Study on optical performance of red-emitting phosphor: $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ /light conversion agent for long-lasting luminous fibers

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Abstract

A novel luminous phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ /light conversion agent with both red luminescence characteristics and persistent luminescent performance were prepared. According to the intermediary color law, the color purity of red emission can be controlled by the doping ratio of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ composite luminous material. The anticipated luminescence properties could be realized precisely by adjusting the ratio. The microscopic morphology of the composite material, energy dispersive spectrometer, X-ray diffraction, FT-IR spectra, emission spectrum, CIE chromaticity diagrams and afterglow properties were examined. The brief outlines about some phenomena aspects and detailed physical descriptions as well as manuals were available. From the analyses of CIE chromaticity diagrams and afterglow properties, the doping ratio of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ can influence afterglow brightness and red emission purity. The samples show great optical performance.

1. Introduction

The rare earth luminous phosphor is a kind of environmentally friendly and sustainable self-luminous functional material, which can absorb the ultraviolet for 10 min and then emit light continuously for more than 10 h. Since scientists founded that the rare earth can activated alkaline earth metal aluminate in 1990s, it has been attracting a lot of interests and further research [1]. The rare earth co-doped long-lasting phosphors play important roles in the fields of home decorations, children toys, emergency signs, the in-vivo medical imaging, and many kinds of applied fields because it exhibits excellent photoresistance and a very bright afterglow [2][3][4]. As for Eu^{2+} and Dy^{3+} co-doped luminous phosphor, it's characteristics due to the level's transition of Eu ions. After excitation of Eu^{2+} from $4f^7$ to $4f^65d^1$, a trap level released by Eu^{2+} is captured by Dy^{3+} and forming the afterglow phenomenon when electrons escape from the trap level [5].

In recent years, there has been an increasing interest in the photochromic of the fiber which determines the application of the fiber. Throughout this paper, the term 'photochromic' will refers to the color of light emitted by the fiber itself after excited by ultraviolet light in a non-illuminated environment. As for enrich the color diversity of luminous fiber, it is very important to study the red-emitting luminous fiber. Researchers tried a lot to solve this problem. For examples, researchers tried to coat red emitting color convert on the surface of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ or use $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$ as the luminescent centre, but it's difficult to satisfy requirement of both afterglow and photochromic properties [6][7][8]. While some studies have carried out on the photochromic of the fiber, further research is still required to obtain full-color emission and stable materials. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ are two kinds of energy-storing materials with excellent optical performance. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, which can emit at 525 nm (green light), has more than 30h's afterglow time; $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$, which can emit at 475 nm (blue light), performs water resisting property and chemical stability. Light conversion agent is a kind of

oxygen anthracene derivative [9]. The red emission that has the broadest excitation band could be excited about from 200 to 550 nm which means that combining rare earth luminescent materials and the light conversion agent can achieve the purpose of red emission.

In the previous work, we founded that $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ can transmit energy to the light conversion agent and convert it into red light emission [10][11], but the light's purity can't meet the need of the full-color emission fiber. Consequently, in this paper, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+} / \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+} /$ light conversion agent was prepared. On the basis of intermediary color law of the Grsassmann Color Law, which means that mixing two non-complementary colors will produce an intermediate color between those two colors, a novel red-emitting luminous material were developed. Figure 1 shows the theory of the Grsassmann color law. And the effect of the doping ratio between the $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ on the luminous performance were investigated.

2. Experiment

2.1 Materials

The materials used for the synthesis were Al_2O_3 (GR), SrCO_3 (AR), MgO (AR), SiO_2 (AR), Eu_2O_3 (99.99%), Dy_2O_3 (99.99%), H_3BO_3 (AR), ethanol (AR), light conversion agent (Rhodamine B) and silane coupling agent (KH560) from Sinopharm Chemical Reagent Co., Ltd., China.

