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Properties of a novel $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} phosphor: Bulk and 1D nanostructure with PVP synthesized by sol-gel and electrospinning

Yuanlin Yao, Zhufa Zhou*, Feng Ye

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

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ABSTRACT

In this study, a sunlight-activated $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} (BSEN) persistent luminescent particles were firstly synthesized by sol-gel method, and then combined with polyvinyl pyrrolidone (PVP) to fabricate one-dimensional functional fiber by electrospinning. XRD, photoluminescence, fluorescence microscope, SEM and TEM were used to investigate the crystal structure, the morphology, the luminescent properties and water resistance of BSEN particles and functional fibers. The results show that BSEN owns a monoclinic crystalline and can be effectively and repeatedly excited by both ultraviolet and sunlight. The BSEN particles were water-resistant and uniformly dispersed in the PVP fibers. Both BSEN particles and functional fibers possessed broad excitation spectra from 250 nm to 450 nm with maximum at 341 nm and exhibited a fluorescent and phosphorescent emission band from 365 nm to 650 nm with maximum at around 489 nm with long afterglow up to 240 min. The new functional fiber has potential to be used in flexible coating, textile and optical display.

1. Introduction

Persistent luminescent material, which can emit visible or near-infrared light for a long time after the excitation source been cut off, is a potential solution to the energy issue [1,2]. Persistent luminescent material has various applications in in-vivo imaging [3], nano probe [4], night vision [5] owing to its long afterglow. Many persistent luminescent materials are in application. For example, ZnS:Co, Cu [6] is used for watch dials but sensitive to moisture. $SrAl_2O_4:Eu^{2+}$, Dy^{3+} has super long afterglow and high brightness but bad hydrolysis resistance [7]. $M_2MgSi_2O_7:Eu^{2+}$,Dy^{3+} (M: Sr, Ca, Ba) possesses excellent afterglow and stable chemical property but lack of color diversity [8,9]. However, very few studies are reported in the sunlight-activated persistent luminescent material. It is economic and environmental friendly to use sunlight to activate persistent luminescent material. So far, the outstanding sunlight-activated material is $Zn_3Ga_2Ge_2O_{10}:Cr^{3+}$, which emits near-infrared light beyond 360 h with excitation spectrum from 300 nm to 650 nm [10].

Sol-gel preparation [11,12] is an effective method to synthesize persistent luminescent material compared to solid-state method [13]. Usually, the latter demands high synthesis temperature, and particles prepared by this method are not small enough. Electrospinning is a facile method to fabricate one-dimensional fibers which draw considerable efforts in research and have various applications in optics, sensors and lasers due to their superior physical and chemical property [14,15].

The secret of sunlight-activated persistent luminescence is to broaden the width of excitation spectra so that the material can be directly activated by solar irradiation. Take $Ba_5Si_8O_{21}:Eu^{2+}$, Dy^{3+} as an example, even if the persistent luminescence can last 8 h after solar irradiation, the width of excitation spectra of Eu^{2+}, Dy^{3+} co-doped $Ba_5Si_8O_{21}$ do not get any broader than Eu^{2+} single doped $Ba_5Si_8O_{21}$ [16]. One effective method to tune the photoluminescence spectra is change the co-doping ions. Therefore, a persistent luminescent material of $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} (BSEN) has been synthesized by sol-gel method, which have broader excitation spectra and low cost due to the rare earth price and act as precursor for electrospinning. The precursors were used to synthesize one-dimensional functional fibers by electrospinning [17,18]. The problem is that, the pure inorganic non-metallic fibers are instable and brittle, thus not suitable for application. To solve this issue, persistent luminescent material were mixed with polymer, and made into fibers by electrospinning [19–21]. Here, polyvinyl pyrrolidone (PVP) and $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} (BSEN) were mixed to synthesize functional fiber through electrospinning. The fiber owns

* Corresponding author.
E-mail address: zhouzhufa@suda.edu.cn (Z. Zhou).

