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Stability of red rare earth luminous fiber emission spectra

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Rare earth strontium aluminate luminous fiber is a novel functional fiber. In order to investigate emission light color stability of the rare earth luminous fiber containing red organic fluorescent pigment, several kinds of rare earth strontium aluminate luminous fibers were prepared by using rare-earth strontium aluminate as the rare-earth luminescent material and fiber-forming polymers such as polymer polyethylene terephthalate (PET) as a matrix and combining them with red organic fluorescent pigment as well as functional additives. Fluorescence spectrophotometer was used to characterize the resulting samples. Results showed that the shape and the peak of emission showed little change, but the emission intensity became weaker as the treatment time increased.

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Keywords: Rare earth luminous fiber, Red organic fluorescent pigment, Emission spectra, $SrAl_2O_4:Eu^{2+}$, Dy^{3+}

1. Introduction

Rare earth luminous fiber is a novel functional fiber, which is made of rare-earth luminescent material and fiber-forming polymer as main raw materials and it was successfully attracted great research interest since being invented in 2004. The fiber has excellent luminescence intensity, a long afterglow time, and is free from harmful radiation [1-2]. 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. It has a wide range of applications, because of its potential to play a vital role in various fields such as embroidery, plush toys, and so on for its excellent luminous properties [3-4].

Alkaline earth aluminates $xMO{\cdot}yAl_2O_3:Eu^{2+}$, RE^{3+} (M = Ca, Sr, Ba) are functional inorganic materials with strong luminescent intensity at the blue/green regions [5-7]. They show high quantum efficiency, long afterglow life, and good chemical stability. Recently, great progresses have been made in aluminate rare earth luminescent materials due to its good water resistance and excellent chemical stability. Phosphor, which is the cure material, used in the luminous fiber is mainly $SrAl_2O_4:Eu^{2+}$, Dy^{3+} currently [5-8]. The color of fiber’s emitting light is rather monotonous at present, which limits the development of rare earth strontium aluminate luminous fibers.

It is well known that Rhodamine B is derivatives of the xanthene dyes class, which are among the oldest and most commonly used of all synthetic dyes that, of their applications were using in cloth and food coloring [9]. The special photophysics properties of these types of molecules cause the vast and increasing up applications in chemistry and physics. And the luminous fiber that can emit red light in the darkness was fabricated through doping red organic fluorescent pigments (the core dye is Rhodamine B). This fiber would inevitably encounter various external conditions in the actual application process, such as air, light, temperature changes, moisture and so on, which are likely to affect its emission spectra, thereby affecting its emission light color. So its emission stability is an important characteristic. But the stability of red rare earth luminous fiber’s emission spectra is not known until now and it is not reported in other literatures.

In order to investigate the stability of emission spectra of rare earth luminous fiber doping red organic fluorescent pigments. In this study, $SrAl_2O_4:Eu^{2+}$, Dy^{3+} was prepared by means of solid-state reaction, and rare earth luminous fibers were prepared through melt spinning by mixing $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and PET chips together, and the emission spectra was tested.

2. Experimental

2.1 Materials

$SrCO_3$ (AR), Al_2O_3 (GR), Eu_2O_3 (99.99%), Dy_2O_3 (99.9%), H_3BO_3 (AR) and organic fluorescent pigments were purchased from Sinopharm Chemical Reagent Co., Ltd China. Polyethylene terephthalate (PET) chips were purchased from Wu Xi Taiji Industry Co, Ltd. (Wuxi, China), and functional additives were supplied by Jiangsu Guoda Complete Wiring Equipment Co,Ltd.(Wuxi, China). The structure of basic organic fluorescent dye used in preparing organic fluorescent pigment was shown in Fig. 1.

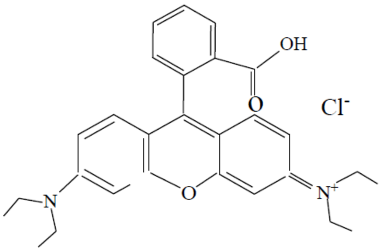


Fig. 1. Molecular structure of organic fluorescent dye

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

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} was prepared by solid-state reaction by 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 °C for 24 h, ground in planetary high-energy ball mill and heated to high temperature 1400 °C for 4 h under a reducing atmosphere, and then re-milled the sintered products and sieved to get the desired samples.

