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ORIGINAL RESEARCH ARTICLE

Synthesis and Luminescent Properties of Eu^{3+}/Tb^{3+} Rare Earth Ions Doped Li_2SrSiO_4 Phosphors

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ABSTRACT

The series of luminescent materials of Eu3 +, Tb3 + doped Li2SrSiO4 were synthesized by a high-temperature solid-state method. The phase purity of the samples was measured by X-ray powder diffraction (XRD). The luminescent properties of the samples were studied by UV-visible excitation spectra and emission spectra The It is found that the strong absorption of Eu3 + doped Li2-xSr1-xEuxSiO4 is from the 250 ~ 290 nm charge transfer band of Eu3 + and the 7F0 → 5L6 absorption transition of 393 nm. The strongest emission of the emission spectra at 393 nm is 614 nm and 701 nm, respectively, from the 5D0 → 7F2 and 5D0 → 7F4 transitions of Eu3 +. Tb3 + doped sample Li2-xSr1-xTb xSiO4 excitation spectrum is mainly composed of Tb3 + ion fd transition and charge transfer band composed of broadband, the strongest absorption at 269 nm, the emission of the main emission of 5D4 → 7F5 transition (542 nm).

KEYWORDS: Rare earth ion; luminescent material; Eu3 +; Tb3 +; Li2SrSiO4

1. Introduction

1.1. Luminescent materials and rare earth elements

Luminous is the process by which an object converts the absorbed energy into optical radiation. When the material is subject to light, such as light, plus electric field or electron beam bombardment and other excitation, the absorption of external energy, in the excited state, it is in the process of transition back to the ground state, part of the excess energy will be released through the form of light or heat out. If this part of the energy is visible or near visible light in the form of electromagnetic waves emitted, resulting in a light phenomenon. This kind of energy in the various types of energy to stimulate the role of light-emitting materials [1,2].

In the luminescent material, rare earth elements play a big role, the role of rare earth far more than other elements. The so-called rare earth elements refers to the lanthanide plus the same group IIIB scandium (Sc) and yttrium (Y), a total of 17 kinds of elements [3-5]. The lanthanides include 15 elements from the 57-171 atomic number in the periodic table. They are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Holmium Ho, erbium Er, thulium Tm, ytterbium Yb, and lutetium. The electron configuration of the lanthanide atoms is: [Xe] 4f0 ~ 145d0 ~ 16s2, 4f electrons from La to Lu are sequentially increased from 0 to 14. The electron layer configuration of scandium and yttrium is different from that of lanthanides, which are [Ar] 3d14s2 and [Kr] 4d15s2, respectively, but they are classified as rare earth elements because of their chemical properties similar to lanthanides. To Gd elements as the boundary, according to the atomic number of rare earth elements are divided into 'light rare earth elements' and 'heavy rare earth elements' [3]. These elements have the same electronic structure of the outer layer, the inner layer 4f electronic energy level is similar, high price, radius, strong polarizability, chemical nature of lively and can be hydrolyzed and other properties, so its application is very extensive.

1.2. Classification of luminescent materials

Luminous materials have different classification methods [2,6,7]: (1) according to the form of excitation energy luminescent materials can be divided into photoluminescence (vacuum ultraviolet light, ultraviolet light or visible light excitation) material, high energy ray excitation (X (By excitation of the electric field), a chemical reaction luminescent material, a mechanical stress luminescent material, a luminescent material, a luminescent material, a luminescent material, a luminescent material, a luminescent material, a luminescent material (The crystal is excited by ionizing radiation and then excited by heat). (2) According to the material, the photoluminescence (excited by ions). (3) According to the application of different functions can be divided into lighting luminescent materials, display with luminescent materials, detection of luminescent materials, etc., can be divided into light-emitting center light-emitting materials, composite luminescent materials and composite luminescent center luminescent materials; (4) According to the different forms of materials can also be divided into powder materials, single crystal materials, glass materials and ceramic materials. In addition, in many luminescent materials, rare earth ions, whether as a matrix ion or activator are of great significance, so we have rare earth ions containing luminescent materials known as rare earth luminescent materials.

