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Researches on preparation and luminescent properties of chromatic rare-earth fiber based on $SrAl_2O_4$: Eu^{2+}, Dy^{3+}

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The chromatic rare-earth fibers based on long afterglow luminescent material $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, which added inorganic pigments of red, yellow, blue and green colors, was prepared by melt-spinning process. The result of X-ray diffraction (XRD) demonstrated that the chromatic luminous fibers had an independent superposition of phase features from both $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and polypropylene. Afterglow decay and excitation-emission spectra were used to analyze the photoluminescence (PL) properties of chromatic rare-earth fibers, and the results indicated that the initial luminescent intensity of white luminous fiber was seen to be more intense. Luminous fibers in white, yellow and green colors were nearly a green emission, which were caused by transition of Eu^{2+}. However, the emission spectrums of red and blue luminous fibers were shown to be red-shifted and blue-shifted, respectively. Furthermore, photo chromic (PC) properties showed that the emitting colors of samples were primarily located in the yellow-green area.

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1. Introduction

Chromatic rare-earth fiber is a novel functional material, which made of rare-earth strontium aluminates and fiber-forming polymer as main raw materials, combining with transparent inorganic pigment and functional additives by a special spinning process [1-2] . Because of its promising applications in various field such as knitted fabrics, woven fabrics, plush toys, art embroidery, and other decorations. Chromatic luminous fiber has successfully attracted great research interest since being invented in 2008[1].

Usually, the luminous fiber without ignorant pigment mainly emits the yellow-green light at night. After the fiber absorbs visible light and stores light energy, it emits light in the darkness for more than 10 hours. Besides, it has excellent luminescence intensity, a long afterglow time, and is non-toxic, non-radioactive, and can be recycled [3-7]. The $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphor, which owns good afterglow property and chemical stability, makes its potential candidate for the luminous fiber. Since the emitting color of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} luminous fiber is mainly distributed in the yellow-green area, it has obvious shortages as well such as single emitting color. Thus, the application of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} luminous fiber is greatly limited.

As a functional luminous fiber, the phenomenon of persistent luminescence of the fiber has been studied by many researchers [8,9]. However, its photo chromic property is also particularly important for study. The rare-earth fibers with different inorganic pigments are still a challenge for photo chromic property. In this work, $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors with long afterglow were synthesized by solid-state reaction method, and on that basis, the chromatic rare-earth fiber containing colored inorganic pigments and luminous phosphors was successfully prepared by the melt-spinning process. Using instruments such as scanning electron microscope, X-ray diffractometer, afterglow tester and fluorescence spectrophotometer to characterize and analyze morphology, crystal structure, afterglow properties, photoluminescence (PL) and photochromic (PC) properties of the chromatic luminous fiber. The results indicated the feasibility of preparing chromatic luminous fiber by melt-spinning process, and its luminescent properties were illustrated in detail. The emission light and the normal reflected light color of chromatic luminous fiber were combined to form brilliant colors. The studies could provide theoretical and experimental references for the development of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} luminescent fiber with more extensive application.

2. Experimental

2.1 Materials

$SrCO_3$(99.5%), Al_2O_3(GR), Eu_2O_3(99.99%) and Dy_2O_3(99.9%) were purchased as raw materials from Sinopharm Chemical Reagent Co,Ltd. All the materials were analytically pure. The fiber-forming polymers (PET chips) were purchased from Wuxi Taiji Industry Co, Ltd. (Wuxi, China).Transparent inorganic pigments and functional additives were supplied by Jiangsu Guoda Complete Wiring Equipment Co, Ltd. The luminous coated fabrics were provided by Changshu Jianghui Fiber-products Co, Ltd. The paper liner and the normal fibers (9.72 tex/2) for Computer-aided embroidery were purchased from Wuxi Yishiman Garment Accessories Co, Ltd.

2.2 Synthesis of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} luminescent materials

$SrCO_3$(99.5%), Al_2O_3(GR), Eu_2O_3(99.99%) and Dy_2O_3 (99.9%) and H_3BO_3(AR) were dispersed by ultra-sonic dispersion in a molar ratio of 1:2:0.01:0.02:0.2 for 15 minimums. Then the five raw materials were ground together in a ball mill, and the powder annealed at 1200°C for 3h in a weakly reducing atmosphere (10%H_2 and 90%N_2) to get the luminescent materials, $SrAl_2O_4$: Eu^{2+}, Dy^{3+}.

