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Effect of light conversion agent on luminous properties of a new down-converting material $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent

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Abstract: A new luminous material $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent that can emit red light in the darkness after being excited was fabricated by combining light conversion agent on to $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles through YsiX3. The morphology of the luminous materials was analyzed by scan electron microscopy (SEM). The emission behavior was evaluated by fluorescence spectrophotometric analysis and the results demonstrated that the emission spectra of samples had a redshift compared to $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and the emission intensity rose dramatically at first and then decreased when the ratio of light conversion agent doping was over 1.4 wt.%. And the emission color of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent was tuned from green ($SrAl_2O_4:Eu^{2+},Dy^{3+}$) to orange-red. Furthermore, the afterglow property was also investigated, and the results indicated that the afterglow brightness reached 6.5 cd/m^2, and as the light conversion agent concentration increased the brightness intensity decreased.

Keywords: $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent; emission; afterglow brightness; afterglow time; rare earths

$SrAl_2O_4:Eu^{2+},Dy^{3+}$ long lasting phosphors, which belong to photoluminescence materials, are kinds of energy-storing materials. The materials can absorb the visible light, store the energy, and gradually release the energy as visible light, which leads to a long persistent afterglow in the darkness[1,2]. The property results in a wide application of the materials in many fields, such as the dial plates of glow watch, warning signs, automobile, ship and other instruments, escape routes, and textiles, etc.[3–5].

In recent years, luminous fiber has attracted much attention since it was invented, because it has more excellent advantages, such as high efficiency, energy-saving, compactness, long operational lifetime and being environmentally friendly[6–9]. It absorbs ultraviolet or the visible light for ten minutes, and then can emit light continually for more than ten hours after removal of excitation resource. For that phosphors used to prepare the luminous fiber are mainly $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $SrMgSi_2O_7:Eu^{2+},Dy^{3+}$, which can emit green and blue light, lacking red ones compared with long-lasting phosphors of three primary colors. It is because that green and blue ones have much better afterglow performance than red phosphor[10,11]. For example, the afterglow time of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (emitting at 520 nm, green)[12] and $CaAl_2O_4:Eu^{2+},Nd^{3+}$ (emitting at 440 nm, blue)[13] is longer than 10 h, while that of $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ (emitting at 617 nm, red) is only 5 h, and the afterglow intensity is lower[14].

In our previous study[15,16], the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ luminous fiber that can emit red light at the wavelength of 600 nm was fabricated by doping red light conversion agent, because that there is an excellent overlap between excitation spectra of light conversion agent and emission spectra of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, which referred to the energy transfer from $SrAl_2O_4:Eu^{2+},Dy^{3+}$ to light conversion agent in the rare earth luminous fiber. When $SrAl_2O_4:Eu^{2+},Dy^{3+}$ was excited, it would emit brightness light; when exposed to light conversion agent in the fiber, part of the light energy was absorbed. For that most of them are converted to be released in the form of light, the electrons in the ground state inside the light conversion agent were stimulated, and transited to the excited state, then the light conversion agent could emit its characteristic red light after being excited. To the best of our knowledge, the new red emitting material can be fabricated by combining light conversion agent to $SrAl_2O_4:Eu^{2+},Dy^{3+}$, but the effect of light conversion agent on the luminous properties of the $SrAl_2O_4:Eu^{2+},Dy^{3+}$-YsiX3-light conversion agent was not clear so far.

In this work, we prepared several kinds of the luminescent material $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent with different concentrations of light conversion agent, and the effect of light conversion agent on the luminous properties of the $SrAl_2O_4:Eu^{2+},Dy^{3+}$-YsiX3-light

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conversion agent were investigated.

1 Experimental

1.1 Materials

$SrCO_3$ (AR), Al_2O_3 (GR), Eu_2O_3 (99.99%), Dy_2O_3 (99.9%), H_3BO_3 (AR), YsiX3 and light conversion agent were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

1.2 Preparation of $SrAl_2O_4:Eu^{2+},Dy^{3+}$

$SrAl_2O_4:Eu^{2+},Dy^{3+}$ was prepared by solid-state reaction using $SrCO_3$, Al_2O_3, H_3BO_3, Eu_2O_3 and Dy_2O_3 of analytical reagent (A.R.) grade as the starting materials. Appropriate amounts of raw materials were mixed and dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30 min in order to get a homogeneous mixture. Then the hybrid was dried at 100 ℃ for 24 h, ground in planetary high-energy ball mill and heated to high temperature 1350 ℃ for 4 h under a reducing atmosphere, then the sintered products were re-milled and sieved to get the desired samples.