1.3. Spectral term of rare earth ions

The electron layer configuration of the ground state atoms is determined by the main quantum number n and the angular quantum number l. For the different lanthanides, when the 4f electrons are sequentially filled with orbits of different magnetic quantum numbers, they must understand their ground state spectral terms (2s + 1LJ) in addition to their electronic layer configurations. The spectral term is a symbol that represents the energy level associated with the electronic arrangement by the angular quantum number l and the magnetic quantum number m and the different combinations between them. When the electrons are filled with different m-values of the 4f sublayer, in turn, the total orbital quantum number L, the total spin quantum number S and the total angular momentum quantum number J and the ground spectral term 2s + 1LJ.

The characteristics of the spectral term of the trivalent lanthanide ion can be summarized as follows: fd (n = 0 ~ 6) and G143 are the pairs of conjugated elements with Gd3 + as the center, Gd3 +, and they have similar spectral terms The number of unpaired electrons on the 4f orbital of the two sides is Gd3 +, and the energy levels are similar. The L and S values of the Gd3 + ions are symmetrical. The total spin quantum number S of trivalent lanthanide ions changes with the increase of atomic number at Gd3 +. The total number of nuclei and angular momentum quantum J show a bimodal periodic change with the increase of atomic number. Due to the unique properties of the rare earth ion spectroscopy, in the crystal or aqueous solution, the different rare earth ions exhibit different colors. Many rare earth compounds have been widely used in glass ceramic coloring, luminescent materials and laser materials and other fields [8].

1.4. Rare earth ion energy level and transition

1.4.1 Rare earth ions 4f energy level and f-f transition

Most of the rare earth material emits light from the electron transition of the 4f shell with the rare earth ions. The 4f orbit is in the interior of the ion and is shielded by eight electrons from the external 5s2 and 5p6 tracks. The crystal field in the matrix lattice has little effect on the light absorption transition of the 4fn electron configuration.

The f-f transition of trivalent rare earth ions is mainly attributed to the electric dipole or magnetic dipole transition of rare earth ions. The choice of the electric dipole transition is: l = ± 1, S = 0, L ≤ 6, J ≤ 6, when J or J '= 0, J = 2, 4, 6; The choice of magnetic dipole transition is: l = 0, S = 0, L = 0, J = 0, ± 1. The electric dipole transition is partially permissible and therefore very sensitive to the symmetry of the crystal, whereas the effect of the symmetry of the crystal on the magnetic dipole transition is not so obvious. The f-f transition of trivalent rare earth ions has the following characteristics: (6) the emission spectrum is linear; (2) the spectrum is rich and can extend from the ultraviolet region to the infrared region; (3) the emission wavelength is less affected by the substrate environment ; (4) the spectral shape of the temperature is relatively small, the temperature quenching small; (5) fluorescence life is generally longer.

1.4.2 Rare earth ions 4f5d energy level and f-d transition

Rare earth ion emission In addition to f-f transition, there is an f-d transition, that is, rare earth ion 4fn configuration and 4fn-15d configuration energy transition between. Because of the rare earth ions exposed to the 5d orbit, the influence of the crystal field environment is relatively large, so the rare earth ions f-d transition and f-f transition spectrum are very different. (2) the emission spectral position is strongly affected by the crystal field, the spectral position can be from the ultraviolet region to the near infrared region; (2) the emission spectrum is affected by the crystal field, and the spectral position can be from the ultraviolet region to the near infrared region; (2) 3) strong emission intensity; (4) fluorescent life is short; (5) luminous intensity by temperature.

1.5. Charge transfer zone of rare earth ions

The electrons migrate from the molecular orbital of the ligand (O, X) to the 4f orbital filled in the rare earth ions, resulting in a broad charge transport band in the spectrum. Tetravalent rare earth ions such as Ce4 +, Pr4 +, Tb4 +, Dy4 + and trivalent rare earth ions such as Sm3 +, Eu3 +, Yb3 + and so on in the near ultraviolet region with a charge transfer zone, the half width of up to 3000 ~ 4000 cm-1, is allowed to transition. In general, the charge transport zone moves toward the low energy direction as the oxidation state increases. Because of the excitation spectrum of rare earth ions, the f-f transition belongs to the narrow band of the forbidden transition, and the intensity is weak, which is not conducive to the absorption of excitation energy. This is one of the reasons why the rare earth ion light emission efficiency is not high. If the energy is absorbed by the charge transport band and the energy is transferred to the luminescent ions, the luminous efficiency of the rare earth ions can be improved.

The charge transport band of rare earth ions has the following characteristics [9]: (1) the smaller the electronegativity of the ligands coordinated with the rare earth ions, the lower the energy of the charge transport band; (2) the coordination of the rare earth ions (3) The higher the oxidation state of the rare earth ions, the lower the energy of the charge transport band.