2.3 Preparation of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} -PET luminous fiber

The chromatic luminous polyester filament (16.67 tex/36 f) was prepared by melt spinning (Fig.1), incorporating the strontium aluminate luminescent particles at 5 wt% [10]. The transparent inorganic pigments in white, red, yellow, blue and green colors mixed with homemade rare earth luminescent materials with mass ratio of 3: 1, respectively. And annealed in a muffle furnace at 1000 °C for 1 hours, then smashed and screened base masteries for chromatic luminous fibers. The fiber-forming polymer (PET chips) were dried in an oven at 110°C for 24 hours, and then mixed with the above obtained colored base masteries (with dosage of 5%) and functional additives in a high-speed mixer. The mixtures were then extruded in a screw masterbatch producer at 270～290 ℃ and melt in a melt-pump at 250℃.Finally, spun to obtain colored luminous fibers samples(Fig.2). In order to describe in an easy manner, the samples are marked as PET-W (fiber without any pigment), PET-Y (fiber with yellow color pigment), PET-G (fiber with green color pigment), PET-B (fiber with blue pigment), PET-R (fiber with red color pigment), respectively.

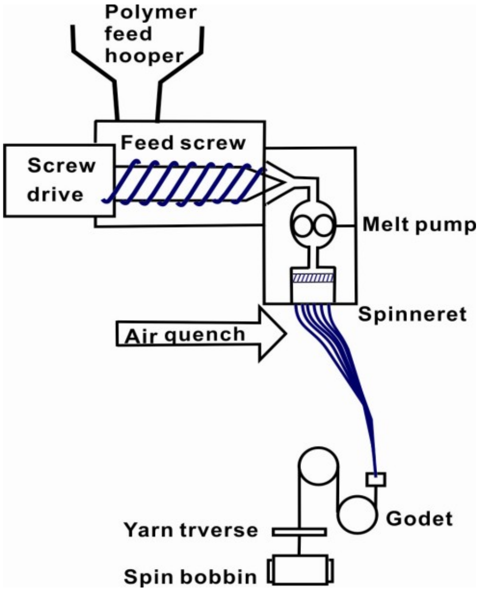

Fig.1. The melt-spinning process of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} -PET luminous fiber

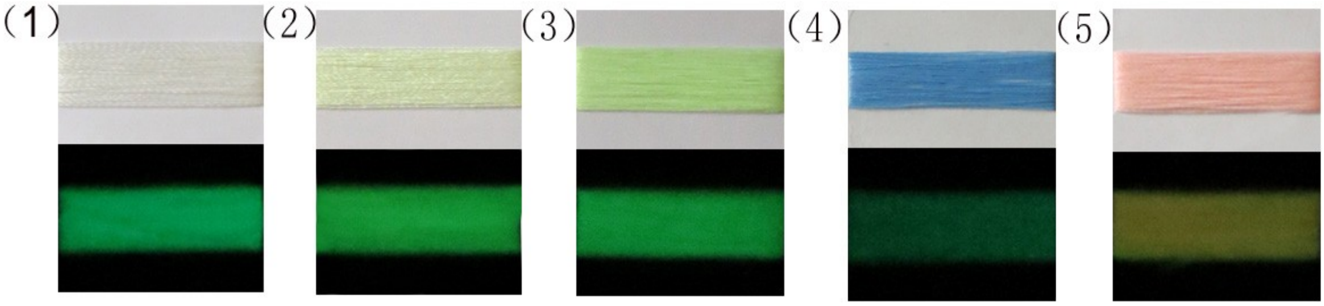

Fig.2. Chromatic luminous fibers with the effect of day and night: (1) white luminous fiber(PET-W), (2) yellow luminous fiber(PET-Y), (3) green luminous fiber(PET-G), (4) blue luminous fiber(PET-B), (5) red luminous fiber(PET-R)

2.4 Characterization

2.4.1 X-ray diffraction

The phase composition and crystal structure and of the samples were recorded on a D8 Advance X-ray diffractometer (Bruker AXS, Germany) using Cu Kα radiation (λ=0.15406 nm) at a voltage of 40 kV and current of 30 mA. The Samples were scanned over the range of diffraction angle from 10°to 70°with a scan speed of 4(°)/min at room temperature.