2.2 Preparation of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$

$\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ was prepared by high-temperature solid-state reaction that is the most common method to synthesis luminescent materials. After weighting out an appropriate amount of Al_2O_3 , SrCO_3 , Eu_2O_3 , Dy_2O_3 , and H_3BO_3 , the raw materials were finely powdered in an agate mortar. And then dissolve the materials to proper amount of ethanol for mixing better in ultrasonic. Until drying all the ethanol of the sample, put the raw materials into the high temperature tubular furnace of 1400 °C for 3 h in a weakly reducing atmosphere. The sintered products were re-milled and sieved to get the desired samples.

2.3 Preparation of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$

$\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ was synthesized using the almost same method that was detailed for $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$, using high-temperature solid-state reaction to preparation. Firstly SrCO_3 , MgO , SiO_2 , Eu_2O_3 , Dy_2O_3 , and H_3BO_3 were weighted and grinded to uniform particles in an agate mortar. After dissolving the samples into suitable ethanol, the homogeneous powder was obtained by using ultrasonic technique. Secondly, the materials were heated in a high temperature tubular furnace of 1400 °C for 3 h in a weakly reducing atmosphere. Finally, the sintered products were re-milled and sieved to get the desired samples after the reactor was cooled to a room temperature.

2.4 Preparation of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$

$\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$ was prepared by heterogeneous precipitation method. $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ were put into a beaker with an appropriate amount of ethanol in different ratio. Subsequently ethanol, light conversion agent (5 wt.%) and KH560 (1.25 wt.%) were added to the materials and then the mixture was stirring for 10 min before putting it in ultrasonic. After agitating the samples of 70 °C for 1h in an enclosed environment, the seal was removed in order to evaporated dry the ethanol. Finally, the sample was dried at 70 °C and it was grinded adequately and sieved to get the desired samples. Figure 2 shows the preparation process of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$. At the same time, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$ were prepared as the comparison sample in the same proportion.

$\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ doped samples: $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ in $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$ (10 wt.%, 30 wt.%, 50 wt.%, 70 wt.%, 90 wt.%).

2.4 Instrumental measurements

2.4.1 Scanning electron microscopy (SEM)

In order to see the coating and dispersion effect of the light conversion agent on the surface of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ accurately, the micro-morphology of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$ was characterized on a SEM (Quanta 200, the Netherlands). All samples were dried and coated with a thin conductive layer of gold and observed at an accelerating voltage of 15 kV.

2.4.2 Energy dispersive spectrometer (EDS)

EDS was used to qualitatively analyze the element distribution in the microscopic region of the composite material on Hitachi SU1510.

2.4.3 X-ray diffraction (XRD)

XRD measurement was tested for confirming whether the mixing of the three materials influence the crystal structure of the composite material. XRD patterns were recorded on a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 0.15406$ nm) at a voltage of 40 kV and current of 30 mA. The scans versus diffraction angle (2θ) were carried out in the range of 10–70°, with a scan speed of 2°/min at room temperature.

2.4.4 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra were examined using the Nicolet IS10. The scanning interval of testing conditions was from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 2 cm^{-1} . Before the test, all the sample and KBr were mixed and ground, and then tableted together.

2.4.5 Luminous properties

The fluorescence spectrophotometer (F-4600 FL Spectrophotometer) with the xenon lamp which set an excitation source at 365 nm excitation light and the slit at 3nm in width was used to test the CIE chromaticity diagrams and afterglow properties of the samples. The afterglow properties of the samples were examined by PR305 afterglow brightness tester, with UV light at 1000 lx for 15 min.