The main difference between the charge transfer state and the fd transition is that: (1) the charge transfer zone usually has no fine structure, and the fd transition is often caused by the d-orbit by the crystal field. (2) The half- (3) The charge transfer zone moves toward the low energy direction with the increase of the oxidation state of the rare earth ions, and the fd transition moves to the high energy direction as the oxidation state increases, such as the lowest absorption of all the tetravalent rare earth ions The band belongs to the charge transfer zone, and all the rare absorption bands of the divalent rare earth ions belong to the fd transition.

1.6. Luminescent properties of rare earth ions

Rare earth luminescent materials with narrow emission band, high color purity, colorful, strong ability to absorb energy, high conversion efficiency, wide emission range (from ultraviolet to infrared), fluorescence life span from nanosecond to milliseconds 6 orders of magnitude, Phosphorescence up to more than 10 hours, the physical and chemical properties of materials stable, can withstand high-power electron beam, high-energy radiation and the role of strong ultraviolet light and so on. Today, rare earth luminescent materials have been widely used in display imaging, new light sources, X-ray sensor screen, nuclear physics detection and other fields, and to other high-tech field expansion [10]. In this study, the emission characteristics of Eu3 + and Tb3 + were studied.

1.6.1 Eu3 + emission characteristics

Eu3 + is almost unaffected by the environment of the ligand crystal field due to the shielding effect of the outer electrons. Therefore, the emission transition is linear in the spectrum. These lines correspond to the 5D0 energy level in the excited state of 4f6 To 7FJ (J = 0, 1, 2, 3, 4, 5, and 6) levels. Since the 5D0 level is not split by the crystal field (J = 0), the splitting of the emission transition is caused by the splitting of the crystal field at the 7FJ level. Usually, the emission lines of Eu3 + are in the red light region, and these lines have many important applications in luminescence and display (color television) and are widely used as the luminescent centers of red phosphors.

The symmetry of the lattice of Eu3 + has a great influence on its transitional emission characteristics. If the lattice occupied by Eu3 + has inversion symmetry, then the electron transition between 4fn electronically arranged energy belongs to parity They can only be used as weakly polar magnetic dipole transitions (the transitional rule is: □ J = 0, ± 1, but J = 0 to J = 0 is the transition Forbidden) or electronic-vibrational dipole transitions occur.

If the lattice of Eu3 + does not have the inversion symmetry, the odd-order phase of the crystal field can be mixed into the 4fn configuration energy level, and the electric dipole transition is no longer strictly forbidden. In the presence of weak lines, the so-called forced dipolar transition (forced electric-dipole transitions). The forced dipole transition must satisfy the following two conditions: there is no inversion symmetry center in the Eu3 + crystal lattice, and the charge transfer transition is at low energy. Some transitions (i.e., □ J = 0, ± 2 transitions) are extremely sensitive to this effect, and even if the lattice of Eu3 + is only slightly deviated from the inversion symmetry center, this transition will dominate the spectrum. 5D0 → 7F2 transitions are super-sensitive forced dipole transitions. When Eu3 + does not have strict inversion symmetry, the emission will dominate the transition of Eu3 +.

In practical applications, the main emission of Eu3 + is required to concentrate on the 5D0 → 7F2 transition (610 ~ 630 nm) to obtain the red light with better color purity [11,12].

So far, Eu3 + has been the rarest earth element for the red and phosphorous UV phosphor, especially for PDP, which has become the indispensable activator of PDP Commercial Red Phosphor (Y, Gd) BO3: Eu3 + [13]. (Y, Gd) BO3: Eu3 + has a main emission wavelength of 593 nm [14], not the best PDP display gamut. Therefore, Y2O3: Eu3 + (the main emission wavelength of 611 nm) are usually used to expand the color gamut of PDP, but the loss of luminescence [15]. In the past few years, YP1-x VxO4: Eu3 + phosphors developed by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences have strong luminous intensity in the vacuum ultraviolet region, and the main emission wavelength is 619 nm, the emission wavelength is longer, Color gamut is a better PDP phosphor. It can be seen, whether it is past, or now, as an activator, Eu3 + is the preparation of PDP with red phosphor is very effective rare earth elements [16].