2.4.2 Luminescent properties

Luminescent properties of samples include afterglow decay properties, photoluminescence (PL) properties and photochromism (PC) properties. The afterglow decay properties of samples were assessed at a room temperature using a PR–305 long-ray fluorescence tester after an excitation illumination level of 1000 lx for 15 min. The excitation spectra and emission spectra of all the samples were measured at room temperature through using a fluorescence spectrophotometer (HITACHI F-4600, Japan) with an emission wavelength of 520 nm and the excitation wavelength was 365 nm. The slit was 2.5 nm in width and the scan speed was 1200 nm/min. Chromaticity diagrams of all the samples were recorded on a PR-650 spectra scan colorimeter using standard light source A as a reference. All measurements were carried out at room temperature.

3. Results and discussion

3.1 Morphology

The pure $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, cross-section of the white luminous fiber and vertical shape of the white luminous fiber were observed by SEM as shown in Fig. 3. Irregularly shaped particles of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} with size about 5μm were clearly visible, as can be seen from Fig. 3 (a). It can be seen from Fig. 3 (b) that the luminescent material could not clearly apparent within the fiber cross-section. Fig. 3 (c) shows the surface of the luminous fiber, from which $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors were found to be distributed in the polyethylene terephthalate randomly. However there was only a small quantity of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} protruding slightly from the fiber surface.

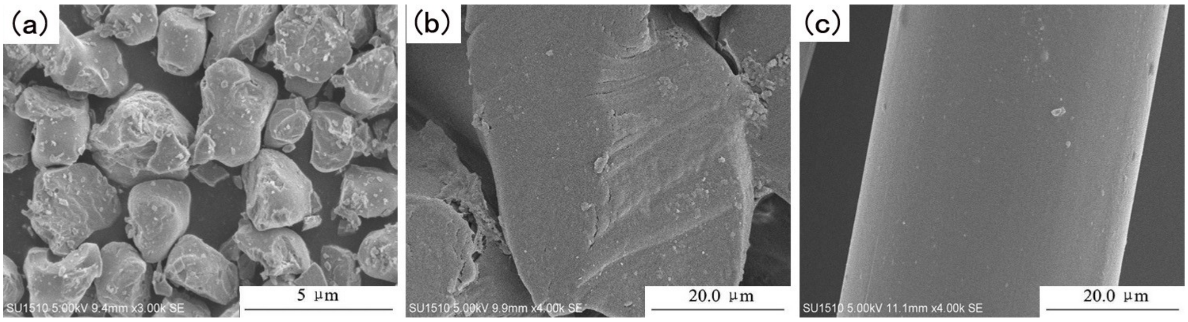

Fig. 3. SEM images of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} (a), cross-section shape of the white luminous fiber (b) and vertical shape of the white luminous fiber (c)

3.2 XRD phase analysis

The X-ray diffraction patterns of the rare earth luminescent material, chromatic rare-earth fiber and the regular polyester fiber are shown in Figure 1. From Fig. 4(a), the diffraction peaks were observed in the strontium aluminate at the diffraction of 2θ at 20.1, 28.5, 29.3 and 35.1. Comparison of the JCPDS standard card (No.34–0379), we confirmed that the sharp peaks correspond to the diffraction peaks of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}. Combining with corresponding MDI software analysis, the luminous material $SrAl_2O_4$: Eu^{2+}, Dy^{3+} is α phase, and it belongs to monoclinic system phosphorus quartz crystal structure with good crystallinity. Crystal parameters obtained from powder diffraction patterns are a=0.8442 nm, b=0.8822 nm, c=0.5161 nm, β =93.41. In addition, the diffraction peak shape of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} fiber was almost the same with that of the regular polyester fiber, this indicated that the crystal lattice of the polymer was not materially affected by the addition of the rare-earth luminous material.