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the properties of luminescence from BSEN and flexibility from PVP.

2. Experimental

2.1. Synthesis and preparation of PVP/$Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} fiber

A series of persistent luminescent materials $Ba_5Si_8O_{21}:0.02Eu^{2+}$, xNd^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08) were synthesized by sol-gel method. The selection of molar ratio of lanthanides in this study is based on the past experience and random [16]. The raw materials were analytical grade $Ba(NO_3)_2$ (Sinopharm Chemical Reagent Co., Ltd, abbreviated as SCR), $Si(OC_2H_5)_4$ (TEOS, SCR), Eu_2O_3 (4N, SCR) and Nd_2O_3 (4N, Aladdin). Firstly, Eu_2O_3 and Nd_2O_3 were dissolved in nitric acid and then stirred with the distilled water. Secondly, $Ba(NO_3)_2$, TEOS and ethanol were added into the solution, and the pH was adjusted to 2 by adding nitric acid dropwise. The solution was stirred at 60 °C until formation of transparent gel. Thirdly, the gel was dried at 110 °C for 12 h. The resulting white gel was then sintered at 1250 °C for 3 h in a graphite reducing atmosphere.

In the following, PVP was dissolved in distilled water with a concentration of 0.2 g/mL and the solution was stirred at room temperature for 2 h. The $Ba_5Si_8O_{21}:0.02Eu^{2+}$, $0.04Nd^{3+}$ particles (10 wt% of the functional fiber) were added in the solution and dispersed in ultrasonic vibrator for 1.5 h. The suspension was loaded in an injector and the injector was fixed on electrospinning equipment. The flow rate was set at 1.5 mL/h and the voltage 15 KV, the distance between collector and syringe needle was 15 cm. The fibers ejected on the collector were the target product. Then the fibers were dried in vacuum oven at 30 °C for 12 h.

2.2. Characterizations

XRD patterns were taken on a Rigaku S/Mx diffractometer (PAN analytical, The Netherlands) using Cu Kα radiation (λ = 1.5406 Å). Excitation and emission spectra and afterglow decay curves were collected by a fluorescence spectrophotometer (Hitachi F-2500, Japan). Absorption spectra were collected by a UV–Vis–NIR spectrophotometer equipped with an integrating sphere (Shimadzu UV-3600, Japan). Morphology images were taken on SEM (Hitachi S-4700, Japan) and TEM (FEI, America). Fluorescence microscopic images were taken on an inverted fluorescence microscope (EVOS, USA) at room temperature.

3. Results and discussion

3.1. XRD analysis of $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} particles

We synthesize a new persistent luminescent material $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} (BSEN) using sol-gel method. Fig. 1 shows the XRD patterns of $Ba_5Si_8O_{21}:0.02Eu^{2+}$ and $Ba_5Si_8O_{21}:0.02Eu^{2+}$, $0.04Nd^{3+}$. The main diffraction peaks are consistent with the monoclinic $Ba_5Si_8O_{21}$ (JCPDS Card No.83–1443, a = 32.675, b = 4.695, c = 13.894, β = 98.10°). There are two conceivable sites that Eu^{2+} ions (1.25 Å) and Nd^{3+} ions (1.109 Å) to be incorporated, one is Ba^{2+} (1.42 Å) sites and the other is Si^{4+} (0.42 Å) sites. Considering the effective ionic radii of cations with different coordination numbers [22], Eu^{2+} ions and Nd^{3+} ions prefer to occupy one of the $[BaO_8]$ site rather than $[Si_3O_8]$ sites. Moreover, no impurities are found in the range of the scanning scope, which reveals that Eu^{2+} ions and Nd^{3+} ions had been incorporated in the monoclinic lattice without distorting the matrix remarkably [16].