3. Results And Discussion

3.1 Morphology analysis

The morphologies of the before and after being coating with light conversion agent were observed by SEM. Figures 3(a)- (b) show the material $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ /light conversion agent with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ doped 50 wt.% after being ground with an agate mortar, while Figs. 3(c)-(e) show the control samples uncoated by light conversion agent. As shown in Figs. 3(c)- (e), the prepared $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ have different particle sizes, and most of the particles have edges and corners. From Figs. 3(d)- (e), we can see that the crystal structure of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ is monoclinic, while for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ is tetragonal. Compared with $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ has a smaller particle size, a smoother surface and fewer edges and corners. Since both particle size is distributed between 5–20 μm uniformly, it can meet the spinning needs of preparing luminous fiber. There are a few particles on the surface of the two materials, which are debris generated during the grinding process after the calcination is completed. The surface of luminescent material becomes rough after coating light conversion agent. This is because silane coupling agent acts as a molecular bridge to tightly coat the light conversion agent on the surface of the material. The hydroxy group formed after the hydrolysis of the alkoxy group on the surface of the silane coupling agent can condense with the hydroxy group on the surface of the inorganic material. It is often used to adjust the interfacial effect of organic and inorganic materials [11]. Therefore, a coating of small particles was formed on the surface which was dense and distributed evenly. As the roughness increases, the particle size of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ /light conversion agent also increases. The uniform attachment of light conversion agent to $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ can effectively transfer energy between $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ and light conversion agent, which is helpful to improve the emission efficiency of red light.

3.2 Structural analysis

Since the brightness and color of the luminous fiber are determined by the activator (Eu^{2+} in this study)

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js arth luminescent material has a great influence

on its luminescence performance [12]. In order to explore whether the addition of light conversion agent will affect the phase structure of luminescent materials, the XRD patterns of the rare earth luminescent materials are illustrated in Fig. 4(a) and Fig. 4(b) shows the XRD patterns of all the samples. The XRD profile indicates that the crystal structure of the sample was mainly $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$. It can be seen that the diffraction peaks mainly at 28.386° , 29.275° , and 29.922° which were assigned to the standard card of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ and at 28.231° and 30.403° which were consistent with $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$ as in the JCPDS Cards NO. 34-0379 and NO. 75-1736 respectively. As shown in Fig. 4, it can be found that the diffraction peak of the samples is well with the different appending proportion of light conversion agent. No extra peaks are observed. The lattice parameters of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$ are listed in Table 1. In addition, with the content of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ increase, the characteristic peak of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ enhanced and the characteristic peak of $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$ weaken. All the curves have the same peak position, which demonstrates that the addition of light conversion agent wasn't changing matrix lattice structure, that means $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ / $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$ / light conversion agent keeping luminescence properties. The coating process of the luminescent materials by the light conversion agent did not damage the luminescent properties of the fibers. The EDS spectra indicated that O, Mg, Al, Sr, Si, and rare earth elements Eu and Dy were presented. The presence of characteristic elements of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{: Eu}^{2+}, \text{Dy}^{3+}$ in the sample shows that the two materials have been successfully combined together.

Table 1
Lattice parameters of rare earth luminescent materials

Materials	Cell size (nm)			Crystal form	
	a	b	c	Crystal system	Bravais lattice
SrAl_2O_4	8.442	8.822	5.161	Monoclinic	Primitive
$\text{Sr}_2\text{MgSi}_2\text{O}_7$	7.996	7.996	5.152	Tetragonal	Primitive

3.3 FT-IR spectra analysis

The FT-IR spectra of light conversion agent and rare earth luminescent materials is shown in Fig. 5. The broaden absorption band of $3000\text{--}3500\text{ cm}^{-1}$ for all the samples is assigned to the symmetric stretching vibration of hydration hydroxyl groups, because the samples absorb the water vapor in the moisture air[13]. For light conversion agent, the peak at 1703 cm^{-1} and 1640 cm^{-1} are attributed to $\text{C}=\text{O}$ and $\text{C}=\text{N}$ stretching in ester carbonyl group respectively, and the banding peak at 715 cm^{-1} is attributed to C-H

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of $\text{SrAl}_2\text{O}_4\text{: Eu}^{2+}, \text{Dy}^{3+}$, it present that peak at