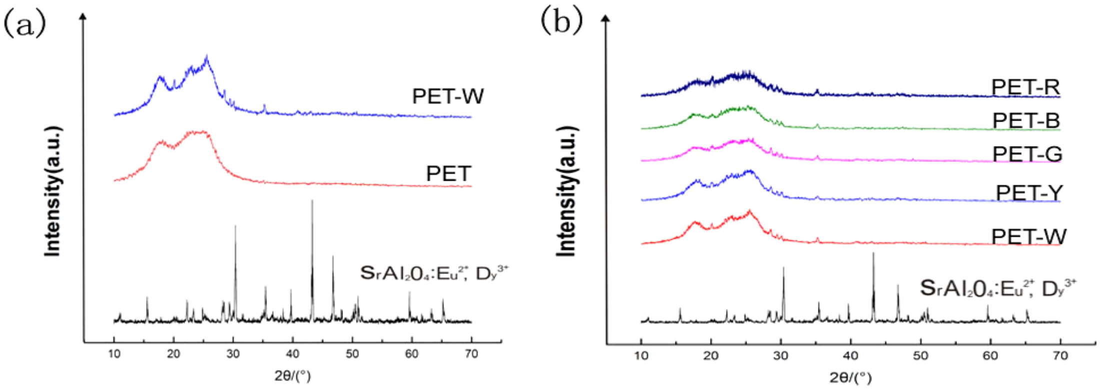

Fig. 4. XRD patterns of the luminous material, chromatic rare-earth fibers and the regular polyester fiber.

From Fig. 4 (b), it can be seen that the peak pattern of red, yellow, blue and green luminous fibers were similar to this white one without inorganic pigment.The spectra pattern of chromatic rare-earth fibers were the superposition of the polyester fiber and the luminous material, which indicated that the lattices of both $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and polyester fiber had not been affected by the high temperature melt-spinning process in the red, yellow, blue and green luminous fiber. However, the only difference was that the red luminous fiber appeared a phenomenon of wide-band spectra, and it implied that the phenomenon was caused by the red inorganic pigment and the lattice of the fiber to some extent was disturbed.

3.3 Afterglow decay properties

In order to investigate the afterglow decay properties of the fibers, afterglow intensity was carried out at room temperature. Figure 5 shows the afterglow decay curves of the colored luminous fibers with the addition of different transparent inorganic pigments. The decay trends of the samples with different inorganic pigments were similar and close to that of the white fiber without any pigment as a whole, but the initial afterglow intensity of the samples were different to some degree. It can be clearly seen that the decay of the entire sample consists of two regimes: one was a fast decay process and subsequent slow decaying process. As we know, the role of Eu^{2+} and Dy^{3+} in the rare earth materials is the luminescent centers and the traps, respectively. The first decay process results from the short survival time of the electron in Eu^{2+} while the slow decay process could be attributed to the deep trap energy center of Dy^{3+}[7].Moreover, the initial afterglow intensity of white luminous fiber (PET-W) was 2.507cd/m^2, which was significantly greater than other samples with inorganic pigments. And the order for the value of the initial afterglow intensity was: white fiber (PET-W) > yellow fiber (PET-Y) > green fiber (PET-G) > red fiber (PET-R) >blue fiber (PET-B).

The main factor that affects the luminous intensity of the fibers is the influence of the inorganic pigments on the color of the light emitted by the luminous fiber. When the luminous fiber is excited by the visible light, most of the strontium aluminates in the fiber are hindered from obtaining excitation energy directly and generating photon transmissions because of the inorganic pigments. It is easy to deduce that some of the photons inevitably encounter inorganic pigments and are absorbed selectively. Therefore, the inorganic pigments have more influence on the transmission of photons emitted by the strontium aluminates. White luminous fiber without inorganic pigments can obtain the most excitation energy, which led to the highest initial afterglow intensity.

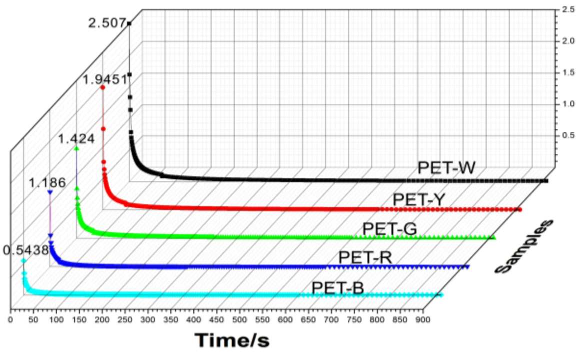

Fig. 5. Decay characteristic of chromatic luminous fibers.

3.4 Spectral characteristics

Spectral characteristics of the five luminous fibers with addition of several different transparent inorganic were investigated in this experiment. Fig. 6 shows the excitation spectra of the chromatic luminous fiber at room temperature. Their excitation spectrum showed a broad band from 340 to 460 nm, which was attributed to the energy levels in Eu^{2+} ion of rare-earth strontium aluminate[11]. More over, the maximum excitation peak was loaded at 451.8 nm, which can be attributed to the addition of red inorganic pigment in the luminous fiber. From Figure 6, it can also be seen clearly that there was a change in the position of excitation peak, showing that the position of excitation peak shifted to the visible-light area and the shift degree of the chromatic luminous fibers were PET-G, PET-W, PET-Y, PET-B, PET-R ranging from small to large.

