

Preparation and luminescence properties of a new material $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ /red organic fluorescent pigment

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Luminescence composite was fabricated by combining red organic fluorescent pigment on to $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ particles. X-ray diffraction (XRD) patterns, PR-305 afterglow brightness tester and Fluorescence spectrophotometer (HITACHI 650-60, Japan) as well as PR-650 Spectra Scan colorimetric were used to characterize the properties of the luminescent composite. The emission behavior was evaluated by Fluorescence Spectrophotometric analysis and the results demonstrated that the emission spectra of samples had a red shift under visible light ($\lambda=520$ nm) excitation. The emission intensity of the red organic fluorescent pigment-doped hybrid increased with the increase of red organic fluorescent pigment concentration, but the afterglow brightness reduced. Furthermore, the emission colors of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ /red organic fluorescent pigment also can be tuned from yellow to orange-red easily by changing the doping concentrations(N) of red organic fluorescent pigment.

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1. Introduction

The long afterglow phosphors Eu^{2+} and Dy^{3+} co-doped aluminates have been greatly improved since 1990s in luminescent brightness, long lasting phosphorescence properties and stability, and it is applied widely in night display material, safety and environmental protection, traffic, decorating material, etc. Many scholars have focused on developing the long lasting luminescent materials [1-4]. The afterglow time of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ can be effectively prolonged by doping Dy^{3+} ion [5]. However, the color of the emitting light is rather monotonous with its emission peak mainly around 520 nm [6].

Recently, much attention has been paid to the red-color long afterglow materials, which became one of the hot and difficult spots in the luminescence field, since the low glow brightness and short afterglow time [7-8]. Many progresses have been made through doping different rare earth ions. Wang, et al [9] reported a red long-lasting phosphor which was mainly consisted with $\text{MgSiO}_3:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Mn}^{2+}$. Its red emission peak at 660 nm could last over 4 h after UV irradiation. Lin et al, made a further study on luminescence properties of MgSiO_3 system $\text{Mn}^{2+}, \text{Dy}^{3+}$ doped and samples co-doped with Dy^{3+} and Mn^{2+} [10], but its luminescence properties were really poor compared with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ [6].

The organic fluorescent pigments can absorb light energy in the sunlight, and the energy absorbed was

disseminated in the form of low-frequency visible fluorescence instead of heat. This emission light and the normal of the reflected light color were combined to form brilliant colors [11].

In this work, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was prepared by means of solid-state reaction, and then it was combined with red organic fluorescent pigment. The composite's luminescence properties and the effect of fluorescent pigments concentration on the emission properties were investigated.

2. Experimental

$\text{SrCO}_3, \text{Al}_2\text{O}_3, \text{H}_3\text{BO}_3, \text{Eu}_2\text{O}_3$ and Dy_2O_3 were employed as raw materials for the solid-state reaction. These five materials were mixed in a molar ratio of Sr : Al : Eu : Dy : B=1:2:0.01:0.02:0.2. The raw materials were ground together in a ball mill to give a homogeneous mixture, and the resulting powder was annealed at 1400 °C for 4 h in the carbon reducing atmosphere to give the strontium aluminate complex $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. The sample $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was equally divided into eleven parts, each part was put into an evaporating dish and then adding octadecyl isocyanate into it. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and octadecyl isocyanate were maintained at 1:1 Afterwards, red organic fluorescent pigment was added into each evaporating dish in the case of stirring and heating constantly for 10 min($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and red

organic fluorescent pigment were combined by octadecyl isocyanate at high temperature. at the same time, octadecyl isocyanate crosslinked. SrAl₂O₄: Eu²⁺, Dy³⁺ and red organic fluorescent pigment were coated. For octadecyl isocyanate itself is transparent, which would not influence the luminescent properties of SrAl₂O₄: Eu²⁺,Dy³⁺/red organic fluorescent pigment), the molar ratio of red organic fluorescent pigment as a dopant was of 0,0.2 at.%,0.5 at.%,0.8 at.%,1.0 at.%,1.2 at.%,1.5 at.%, 2.0 at.%,4.0 at.%,6.0 at.%,8.0 at.% with respect to SrAl₂O₄: Eu²⁺,Dy³⁺, finally the samples were dried at 100 °C for 30 min and the products were milled and sieved to get the desired samples. Fig. 1 shows molecular structure of red organic fluorescent pigment and the preparation process of SrAl₂O₄:Eu²⁺, Dy³⁺/ red organic fluorescent pigment is shown in Fig. 2.