1.6.2 Tb3 + luminescence characteristics

Tb3 + emission from the 5D4 → 7FJ transition, mainly in the green zone, and from the higher level of 5D3 → 7FJ transition also has a certain launch, it is mainly in the blue light area, but it is easy to be broken, which may be through Tb (5D3) + Tb (7F6) → Tb (5D4) + Tb (7F6) transfer process. In practical applications, the main use of Tb3 + 5D4 → 7F5 transition emission of green light (near 540 nm).

The borate activated by Tb3 + has the advantages of good UV absorption, high quantum efficiency, and good luminous brightness and luminous efficiency, which is the main representative of green powder in trichromatic phosphor [17]. Many studies have shown that Tb3 + is in the vicinity of 170 ~ 200 nm in the VUV region, so Tb3 + is incorporated into the matrix material with strong absorption in this band, and the energy can be effectively transferred to the luminescent center Tb3 + through the matrix. In the field of PDP, Mn2 + activated green powder afterglow time is longer, and in the PDP production and use of the process is easy to be oxidized to a higher valence of manganese ions, so that the luminous brightness. Tb3 + activated phosphor have the advantages of narrow bandwidth, stable performance and high quantum efficiency under the excitation of PDP. However, with Tb3 + as the luminescent center and Mn2 + -activated fluorescence Powder, in the luminous brightness and color purity, etc. have yet to be improved.

1.7. Characterization of Rare Earth Luminescent Materials

The characterization methods of rare earth luminescent materials include structural characterization and spectral characterization of materials. These methods of characterization are important means to help us understand the macroscopic and microscopic structures of materials and the properties of light emission. At the same time, the various indicators of luminous materials are to examine whether the material has a direct basis for the application value. The characterization method and performance index used in this experiment are as follows:

1.7.1 Powder diffraction

When the angle between the X-ray of the irradiated sample and the plane of the sample is θ, the crystal faces in the sample that satisfy the diffraction conditions of the Bragg equation, cause the incident X-ray to produce a diffraction line at the 2θ angle. The sample was then scanned to obtain a sample X-ray diffraction pattern. The abscissa in the diffraction pattern is 2θ, and the ordinate is the relative diffraction intensity. For luminescent materials, the X-ray diffraction pattern is often used to compare the X-ray diffraction curves of the light-emitting matrix PDF card or single crystal structure data to determine whether the synthesized luminescent material is a pure phase target product. In addition, the X-ray diffraction pattern can also calculate the particle size of the sample, coordination of environmental changes and other information.

1.7.2 Excitation spectra and emission spectra

The emission spectrum is the recording of the luminescent material at a particular wavelength of light excitation, the emission of different wavelengths of light intensity or energy distribution. The emission spectrum can characterize the luminous intensity of the luminescent material, the strongest emission position,

Emission spectrum shape can reflect the type of light and the transition level and the luminous color of the material and so on.

In addition to vacuum ultraviolet, UV and visible light, the excitation energy of the emission spectrum can also be provided by other excitation sources, such as X-ray and cathode ray electron beams in this paper.

The excitation spectrum is the relationship between the intensity of a particular emission wavelength and the wavelength of the excitation light under the excitation of different wavelengths. The excitation light distribution and the optimum excitation wavelength for a particular emission of the luminescent material can be determined from the excitation spectrum. Although it is the ability to characterize the light-absorbing material to absorb light, the excitation spectrum and the absorption spectrum are different, because not all of the absorbed light contributes to the light emission. The excitation spectrum is the same as the emission spectrum. The abscissa is the emission wavelength, often expressed in nanometers (nm), and the ordinate is the excitation (emission) intensity (I), often expressed as the relative intensity (a.u.) of any unit.

1.8. Application of Rare Earth Luminescent Materials

Rare earth luminescent material has the advantage of high conversion rate can be emitted from the UV, visible to the infrared wavelength of light, and the physical and chemical properties of stability. At the same time, the absorption of light from the rare earth ions takes place between the different energy levels of the inner layer 4f electrons, resulting in a narrow spectrum of absorption spectra, thus showing a bright and pure color. Since the Y2O3: Eu was used as a phosphor in 1964, rare earth luminescent materials have developed rapidly. Most rare earth elements are used more or less for the synthesis of fluorescent materials. Rare earth luminescent materials have become the display, lighting and optoelectronic devices And other areas of the supporting material, and there has been new rare earth phosphor appears.

At present, rare earth luminescent materials are mainly used for color TV tube, computer monitors, lighting, medical equipment and so on. Rare earth luminescent materials are the largest amount of color cathode ray tube, computer monitors, rare earth trichromatic fluorescent lamps, PDP display.