2.3 Preparation of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment

PET chips were dried in an oven at 110 °C for 24 h, and then mixed with a scheduled mass of rare-earth luminescent material functional addictives (dispersant) in a high-speed mixer. The mixtures were then extruded in a twin-screw master batch producer at 270-290 °C to get master batches for spinning application. After being dried at 110 °C, the master batches were melted and spun to obtain the luminous fiber, incorporating the strontium aluminate luminescent agent at 5 wt% and red organic fluorescent pigment at 0.5 wt%.

2.4 Sample preparation

2.4.1 Durability test

Samples were placed in ordinary circumstances last for one year, emission spectra of the samples were tested every three months.

2.4.2 Light fastness test

Samples were placed in light fastness tester (ATLAS-150S) for 5 hours, temperature 50 °C, and emission spectra of the samples were tested every one hour.

2.4.3 Acid and alkali resistance test

Samples were placed in the solution of hydrochloric acid (0.5wt%) and sodium hydroxide solution(0.5 wt %) for 0.5, 1, 3, 5min, respectively.

2.4.4 Washable performance test

Samples were washed for 1h, 2h, 3h respectively, and then the emission spectra were tested.

2.5 Characterization

2.5.1 Luminous properties

The emission spectra of all the samples were measured at room temperature through using a fluorescence spectrophotometer (HITACHI 650-60, Japan) with a Xe flash lamp as an excitation source; the slit was 2.5 nm in width; the excitation wavelength was from 200 nm to 700 nm and the scan speed was 120 nm/min.

3. Results and discussion

3.1 Durability of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment

The emission spectra of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment samples are shown in Fig. 2, which were placed at room temperature for 12 months, respectively, and the emission spectra of the samples were tested every three months.

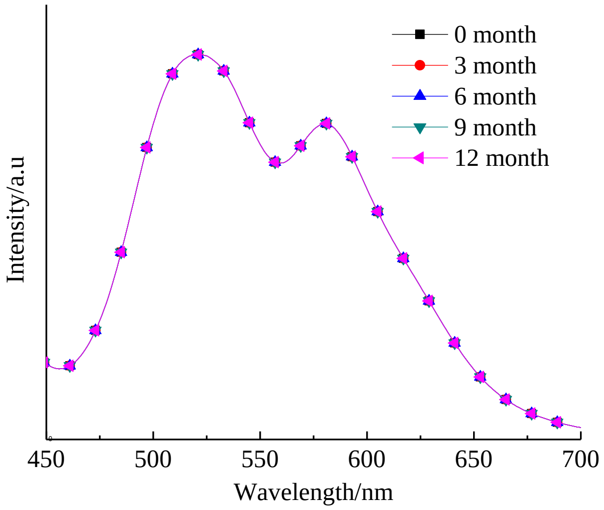


Fig. 2. Emission spectra of luminous fiber placed at room temperature for different time

It is well known that the shape and the intensity of the emission spectra of PET-$SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment samples are due to the number of electrons, which belong to $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and red organic fluorescent pigment, that transit to the excited state and the energy level of this state. As we all know, when the $SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment are irradiated in the same excitation light, then the number of electrons and the energy level of the excited state are the same. From Fig. 2 it can be seen that luminous fibers were excited in the same condition and the emission spectra of samples had a broad band emission accompanied with the peaks around λ =520 nm and 580 nm , which was due to the 5d–4f transition of Eu^{2+} ions of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and the characteristic emission of the red organic fluorescent pigments. All the samples had similar emission spectra with the strontium aluminate luminescent agent at 5 wt% and red organic fluorescent pigment at 0.5 wt%. Regardless of the change of the storage time, the position of the emission peak and the shape showed no change, indicating that the change of the storage time hardly influenced the crystal structure of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and the red organic fluorescent pigment.

From the analysis above we obtained the conclusion that the emission properties were stable no matter how long it has been placed in the same atmosphere.

3.2 Light fastness of PET-$SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment

Light fastness has been to be a subject of great interest in textile industry since the fabrics are widely used in automobile colored upholstery and are exposed to direct sunlight and temperature above 50 °C. Fig. 3 shows the emission spectra of PET-$SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment samples that were exposed to direct sunlight and temperature at 50 °C for different time. From Fig. 3, it can be seen that the emission spectra of rare earth luminous fiber containing red organic fluorescent pigment had a similar emission spectrum with each other under the same condition just different time. The shape and the peak of emission showed little change, but the emission intensity became weaker as the time exposed to direct sunlight and temperature at 50 °C increased. It was mainly related to the luminescence properties of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and red organic fluorescent pigment. As is mentioned above, the luminescence of rare-earth luminescent material is generated by the transition of 4f electrons of rare-earth ion. When it was excited by the sunlight, the electrons transited between 4f and 5d shells. Therefore, the matrix lattice structure of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} were not changed, which ensured the luminescence properties of $SrAl_2O_4$:Eu^{2+}, Dy^{3+}.