3.2. Morphologies of PVP/$Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} functional fiber

Fig. 2 shows the SEM and TEM images of BSEN particles and PVP/BSEN functional fibers. Fig. 2a shows the fine size distribution of BSEN particles after being sintered at 1250 °C with an average size of 0.45 μm. Fig. 2b shows that the functional fibers are randomly oriented and possess relatively uniform diameter. Because the process of electrospinning is complicated, every factor can affects the result more or less, including the orifice size, collector distance, flow rate and voltage. Therefore, it is hard to control the diameter of fibers precisely. The functional fibers would have evaporated liquid solvent since synthesized and shrinked a little which can be seen in Fig. 2c that some tiny wrinkles appeared on its appearance. Fig. 2d shows various shapes and sizes of BSEN particles are randomly distributed in the PVP fibers successfully and the functional fibers' diameter is approximately 2 μm.

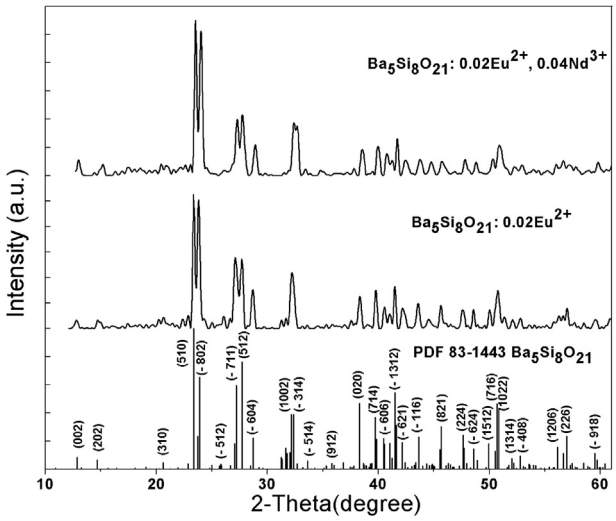

Fig. 1. XRD patterns of $Ba_5Si_8O_{21}:0.02Eu^{2+}$ and $Ba_5Si_8O_{21}:0.02Eu^{2+}$, $0.04Nd^{3+}$ particles. JCPDS Card No. 83–1443.

3.3. Photoluminescence of $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} particles and PVP/$Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} fiber

In this work, a series of persistent luminescent material $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} were synthesized by sol-gel method. All the samples show single monoclinic crystalline. For the purpose of confirming the best doping ratio of Eu/Nd, the univariate analysis of doping concentration of Nd^{3+} was conducted. As shown in Fig. 3a, the excitation spectra of BSEN particles cover a broad band from 250 nm to 450 nm with a maximum at 341 nm which correspond to the absorption spectra in Fig. 3c. Under the excitation of 341 nm, the BSEN particles exhibit an asymmetric broad band from 365 nm to 650 nm with a maximum at 489 nm which can be ascribed to the typical transition of the excited state ($^4f^5d^1$) to the ground state ($^4F_7$) configurations of Eu^{2+} ions [23]. The PL spectra reveal that the Eu^{3+} ions are reduced to Eu^{2+} because the typical emission peaks of Eu^{3+} around 580 nm, 590 nm, 612 nm, 650 nm and 698 nm due to the transition $^5D_0 \rightarrow {}^7F_{J\ (J=0,\ 1,\ 2,\ 3,\ 4)}$ are not found [24]. It is indicated that the emitter center is Eu^{2+} ions, and there are three nonequivalent Ba^{2+} sites in the matrix which can be substituted by the Eu^{2+} ions [16], therefore the asymmetric emission spectra are well-fitted by three Gaussian profiles (dark yellow dashed lined) in Fig. 3b.

Moreover, compared with the PL intensity of $Ba_5Si_8O_{21}:Eu^{2+}$, the PL intensity of $Ba_5Si_8O_{21}:Eu^{2+}$, Nd^{3+} is enhanced along with the increase of the concentration of Nd^{3+} at the beginning and reaches the highest intensity when the concentration of Nd^{3+} at 0.04 and then starts to decrease. The reason can be ascribed to the