1.3 Preparation of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent

$SrAl_2O_4:Eu^{2+},Dy^{3+}$ and ethanol were put into an evaporating dish, then added with nitrate. After that the YsiX3 was added half an hour later. Afterwards, light conversion agent was added into compound above in the case of stirring and heating constantly for 30 min, then $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and light conversion agent were combined. Finally the samples were dried at 100 ℃ for 30 min and the products were milled and sieved to get the desired samples. The structure of light conversion agent and the preparation process of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent are shown in Fig. 1.

The samples' ratio of doped light conversion agent to

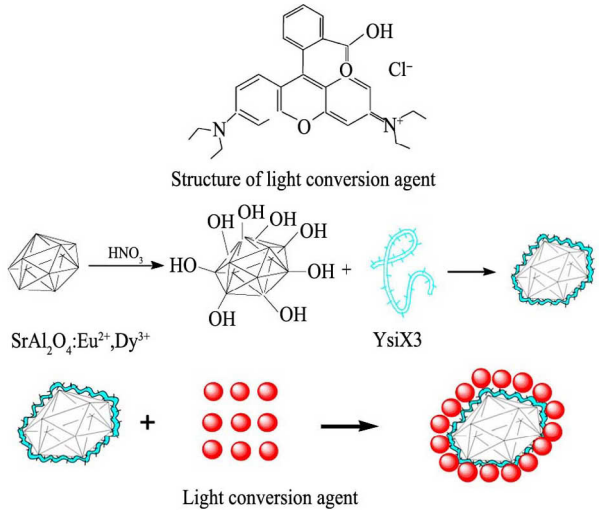

Fig. 1 Preparation process of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent

$SrAl_2O_4:Eu^{2+},Dy^{3+}$ is given as follows:

Light conversion agent doped samples: light conversion agent ($1^{\#}$: 1.2 wt.%, $2^{\#}$: 1.3 wt.%, $3^{\#}$: 1.4 wt.%, $4^{\#}$: 1.5 wt.%, $5^{\#}$: 0).

1.4 Scanning electron microscopy

In order to investigate the distribution of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent with different light conversion agent concentrations, the longitudinal structures of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent were observed using scanning electron microscopy (SEM) on an SEM microscope (Quanta 200, the Netherlands), at an accelerating voltage of 20 kV. All samples were dried and coated with gold before scanning.

1.5 X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu Kα radiation (λ=0.15406 nm) at a voltage of 40 kV and current of 30 mA. Samples were scanned over the range of diffraction angle 2θ=10°–70°, with a scan speed of 4(°)/min at room temperature.

1.6 Luminous properties

The emission spectra of all the samples were measured at room temperature with an excitation wavelength of 360 nm using a fluorescence spectrophotometer (HITACHI 650-60, Japan) with a Xe flash lamp as an excitation source; the slit was 1–5 nm in width; the excitation wavelength was from 200 to 800 nm and the scan speed was 120 nm/min. Chromaticity coordinates were tested and chromaticity diagrams were obtained by using a PR-650 SpectraScan colorimeter (Photo Research Inc.). Afterglow decay curves were tested using a PR-305 afterglow brightness tester (excitation illumination: 1000 lx, excitation time: 15 min). All measurements were carried out at room temperature. Before testing, samples must be placed in the darkness for more than 15 h to be certain that afterglow illumination has been attenuated completely.

2 Results and discussion

2.1 SEM analysis and the composition of samples

Fig. 2 shows the SEM images of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent with different light conversion agent concentrations. From this figure it can be found that particles of light conversion agent were smaller than that of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, therefore it can be completely coated on phosphor surface in the fabrication process of $SrAl_2O_4:Eu^{2+},Dy^{3+}$/light conversion agent.

Irregularly shaped particles with sharp edges are clear visible in Fig. 2(e), and it was smooth on the surface of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ as shown in Fig. 2. From Fig. 2(a–d), it is indicated that a light conversion agent was com-