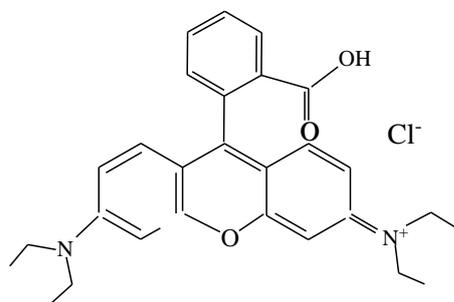


Fig. 1. Molecular structure of red organic fluorescent pigment.

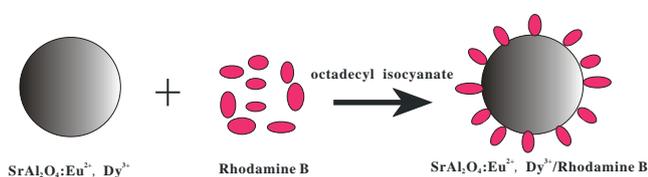


Fig. 2. Preparation of SrAl₂O₄:Eu²⁺, Dy³⁺/ red organic fluorescent pigment.

Characterization

X-ray diffraction

X-ray diffraction (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. Samples were scanned over the range of diffraction angle $2\theta = 10\text{--}70^\circ$, with a scan speed of $4^\circ/\text{min}$ at room temperature.

Luminous properties

The excitation and emission spectra of all the samples were performed at room temperature with an emission wavelength of 605 nm and excitation wavelength of 520 nm using a fluorescence spectrophotometer (HITACHI

650-60, Japan) with a Xe flash lamp as an excitation source; the slit was 1 nm-5 nm in width; the excitation wavelength was from 200 nm to 600 nm, the emission wavelength was from 200nm to 800 nm and the scan speed was 120 nm/min. Chromaticity diagrams were obtained using a PR-650 Spectra Scan colorimeter (Photo Research Inc.) and the excitation wavelength is 365 nm. Afterglow decay curves were tested using PR-305 afterglow brightness tester (excitation illumination: 1000 lx, excitation time: 15 min, excitation wavelength is 365 nm). All measurements were carried out at room temperature. Before the testing, samples must be placed in the darkness for more than 15 h to be certain that afterglow illumination has been attenuated completely.

3. Results and discussion

3.1 XRD analysis

From the research, we got the knowledge that the lattice constants of pure monoclinic phase diffraction peaks of SrAl₂O₄:Eu²⁺, Dy³⁺/Rhodamine B were $a = 8.442$ Å, $b = 8.822$ Å, $c = 5.160$ Å, and $\beta = 93.415$ Å and the samples were all low-temperature monoclinic phase (α -phase) in contrast to JCSDS date file (No. 34-0379), which were the characteristic diffraction peaks of SrAl₂O₄. Except this, no other peak was identified in the pattern. From the analysis above, it can be seen that the complex manufacturing process and organic fluorescent pigment did not destroy the phase of SrAl₂O₄:Eu²⁺, Dy³⁺, which ensured the luminescent properties of SrAl₂O₄:Eu²⁺,Dy³⁺.

3.2 Emission spectra

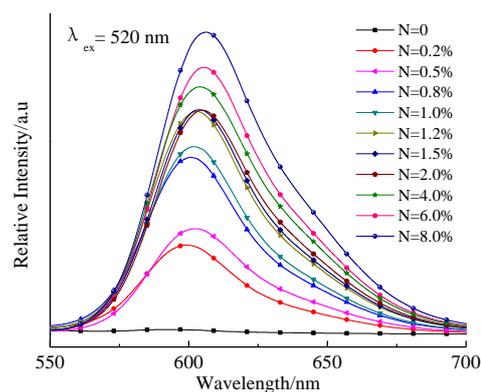


Fig. 3. Emission spectra of SrAl₂O₄:Eu²⁺, Dy³⁺/ red organic fluorescent pigment.

