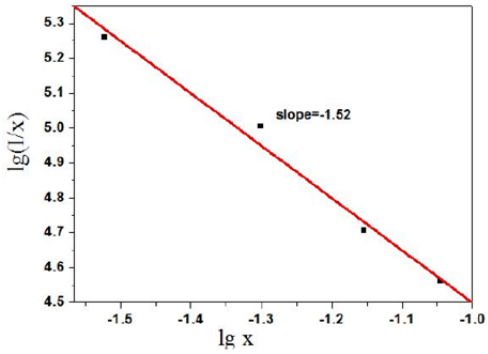

Figure 5: Curve of log (I/x) vs. log x in Na3YSi2O7: x Sm3+ phosphors

5. Conclusion

This paper uses the high temperature solid phase method, and taking Na3YSi2O7 as matrix compound, prepares a series of white LED luminescent materials doped with rare earth, and studies the luminescence properties of the material, the thermal stability, concentration quenching and its mechanism in detail. The results are summarized as follows: Na3YSi2O7: Sm3+ phosphor white LED is synthesized by using high temperature solid phase method. By using X- ray diffraction (XRD) and fluorescence spectroscopy and fluorescence spectroscopy at different temperatures, the phosphor and luminescence properties are characterized. At the same time, the concentration quenching mechanism of phosphor powder is analysed.

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