844 cm^{-1} and 778 cm^{-1} belong to Al-O and Sr-O stretching vibration peak, besides the peak band at 1483 cm^{-1} is present symmetric stretching vibrations of the Sr-O-Al bonds[14]. As for $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , the banding peak at 565 cm^{-1} is due to the bending vibration of Si-O and the other obvious peak at 474 cm^{-1} correspond to the stretching vibration from Mg-O[15]. The FT-IR spectra of SrAl_2O_4 : Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} are consistent with the standard map. In the spectra of composite particle, the peak band at 1644 cm^{-1} , 1485 cm^{-1} , 474 cm^{-1} and 563 cm^{-1} based on the stretching vibrations of C = N, Sr-O-Al, Mg-O and bending vibration of Si-O, which insured the composite particle is combined by light conversion agent, SrAl_2O_4 : Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} .

3.4 Photoluminescence analysis

In order to determine the effect of light conversion agent on red-emitting property of SrAl_2O_4 : Eu^{2+} , Dy^{3+} / $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} composite luminous materials, the emission spectra of SrAl_2O_4 : Eu^{2+} , Dy^{3+} , $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , light conversion agent, and composite luminous materials were shown in Fig. 5. As can be seen from Fig. 6(a), the emission peak of light conversion agent, SrAl_2O_4 : Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} were located at 610, 525, and 475 nm, respectively, corresponding to the red, green and blue photochromic area. Besides, the light conversion agent has a strong excitation band from 400 to 570 nm. Therefore, the light conversion agent can be greatly excited by SrAl_2O_4 : Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} after excited. But the bioluminescence of the light conversion agent belongs to instant luminescence, which means it has very short luminescence time. The purpose of red emission can be achieved by energy transmit from rare earth materials to light conversion agent. Hence, it's feasible for using rare earth materials to excite light conversion agent for long-persistent red emission.

Figure 6 depicts the emission spectra with various content of SrAl_2O_4 : Eu^{2+} , Dy^{3+} in SrAl_2O_4 : Eu^{2+} , Dy^{3+} , $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , light conversion agent. We can see that there are two emission peaks in the spectrum occurring at 450–550 nm and 604 nm, which means photochromic property of luminescent power was composed of SrAl_2O_4 : Eu^{2+} , Dy^{3+} , $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} and light conversion agent. The emission peak at 450–550 nm is generated by the ionic transition in the rare earth luminescent material, indicating that mixing the two luminescent materials and the light conversion agent does not change the crystal structure of the material. When irradiated by excitation light, Eu^{2+} ions in SrAl_2O_4 : Eu^{2+} , Dy^{3+} / $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} emerged energy level transitions, from $4f^65d^1$ to $4f^7$. With the increment of the SrAl_2O_4 : Eu^{2+} , Dy^{3+} , the emission peak has right-shift in the wavelength range of 450–550 nm and the peak are very weak comparing with the peak at 604 nm, whilst the spectra relative intensity increased gradually at 604 nm. This phenomenon indicated that transfer efficiency between SrAl_2O_4 : Eu^{2+} , Dy^{3+} and light conversion agent was more efficacious than $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} . Because the smaller particle sizes of SrAl_2O_4 : Eu^{2+} , Dy^{3+} had a higher specific surface area to contact more light conversion agent molecule, and it indicated that the light conversion agent was excited better by the luminous energy that

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js mission peak in the range of 450–550 nm that

was weakened reflected that the fluorescence resonance energy transfer (FRET) could have occurred. Rare earth luminescent materials are used as luminescent donors, and part of the energy is transferred from the rare earth luminescent materials to the light conversion agent, resulting in the attenuation of the donor's autofluorescence intensity[16]. Meanwhile, the difference in the ratio of luminescent materials has no effect on the degree of red shift of the light conversion agent, indicating that it's decided by addition of light conversion agent.