The emission spectra of the mixture doping with different concentration of red organic fluorescent pigment were observed by HITACHI 650-60 and shown in Fig. 3. The results observed from Fig. 3 demonstrated that the

shape of the emission spectra remained unchanged as red organic fluorescent pigment concentration increased, and all samples displayed their main emission peaks around 595-605 nm. It is also found that the emission intensity increased gradually as the concentration of red organic fluorescent pigment increased. Additionally, a red shift for the emission band can be observed from low red organic fluorescent pigment concentration to high red organic fluorescent pigment concentration (0.2% to 8.0%), and the emission peak of the mixture moved to longer emission wavelength (595 nm to 605 nm), which presumably attributed to the $S_2, S_1 \rightarrow S_0$ transition of Rhodamine B. This may be caused by two factors. First, it may be due to the increasing of red organic fluorescent pigment concentration, which leads to interactions between neighboring molecules, lowers their excited state energy and produces a red shift in the spectra. Secondly, a self absorption process. When the concentration of the solution was excessively large, part of red organic fluorescent pigment became aggregation state, forming dimer or trimer. The first electronic (due to the first excited electronic singlet state's energy of dimer or trimer) was lower than that of the monomer, therefore the emission wavelength red shift [12]. So with the increase of red organic fluorescent pigment concentration, the self-absorption of red organic fluorescent pigment will increase, which leads to the red shift of the emission band.

3.3 Analysis of energy transfer from $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ to red organic fluorescent pigment

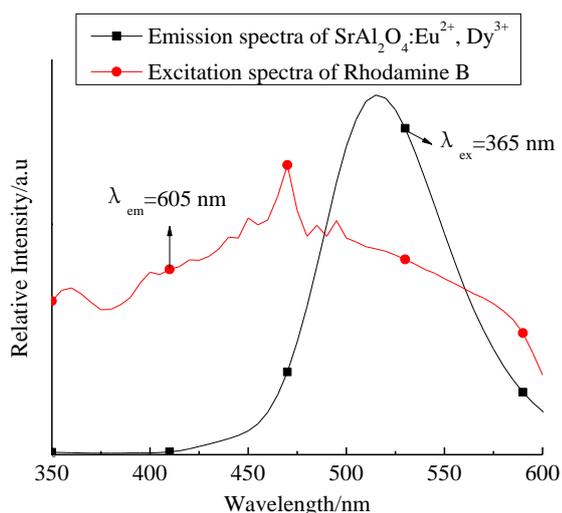


Fig. 4. The excitation spectra of red organic fluorescent pigment and the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

Fig. 4 shows the excitation spectra of red organic fluorescent pigment and the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. From Fig. 4 it can be seen that the

excitation spectra presents broad band of continuous wavelength, which shows a wide range from ultraviolet to visible light between 350 nm and 600 nm, and the main excitation peak was located at about 470 nm. According to Dexter energy transfer theory, effective energy transfer could happen in case that the emission spectra of sensitization ion and the excitation spectra of activation ion must have overlaps. From Fig. 4 it can be seen that there was a good overlap between the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ around 460~580nm and excitation spectra of red organic fluorescent pigment around 350~600 nm. From the analysis above we knew that there was energy transferred from $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ to red organic fluorescent pigment.

Literature reported that molecules of organic fluorescent pigments usually stay in the lowest energy state (S_0), and the electrons transited to a higher energy orbit in an excited state (S_1 or S_2) when absorbing ultraviolet and visible energy, then it will transit back to the minimum vibration level of molecular's lowest excited state (S_1). Finally they recurred radiative transition to the ground state, and in which state electrons span in pairs accompanied by the generation of fluorescence [12]. In the process of emitting, the electrons of Rhodamine B transited to a higher energy orbit in an excited state (S_1) and part of them in an excited state (S_2) after absorbing energy and disseminated by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, then they transited back to lowest energy state (S_0) due to high and unstable energy, and the energy was disseminated in the form of low-frequency visible fluorescence.

3.4 Chromatography analysis

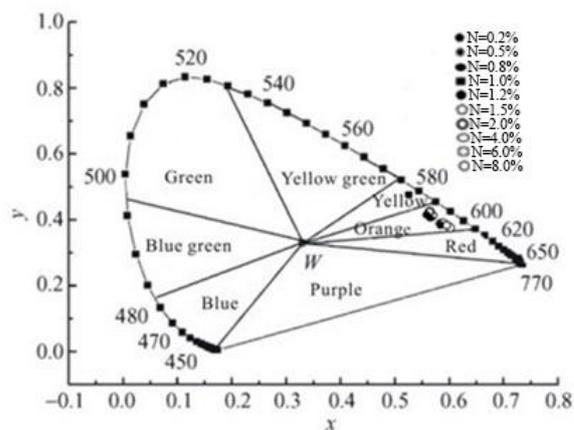


Fig. 5. Location of samples on CIE 1931 chromaticity.