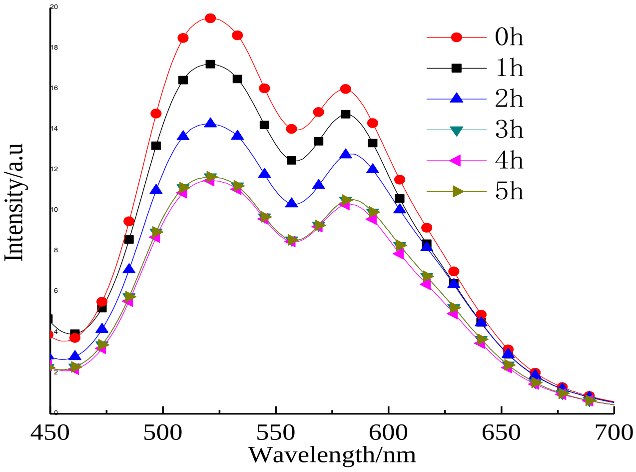


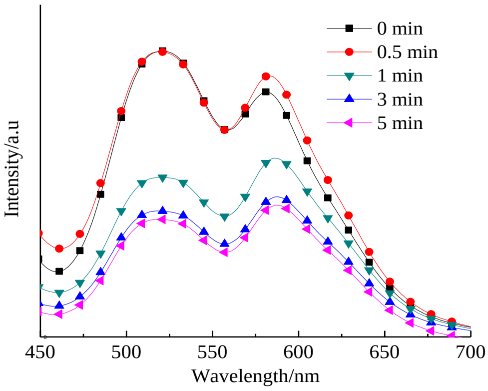
Fig. 3. Emission spectra of luminous fiber exposed to direct sunlight for different time

In our previous study, it is reported that there was a small quantity of particles protruding slightly from the fiber surface, which included $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and red organic fluorescent pigment. And we expect that the structure of the red organic fluorescent pigment was destroyed when it was exposed to sunlight, which would influence the luminescence properties of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and the destroyed red organic fluorescent pigment covered the surface of the luminous fiber, which lead to lower the emission intensity of the red organic fluorescent pigment and $SrAl_2O_4$:Eu^{2+}, Dy^{3+}. This research also deduces that the sunlight has a great influence on its luminous properties of red organic fluorescent pigments on the surface of the luminous fiber and the fluorescent pigments inside the fiber are less affected by sunlight. Which we can see from Fig. 3 that when the luminous fiber is exposed to the sunlight for more than 3 hours, its emission intensity and shape has little change.

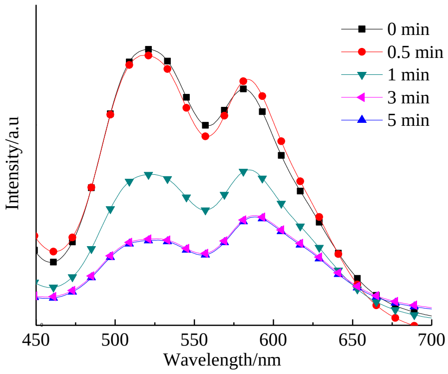
3.3 Acid and alkali resistance of PET-$SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment

Luminous fibers may be in a weak acid or weak alkaline environment in the course of application, in order to investigate the acid-alkali resistance of red emission luminous fiber. PET-$SrAl_2O_4$:Eu^{2+}, Dy^{3+}- red organic fluorescent pigment samples were put into the hydrochloric acid solution for several minutes.

Fig. 4 shows the emission spectra of luminous fiber with acid and alkali treatment for different time. From Fig. 4 it can be seen that the principle of emission spectra were similar with each other containing two emission peaks around 520 nm and 580 nm. However, the emission intensity was different from each other as the acid treatment time changed. The intensity of emission peak around 520 nm dropped and emission peak around 580 nm increased greatly at first and then decreased gradually when the treatment time was over 0.5 minute. We deemed that it was affected by $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and red organic fluorescent pigment on the surface of the luminous fiber, and when luminous fiber was dipping in the acid-alkali solution, it would penetrate to the internal of the fluorescent pigment, which might influence the polarity of fluorescent pigment. And it will lead to more and more electrons transited between the ground state and the excited state of fluorescent pigment. But as the treatment time increased, the acid-alkali solution penetrating to the internal of the luminous fiber increased, which would cause the structure change of the pigment. $SrAl_2O_4:Eu^{2+}$, Dy^{3+} will be hydrolysis when it faced with acid or alkali.