1.8.1 Luminescent materials for lamps

In the early 1970s, M. Koedam et al. used an electronic computer to optimize the light efficiency and color rendering index of the lamp. Theoretically, the four visible mercury spectra in the low-pressure mercury lamp were, 550,610 nm each have a narrow line, can make the color rendering index and light efficiency at the same time improve. (Ce, Tb) MgAl11O19 (543 nm), blue powder BaMg2Al16O27: Eu2 + (451 nm) and red powder Y2O3: Eu3 + (611 nm) were developed in Verstegen, Netherlands so that the application of rare earth trichromatic fluorescent lamp achieve. By the above three kinds of materials according to a certain proportion of mixing, can be made from 2300 to 8000 K color temperature of the various fluorescent lamps, color rendering index greater than 80, light efficiency greater than 80 lm / W. Blue LED in the 1990s technology and industrialization in a great way to promote and achieve the development of white light, optoelectronics, lighting engineering has become another major achievement. Among them, the white light LED combination of yellowing Ce3 + doped (Y, Gd) 3 (Al, Ga) 5O12 with blue-emitting InGaN chip is the mainstream of the current development. At present, its luminous efficiency has been much higher than incandescent, expecting to meet and exceed fluorescent lamps in the future. Is expected to become the fourth generation of new lighting source, to achieve energy saving and green lighting. It can be asserted that with the development of technology, rare earth luminescent materials will play an increasingly important role in the future lighting field.

1.8.2 Cathode ray luminescent material

The rare earth luminescent materials used in color cathode ray tubes and computer displays are cathode ray luminescent materials. CRT (cathode ray tube) phosphor is the earliest application of rare earth in luminescent materials. The popularity of color TV and the vigorous development of PC so that this classic new material growth, there are still 7% annual growth rate, but also faced with the challenges of flat panel display. Color TV and color display with the basic process of phosphor formed in the 1970s, the United States RCA is the originator of this technology, but Japan's Nichia, Kassei, and other companies for this area continued to inject a new technical content, so that the brightness of the screen, contrast, clarity, daylight readability, life and other indicators have been greatly improved. Currently used color TV red phosphor with Eu3 + ion activated YVO4: Eu, Y2O2S: Eu and so on. Red phosphors made with rare earth are bright and stable, and their luminous properties greatly exceed that of rare earth-free powders. As a result, the demand for pure europium oxide and pure yttrium oxide has increased dramatically. Y2O2S: Eu, but also the content of Eu3 +, the green powder is Tb3 + activated rare earth sulfur oxides Y2O2S: Tb, Dy and Gd2O2S: Tb and the green powder is Tb3 + activated rare earth sulfur oxides Y2O2S: Tb, Dy, and Gd2O2S: Tb, Dy efficient green phosphor with a particle size of 4 to 6 μm. It has been reported that blue powder will also be replaced by rare earth luminescent materials zinc, strontium sulfide phosphor. Large screen projection TV red powder is also Y2O2S: Eu, green powder for the Tb3 + activated rare earth luminescent materials, projection TV with the annual consumption of several tons of rare earth oxide phosphor.

1.8.3 X-ray luminescent materials

In the case of medical X-ray photography, a screen is used to convert an X-ray image into a visual image. The new X-ray screen, which is mainly based on rare earth phosphor, has been paid more and more attention by X-ray luminescent materials. Over the past decade, several rare earth phosphors have been found, which not only have the same photographic effect as CaWO4 but also have a high efficiency under X-ray excitation. This can reduce the patient’s exposure to X-ray radiation by 75%, improve the image quality, extend the life of the X-ray tube, and reduce the X-ray diagnostic power consumption, improve the success rate of the film. X-ray sensor screen also has a variety of high-sensitivity X-ray screen using Gd2O2S: Tb phosphor. Compared with other phosphors, Gd2O2S: Tb can emit high efficiency white or green light by X-ray excitation.

1.8.4 Electroluminescent materials

Electroluminescence is the direct conversion of electrical energy into light energy. It is characterized by low operating voltage, high energy conversion efficiency, small volume, light weight, wide working range and fast response speed. Rare earth doped ZnS, CaS and SrS thin film electroluminescent devices in the flat panel display cut a striking figure. To achieve color electroluminescent flat panel display, the current research and development of rare earth doped rare earth thin film materials.