Almost all samples' colors were located in the orange-red area that the human eye has the greatest sensitivity, which we can see from Fig. 5. However, there was a significant difference in the color rendering index between them. The emission color was closer to red color and color purities were similar as the doping of red organic

fluorescent pigment increased. From the analysis mentioned above, we can refer to the conclusion that it could make the emission spectra of SrAl₂O₄:Eu²⁺, Dy³⁺ red shift when it was combined with red organic fluorescent pigment.

3.5 Afterglow curve

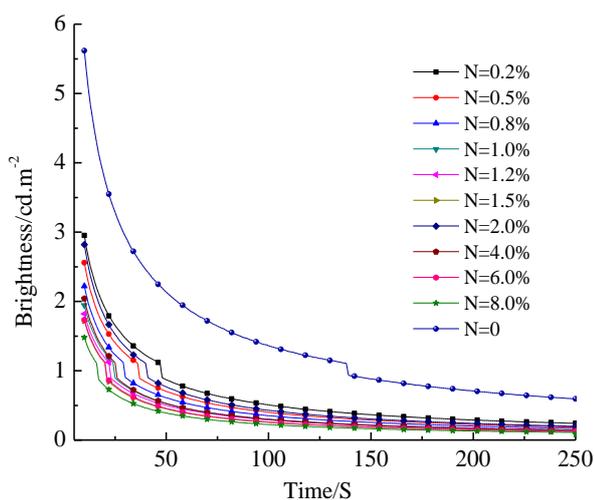


Fig. 6. Afterglow curve of SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment.

Fig. 6 shows the afterglow decay curves of SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment in which the concentration of red organic fluorescent pigment were from 0 to 8%. From Fig. 6 it can be seen that the principle of afterglow decay was similar to each other containing a fast and slow decay. However, the afterglow brightness and time were different from one to another prepared with different red organic fluorescent pigment concentration. The brightness of SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment doping with different concentrations of organic fluorescent pigments (N = 0.2%, 0.5%, 0.8%, 1.0%, 1.2%, 1.5%, 2.0%, 4.0%, 6.0%, 8.0%) declined significantly than that SrAl₂O₄:Eu²⁺, Dy³⁺, and as the concentration of organic fluorescent pigments increased, the afterglow brightness of the composite decreased gradually. From the analysis above we knew that a part of the organic fluorescent pigments covered on the surface of SrAl₂O₄:Eu²⁺, Dy³⁺, and part of the exciting light energy was absorbed and reflected by pigments. On the other hand, part of the light energy emitting by phosphors was absorbed and reflected by pigments to some extent. As the ratio of pigments increased, the brightness decreased.

From the description above, it can be concluded that the afterglow brightness of SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment was composed of two parts. One was the brightness in the 520 nm wavelength, which emitted by SrAl₂O₄:Eu²⁺, Dy³⁺. The other was the light

formed by the emitting light of pigments, the wavelength of which was shifted to red because of the selective absorption of the pigments. And as the concentration of red organic fluorescent pigment increased, the energy transferred from SrAl₂O₄:Eu²⁺, Dy³⁺ to red organic fluorescent pigment increased and the light energy reflected by pigments became more and more, which led to lower afterglow brightness

4. Conclusions

Samples (SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment) can emit red light were synthesized and their luminescence properties were characterized. Excitation, emission spectra and chromatography analysis suggested that it had a wide range of excitation wavelength from ultraviolet to visible light between 350 nm and 600 nm. All samples displayed their main emission peak around 600 nm and color of emission by SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment were located in the orange-red area. The emission intensity increased gradually as the concentration of red organic fluorescent pigment increased, and the emission peak moved to longer emission wavelength from 595 nm to 605 nm. Results from PR-305 afterglow brightness tester demonstrated that the afterglow brightness of SrAl₂O₄:Eu²⁺, Dy³⁺/red organic fluorescent pigment declined significantly than that SrAl₂O₄:Eu²⁺, Dy³⁺, and as the concentration of organic fluorescent pigments increased, the afterglow brightness decreased gradually.

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