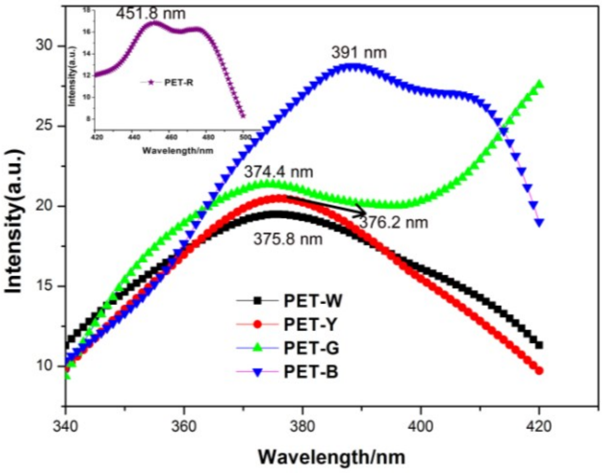

Fig. 6. Excitation spectrum of the chromatic luminous fibers (λ_{em}=520 nm)

Fig. 7 shows emission spectra of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} -PET luminous fibers of different colors. The emission peak of white luminous fiber was located at 506.4 nm, which belonged to the transition of Eu^{2+} ions and kelly-light areas. The shapes of emission spectra of chromatic luminous fibers were similar to that of the fiber without any pigment, but the emission peak produced red-shift or blue-shift compared with the white luminous fiber. The blue luminous fiber showed obvious blue-shift phenomenon with the emission peak at 446.4 nm. In addition, the emission spectra of red luminous fiber were still broad band and the emission peak exists at around 585.6 nm, which originated from the transitions of $_4F^{9/2}$ to $_6H^{15/2}$ ($_6H^{13/2}$) [7]. As we know, another characteristic emission peak of Dy^{3+} is found in the red luminous fibers, indicating that the luminescence center is formed by both Eu^{2+} ions and Dy^{3+} ions existed in $SrAl_2O_4$ host lattice. Meanwhile, the emission peaks of yellow and green luminous fibers had a slightly red-shift phenomenon, and with a peak of 512.8nm and 517.4 nm, respectively. It is deemed that the shift of emission spectra relates to selective absorption of light for transparent inorganic pigment.

By the above analysis, chromatic $SrAl_2O_4$: Eu^{2+}, Dy^{3+} -PET luminous fibers with addition of different kinds of transparent inorganic pigments can enrich the spectral lines , which provides a fundamental guarantee for the development of chromatic luminous fibers .

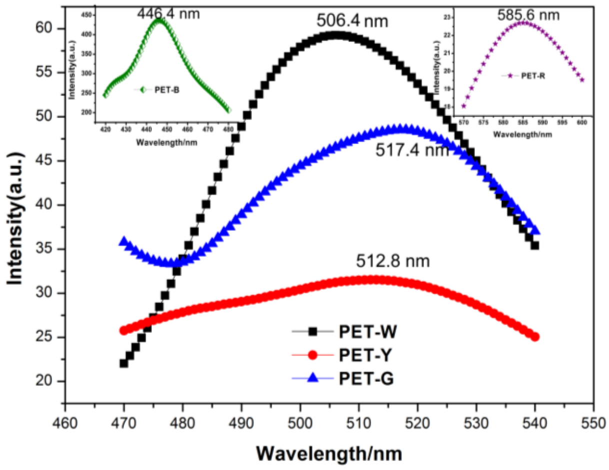

Fig. 7. Emission spectrum of the chromatic luminous fibers (λ_{ex}=365 nm)

3.5 photochromism (PC) properties

Fig. 8 shows the CIE 1931 chromaticity diagram of chromatic luminous fiber. The colors of these five samples were primarily located between yellow-green areas, where human eyes had the greatest sensitivity. Therefore, the luminous fiber samples can be easily seen in the darkness. Moreover, O point represents white illuminant, and we could draw straight lines from O point to wavelength points in Fig. 8. Thus the color of any light source can be represented as an (x, y) coordinate on the diagram, which can be calculated by drawing straight lines from O point through the (x, y) coordinates of samples, until the lines intersect the outer locus of points along the spectral edge of the 1931 CIE chromatic diagram. For example, color purity of the blue luminous fiber is marked as P in Fig. 8 and this purity can be calculated as follows:

$$\mathbf{P} = \frac{\overrightarrow{OP}}{\overrightarrow{ON}} = \frac{x_P - x_O}{x_N - x_O} \tag{1}$$

Where XP, XO, XN are the abscissa of P, O, and N point in the chromatic diagram respectively. The chromaticity coordinates and relevant color parameters are summarized in Table 1.