3.5 Afterglow properties analysis

Figure 7 shows the afterglow properties of SrAl₂O₄: Eu²⁺, Dy³⁺ + doped of SrAl₂O₄: Eu²⁺, Dy³⁺/Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺/light conversion agent luminous materials. The samples were irradiated by UV light for 15 min, after that they were moved into the brightness meter. The initial afterglow brightness (at 10 s) contrast curves of the five samples are shown in the inset picture of Fig. 7. The decay curves have been calculated by fitting the decay data using the following equation:

$$I = A_1 \times \exp\left(-\frac{t}{\lambda_1}\right) + A_2 \exp\left(-\frac{t}{\lambda_2}\right) + A_3 \exp\left(-\frac{t}{\lambda_3}\right) + R \quad (1)$$

In this attenuation formula, I stand for afterglow intensity; t stand for the time; R stand for initial brightness; A_1 , A_2 , and A_3 are constants; λ_1 , λ_2 and λ_3 represent the decay time of three different periods of exponential decay for the exponential components which could be obtained by using Origin 8.0. The attenuation of afterglow is divided into three stages, which are the initial fast attenuation stage, the subsequent slow attenuation stage and the final afterglow brightness stabilized stage. From Fig. 7, it can be observed that the attenuation of the afterglow curve conforms to the exponential decay law. The existence of light conversion agent will affect the partial afterglow performance of the material. This is because the light agent will be coated on the surface of the composite luminous powder and part of the excited light will be absorbed and reflected by the light conversion agent. In addition, the light conversion agent will absorb some of the energy emitted by SrAl₂O₄: Eu²⁺, Dy³⁺ and Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺, resulting in a loss of energy and afterglow performance.

Besides, as it shown in Fig. 7, with the increase of SrAl₂O₄: Eu²⁺, Dy³⁺ percentage, the initial luminance of excited material also increased. The initial brightness of all the samples with different SrAl₂O₄: Eu²⁺, Dy³⁺ additive ratios could more than 10 mcd/m² except the sample 10%. The decay curves of SrAl₂O₄: Eu²⁺, Dy³⁺/Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺/light conversion agent is a composite of the afterglow properties of SrAl₂O₄: Eu²⁺, Dy³⁺, Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ and light conversion agent. It revealed that the afterglow performance of composite luminescent materials is positively correlated with SrAl₂O₄: Eu²⁺, Dy³⁺ concentration. It's because that the afterglow properties of rare earth materials are determined by their lattice structure [17]. Compared with Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺, the number of electrons in the energy level transition of SrAl₂O₄: Eu²⁺, Dy³⁺ are more than Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ when excited by the light. Accordingly, the afterglow brightness and afterglow time of SrAl₂O₄: Eu²⁺, Dy³⁺ is better than Sr₂MgSi₂O₇:

Eu^{2+} , Dy^{3+} . Consequently, the higher the $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ content, the better the afterglow performance in $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$. From the analyses above, it is well known that the composite luminescent material which have a great afterglow performance and can emit high-brightness and long-lasting light in a dark environment is of value in actual practice. The afterglow performance can be changed by changing the ratio of material components.

3.6 Fluorescence characteristics

The color coordinates and color purity are depicted on Fig. 8. Besides, the chromaticity diagram is partitioned by color. The term “purity” for CIE 1931 chromaticity diagram will refers to how close the color of the sample is to the spectral color of the same dominant wavelength. The chromaticity diagram needs to be partitioned because only the purity calculation in a same color area is meaningful. Figure 8 inset picture shows the calculation method of color purity. In the chromaticity diagram, O is the CIE1931 standard light source point, which is equivalent to the light color of the noon sunlight; R_1 is the target point; R_2 is the intersection point of extending O and R_1 outward to the spectral trajectory; M, N are the intersection of the triangle area formed by points O, R_1 and R_2 . The color purity of R_1 can be calculated as follows. And the color parameters of the samples are listed in the Table 2.