1.8.5 Long afterglow fluorescent material

The long afterglow phosphor (commonly known as luminous powder) is a kind of energy that can receive natural light (daylight) and various light sources (fluorescent lamps, incandescent lamps, etc.) and store light energy, and then release visible light for a long period of time Of the new storage materials, usually in the dark to continue to light 8-10 hours, it is called long afterglow fluorescence material. Rare earth long afterglow material has the advantages of high luminous brightness, long afterglow time, radiation resistance, long life, long-term exposure to sunlight and no failure. It is also a long afterglow fluorescence material without radioactive hazards. Has attracted wide attention since the 1980s, and has been widely used in advertising, road signs, indoor indicators, luminous watches, boats, and lighthouse and so on. In recent years, long afterglow fluorescence materials developed rapidly, in addition to the emergence of new fluorescent materials, due to the theory of fluorescent materials and manufacturing technology development, many traditional fluorescent materials have been given new application characteristics. At the same time, the application of the market continues to expand, but also to promote this area of research is very active.

In addition, rare earth luminescent materials have many other uses. Such as infrared up conversion luminescent materials, due to the rapid development of portable infrared lasers (laser pens) in recent years, people can use infrared light conversion materials to prepare anti-counterfeit labels, because the infrared conversion material is inkless color, and excited infrared Light source is also invisible to the human eye, so it is now using the UV excitation light identification material concealment is good, is a highly technical anti-counterfeiting technology. Such as quantum cutting materials, with the requirements of green lighting, people urgently asked the development of mercury-free fluorescent lamps, for mercury fluorescent lamps, mercury vapor excitation at 254 nm, if the average wavelength of visible light at 500 nm, the phosphor quantum efficiency of 100%, The energy conversion efficiency is 51%. The mercury-free fluorescent lamp has an energy conversion efficiency of 34% with an inert gas discharge as the excitation light source (Xe, 172 nm) so that the mercury-free fluorescent lamp is competitive and must use high quantum efficiency. The luminescent material is cut at 100% quantum to improve its energy conversion efficiency.

2. Experimental parts

2.1. Experimental drugs and equipment

The main reagents used in this experiment are shown in Table 1.

Table 1. Major reagents and purity

Reagent Name	chemical formula	purify	type	manufacturer
Anhydrous lithium carbonate	Li_2CO_3	C.P.	73.89	Guangzhou Guanghua Chemical Factory Co., Ltd
Strontium Carbonate	$SrCO_3$	A.R.	147.63	Guangzhou Guanghua Chemical Factory Co., Ltd
Quartz sand	SiO_2	A.R.	60.08	Guangzhou Guanghua Chemical Factory Co., Ltd
Europium	Eu_2O_3	99.99%	351.93	Guangdong Nonferrous Metals Research Institute
Nonferrous Metals	Tb_4O_7	99.99%	747.70	Guangdong Nonferrous Metals Research Institute

The experimental sample synthesis equipment for the Shanghai experimental furnace production of 8-10-12 box resistance furnace, rated power 15 kW, the maximum control temperature of 1600°C.

2.2. Synthesis of samples

2.2.1 Preparation of Li2SrSiO4: Eu3 +

A series of different concentrations of Li2-xSr1-xEuxSiO4 (x = 0.005, 0.01, 0.03, 0.05, 0.07, 0.09, 0.12 and 0.15) were synthesized.

Synthesis method: the sample using traditional high-temperature solid phase synthesis. According to the chemical formula of the synthesized compound, according to the stoichiometric ratio of different elements, accurately weighed a certain amount of raw materials in the ceramic mortar fully mixed grinding. The raw material mixture after grinding was transferred to an alumina crucible and then placed in a capped large crucible, heated to 800 °C in a resistance furnace for 6 h. After the reaction product is naturally cooled in the resistance furnace, it is taken out in the ceramic mortar to obtain the final sample, and the bag is marked as the final sample.

2.2.2 Preparation of Li_2SrSiO_4: Tb^{3+}

A series of different concentrations of $Li_{2-x}Sr_{1-x}Tb_xSiO_4$ (x = 0.005, 0.01, 0.03, 0.05, 0.07, 0.09, 0.12 and 0.15) were synthesized.