(1) acid treatment



(2) alkali treatment

Fig. 4. Emission spectra of luminous fiber with acid-alkali treatment for different time

Based on the above discussions, it is clear that the emission intensity of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment was obviously influenced by the acid-alkali solution.

3.4 Washable performance of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment

Emission spectra of luminous fiber after being washing for different time are shown in Fig. 5. From Fig. 5 it can be seen that the emission intensity of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment after being washed for more than one hour was lower than that of the luminous fiber without washing treatment. And when it was washed for more than one hour, the luminous fibers have similar emission spectra with the same emission intensity and the same shape. It was deemed that there would be two reasons for this phenomenon. Firstly, one of the possible reasons could be ascribed to the fact that part of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and red organic fluorescent pigment moved to the surface of the luminous fiber in the preparing process of this luminous red fiber and easily affected by washing. When it was being washed, the particles would drop down, which caused the emission intensity decreased. Secondly, the particles inside the fiber were less affected by washing, which resulted in little change of the emission spectra as the washing time increased.

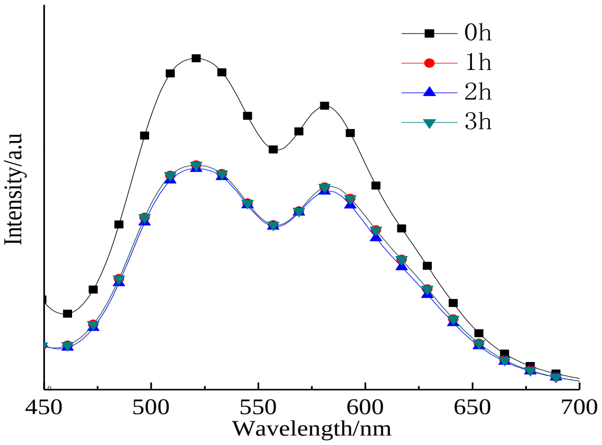


Fig. 5. Emission spectra of luminous fiber after being washing for different time

The results showed that washing time had a certain effects on the emission intensity of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment. Even in the same washing conditions just with different washing time, the luminous fiber would possess emission spectral line with different intensity.

4. Conclusions

In order to investigate the emission stability of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment. $SrAl_2O_4:Eu^{2+}$, Dy^{3+} was prepared by means of solid-state reaction, and rare earth luminous fibers were fabricated through melt spinning by mixing $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, organic fluorescent pigments (Rhodamine B) and polymer polyethylene terephthalate (PET) chips together, and it was treated in different environments. The emission properties were studied through testing their emission spectra. The conclusions are summed up as follows:

(1) The emission properties were stable no matter how long it has been placed in the same atmosphere.

(2) The shape and the peak of emission showed little change, but the emission intensity became weaker as the time exposed to direct sunlight and temperature at 50 ^oC increased, and when the luminous fiber is exposed to the sunlight for more than 3 hours, its emission intensity and shape has little change.

(3) The emission intensity of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment was obviously influenced by the acid-alkali solution.

(4) Washing time had a certain effects on the emission intensity of PET-$SrAl_2O_4:Eu^{2+}$, Dy^{3+}- red organic fluorescent pigment. Even in the same washing conditions just with different washing time, the luminous fiber would possess emission spectral line with different intensity.

Acknowledgments

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References

[1] Y. H. Yan, M. Q. Ge, Text Res J **1819**, 82 (2012).
[2] M. Q. Ge, X. F. Guo, Y. H. Yan, Text Res J **677**, 82 (2012).
[3] J. S. H. Zhang, M. Q. Ge, J Text I **767**, 9 (2011).
[4] X. F. Guo, M. Q. Ge, J. M. Zhao Fiber Polym **875**, 7 (2011).
[5] W. Xie, J. Quan, H. Y. Wu, L. X. Shao, al et. J Alloy Compd **97**, 514 (2012).
[6] B. M. Mothudi, O. M. Ntwaeaborwa, J. R. Botha, H. C. Swart, Physica B: Condensed Matter **4440**, 404 (2009).
[7] P. T. Ji, X. Y. Chen, Y. Q. Wu, Appl Surf Sci **1888**, 258 (2011).
[8] D. Q. Chen, J Eur Ceram Soc **4069**, 34 (2014).
[9] Jahanbakhsh Ghasemi, Ali Niazi, Mikael Kubista, Spectrochim Acta A **649**, 62 (2005).

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