$$P = OM / ON = (X - X_0) / (X_2 - X_0)$$

2

According to the Fig. 8 above, we can see that comparison samples $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$ was at ORANGE area, and meanwhile $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$ was at RED area. All the samples of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$ were at the area between $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}/ \text{light conversion agent}$. When adding less $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$, the samples photochromic shift towards cool-tone; When the proportion of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ increases, the samples photochromic are closer to the warm-tone on the contrast. This is because color is the effect of different absorption, reflection or transmission caused by light acting on an object. The light color of the luminous material we see is a mixture of different light colors through the additive color principle. Owing to the difference in the amount of the two light color materials added, different samples showed different light colors. The sample 10%, 30% and 50% are in the RED area, and others are in the ORANGE area in the meanwhile. Therefore, the purity of the samples at RED area were calculated as listed in Table 2. We can find that at RED area, with the increase of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ proportion, the purity of the samples will promote at RED area. From 3.3, It can be seen that the difference in the ratio of luminescent materials has no effect on the degree of red shift of the light conversion agent. However, through the analysis of sample purity in Fig. 8, changing the $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ ratio will not change the degree of red shift of the sample emission spectrum, but it will affect the red-light emission purity. The higher the proportion of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ added, the higher the purity of the red light emitted after excitation.

Table 2 Color parameters of the rare earth luminescent materials

Samples	x	y	Photochromic classification	Purity (%)
10%	0.56733	0.33519	RED	67.80%
30%	0.55161	0.33763	RED	70.78%
50%	0.57670	0.35254	RED	79.47%
70%	0.56169	0.36386	ORANGE	/
90%	0.58195	0.37635	ORANGE	/
SrAl ₂ O ₄ : Eu ²⁺ , Dy ³⁺ / light conversion agent	0.5734	0.3954	ORANGE	/
Sr ₂ MgSi ₂ O ₇ :Eu ²⁺ , Dy ³⁺ / light conversion agent	0.5543	0.3146	RED	55.67%

4. Conclusion

Herein, a novel red-emitting luminous material was prepared. On the basis of intermediary color law of the Grsassmann color law, two different photochromic luminescent materials and light conversion agent were mixed to obtain a red emission powder, which has both red luminescence characteristics and persistent luminescent performance. On the micro scale, the light conversion agent was completely coated on the phosphor that mixing by SrAl₂O₄: Eu²⁺, Dy³⁺ and Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ which has dense and distributed evenly coating layer. By utilizing the purplish red of Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺/light conversion agent and the orange red of SrAl₂O₄: Eu²⁺, Dy³⁺/light conversion agent, the red emission powder was obtained. The afterglow performance was greatly influence by SrAl₂O₄: Eu²⁺, Dy³⁺. When the SrAl₂O₄: Eu²⁺, Dy³⁺ doped ratio is 50%, SrAl₂O₄: Eu²⁺, Dy³⁺/ Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺/light conversion agent has a red emission purity at 79.47%.

Declarations

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Figures

Figure 1

The theory of the Grassmann color law.

Figure 2

Preparation process of SrAl₂O₄: Eu²⁺, Dy³⁺/Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺/light conversion agent.

Figure 3

SEM pictures of (a)(b) 50% $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$; (c)(d) (e) 50% $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$

Figure 4

XRD patterns of (a) the raw materials of composite luminescent material; (b) all the samples of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$ /light conversion agent in different adding proportion. Energy dispersive spectrum of (c) 50% $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$ /light conversion agent

Figure 5

FT-IR spectra of the samples of light conversion agent, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ and composite particle

Figure 6

Emission spectra of (a) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$, and light conversion agent; (b) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}/\text{light conversion agent}$

Figure 7

Afterglow decay curves of SrAl₂O₄: Eu²⁺, Dy³⁺ / Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ / light conversion agent with the inset showing the initial brightness of samples at 10 s.