Synthesis method: the sample using traditional high-temperature solid phase synthesis. According to the chemical formula of the synthesized compound, according to the stoichiometric ratio of different elements, accurately weighed a certain amount of raw materials in the ceramic mortar fully mixed grinding. The raw material mixture after the grinding was transferred to an alumina crucible and then placed in a capped large crucible (a large crucible bottomed with a layer of toner) and heated at 800 °C in a carbon monoxide reduction atmosphere (supplied from toner) for 6 h The After the reaction product is naturally cooled in the resistance furnace, it is taken out in the ceramic mortar to obtain the final sample, and the bag is marked as the final sample.

2.3. 2.3 Test of samples

The characterization of the samples was determined by the Rigaku D/max 2200 vpc X-ray powder diffractometer. The test conditions were: graphite monochromatic, CuKα ray (λ = 1.541 Å), operating voltage 40 kV, current 30 mA, The speed is 10 °/ min.

The emission spectra and fluorescence decay curves of the samples were measured by FLS920 combined fluorescence lifetime and steady state fluorescence spectrometer from Edinburgh, UK. The Xe lamp used to test the fluorescence spectrum of the excitation light source is 450 W.

3. Results and discussion

3.1. Study on Luminescence Properties of $Li_{2-x}Sr_{1-x}Eu_xSiO_4$

3.1.1 XRD characterization of samples

To investigate the phase purity and phase structure of the synthesized samples, two samples with the lowest concentration (x = 0.005) and the highest concentration (x = 0.150) were selected as the representative of the powder XRD test. The XRD pattern of the sample $Li_{2-x}Sr_{1-x}Eu_xSiO_4$ (x = 0.005, x = 0.150). Li_2SrSiO_4 structure for the hexagonal system, space group P3121, and Li_2EuSiO_4 have the same structure. It can be seen that the XRD of the representative sample is in good agreement with the standard card Li_2EuSiO_4 (JCPDS card 470-120), especially the sample with low Eu^{3+} ion doping concentration (b: x = 0.005). This indicates that the composite sample with Eu^{3+} ion doping concentration x = 0.005 is the target product of pure phase. However, the diffraction curve of the sample with high concentration (c: x = 0.150) can be observed at 28.4 ° and 31.5 °, and the weak diffraction peak (see the solid point of curve c in Figure 1) shows that Eu^{3+} ion doping concentration x = 0.150 The synthesis of the sample is not enough purity, may be caused by insufficient sintering time.

3.1.2 Excitation spectra of $Li_{2-x}Sr_{1-x}Eu_xSiO_4$

Excitation spectrum of the sample $Li_{2-x}Sr_{1-x}Eu_xSiO_4$ (x = 0.005, x = 0.150). It can be seen from the figure, the excitation spectrum of 230 ~ 350 nm range of broad peaks and 350 ~ 430 nm range of sharp components. Among them, the broadband excitation peak in the figure is the charge transfer between the $O^{2-} \rightarrow Eu^{3+}$ ions to form the charge transfer band (CTB) [18]. For the sample $Li_{1.995}Sr_{0.995}Eu_{0.005}SiO_4$ (curve a), the maximum value is at 269 Nm, while in the sample $Li_{1.850}Sr_{0.850}Eu_{0.150}SiO_4$ (curve b), the maximum value of the charge transfer band is at 287 nm. In the main absorption peak that can be observed, with the increase of the doping concentration, the charge transfer band is redshifts, that is, moves toward the low energy direction. The excitation peaks are located in the range of 355 to 421 nm, which correspond to the f-f transition emission of Eu^{3+} ions. The strongest absorption is at 393 nm, corresponding to the $^7F_0 \rightarrow {}^5L_6$ absorption transition of Eu^{3+}.

3.1.3 Emission spectra of $Li_{2-x}Sr_{1-x}Eu_xSiO_4$

At 393 nm excitation, the emission spectrum of the sample Li2-xSr1-xEuxSiO4 (x = 0.005, x = 0.150) is shown in Fig. The characteristic shows that the emission peak belongs to 5D0 → 7FJ (J = 0 ~ 4) of Eu3 +, and the strongest 602 ~ 644 nm emission is 5D0 → 7F2 transition emission of Eu3 +. The maximum wavelength is 614 nm. 5D0 → 7F2 transition for the electric dipole transition (also known as the ultra-sensitive transition), its crystal field is very sensitive. In addition, there is sub-strong 692 ~ 717 nm emission, belonging to Eu3 + 5D0 → 7F4 transition emission, the maximum wavelength of 701 nm. It is worth mentioning that Eu3 + 5D0 → 7F2 and 5D0 → 7F4 for the dominant emission, for improving the color purity of the luminescent material is helpful, so the sample Li2-xSr1-xEuxSiO4 light color is relatively red.

3.2. 3.2 Study on Luminescence Properties of Li2-xSr1-xTbxSiO4

3.2.1 XRD characterization of samples

XRD patterns of the two representative concentrations of the sample Li2-xSr1-xTbxSiO4 minimum concentration x = 0.005 and the highest concentration x = 0.150. It can be seen that the low concentration (x = 0.005) represents the XRD pattern of the sample and the standard card Li2EuSiO4 (JCPDS card 470-120) is very consistent, indicating that the synthesized sample Li1.995Sr0.995Tb0.005SiO4 is the pure phase of the target product The For the high concentration (x = 0.150) of the synthetic sample Li1.850Sr0.850Tb0.150SiO4, the XRD is consistent with the standard card, but its diffraction curve at 31.9 ° can be observed obvious diffraction peak (see Figure 4 curve c Solid Point), indicating that the synthetic sample Li1.850Sr0.850Tb0.150SiO4 purity is not enough, the reaction is not thorough enough. The reason may be: 1, sintering time is insufficient; 2, a constant temperature is not high enough.

3.2.2 Excitation spectra of Li2-xSr1-xTbxSiO4

We investigated the excitation spectra of Li2-xSr1-xTbxSiO4 (a: x = 0.150, b: x = 0.005) with different doping concentrations of 542 nm emission of Tb3 + ions, as shown in Fig. As can be seen from the figure, the excitation spectrum in the range of 200 ~ 310 nm for the two strong absorptions of broadband. The absorption band at which the low energy peak is located at 269 nm may be the transitional absorption of the spin-up of the f-d transition, while the higher energy peak at 250 nm may come from the Tb3 + → O2-charge transfer state. A series of spikes in the range of ~ ~ 310 nm to 450 nm is the f-f transition peak of Tb3 +. The peak at 378 nm is the most obvious, which is the characteristic band of 7F6 → 5L10 of Tb3 +, and the other f-f absorption peaks is weak. In addition, the difference in the excitation spectra of the two samples with different doping concentration is mainly reflected in the intensity difference, and the strength of the sample with high doping concentration is much stronger.

3.2.3 Emission spectra of Li2-xSr1-xTbxSiO4

The emission spectra of Li1.995Sr0.995Tb0.005SiO4 (a, 247 nm excitation) and Li1.850Sr0.850 Tb 0.150SiO4 (b, 269 nm excitation). It can be seen that the fluorescence emission spectra of Tb3 + ions in Li2SrSiO4 are at 487,542,584,620 nm, and their peaks correspond to 5D4 → 7F6, 5D4 → 7F5, 5D4 → 7F4, 5D4 → 7F3 transition of Tb3 + ions respectively, of which 5D4 → 7F5 transition emission is the strongest, is Tb3 + ion characteristic emission, other transition intensity are relatively weak. So the sample is green. Similar to the excitation spectrum, the emission peak intensity of the sample with high doping concentration is stronger than that of the sample with low doping concentration, which indicates that increasing the concentration of dopant ions in a certain concentration range can improve the luminous intensity of the sample.

4. Conclusions

(X = 0.005, 0.01, 0.03, 0.05, 0.07, 0.09, 0.12, 0.15) were synthesized by high temperature solid phase method. The effects of low concentration (x = 0.005) and high concentration (x = 0.005) X = 0.150). The results show that: (1) the fluorescence intensity increases with the increase of Eu3 + concentration. (2) The broadband excitation peak at 250 ~ 290 nm is the charge transfer between O2- → Eu3 + ions to form CTB band. (3) The narrow peaks appearing in the range of 355 ~ 421 nm, which correspond to the f-f transition emission of Eu3 + ions; (4) the Eu3 + at 614 nm is strong the emission is from the 5D0 → 7F2 transition, the sample is strong red.

(X = 0.005, 0.01, 0.03, 0.05, 0.07, 0.09, 0.12, 0.15) were synthesized by high temperature solid phase method. The effects of low concentration (x = 0.005) and high concentration (x = 0.005) X = 0.150). The results show that: (1) the fluorescence intensity increases with the increase of Tb3 + concentration; (2) The strong excitation peak of Tb3 + is located at 269 nm at 542 nm; (3) The fluorescence emission of Tb3 + ions in Li2SrSiO4 The strongest emission of the spectrum is 5D4 → 7F5 transition emission (542 nm), the sample is green.

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