From table 1, the color purities of chromatic rare-earth fibers were similar, but higher than that of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphor except the blue luminous fiber. The main reason for this phenomenon is that the color of emitting light is caused by adding blue inorganic pigment and can be absorbed selectively by the pigment. As far as we know, the color of blue inorganic pigment is far apart with the emitting color of yellow-green light from $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, but the other colors of inorganic pigments such as yellow, green and red, which are added in to luminous fibers are close to this yellow-green emitting color. Moreover, the value of the color rendering indexes of these five samples was all above 70, which was higher than that of phosphor (39.4). In addition, the hue of light colors for samples can be used to characterize the dominant wavelength, and the dominant wavelength of luminous fibers in white, yellow, green and blue color was almost similar. However, the luminous fiber in red color had the maximum dominant wavelength. Due to the absorption towards the light of pigments, red-shift phenomenon had occurred in the red luminous fiber. To a certain extent, the emission spectrum was drawn by red inorganic pigments and light color tends to hue of the red pigment.

From the above analysis, we reach the conclusion that chromatic luminous fibers with different inorganic pigments affect their emitting colors in the night. Beside, these emitting colors are mainly located in the yellow-green area due to the luminescent materials such as $SrAl_2O_4$: Eu^{2+}, Dy^{3+} in the fiber. Thus, these materials and inorganic pigments make the luminous fibers have good ornamental value and recognition ability in the darkness.

Table 1. Chromaticity coordinates and light color parameters.

Samples	Chromaticity coordinates		Dominant wavelength /nm	Color rendering Index(Ra)	Purity/%
	X	Y			
$SrAl_2O_4$: Eu^{2+}, Dy^{3+}	0.3012	0.5634	519	39.4	54
PET-W	0.2536	0.6097	524	92.0	69
PET-Y	0.2687	0.6521	533	91.4	76
PET-G	0.2054	0.5609	514	76.6	59
PET-B	0.1989	0.3387	493	70.5	47
PET-R	0.4684	0.3533	588	88.7	73

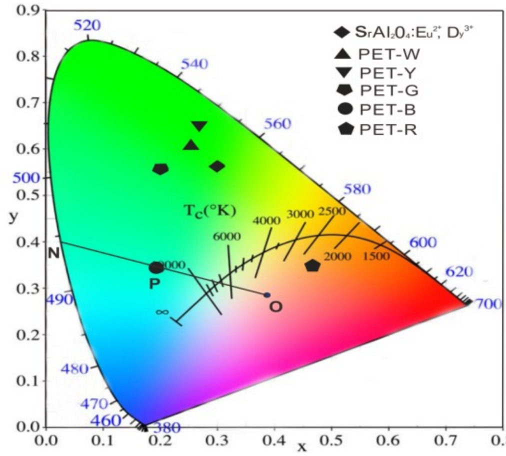

Fig.8. The location of samples on CIE 1931 chromaticity diagram.

4. Conclusions

Chromatic luminous fibers based on $SrAl_2O_4$: Eu^{2+}, Dy^{3+} were prepared and their luminescent properties were characterized. The lattices of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} fiber in the white, yellow, green and blue luminous fibers had not been destroyed. However, the lattice of red luminescent fiber had been distorted, producing emission at 580 nm due to the $_4F^{9/2}$ $_6H^{15/2}$ ($_6H^{13/2}$) transition of Dy^{3+}. In addition, the chromatic luminous fibers might have both the spectral characteristics of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and the physicochemical properties of polypropylene fibers, as well as proved the feasibility of preparing the chromatic rare-earth fibers by melt-spinning method.

The decay characteristics of chromatic luminous fibers were similar to $SrAl_2O_4$ phosphors and the decay processes controlled by the different depth of trap levels including rapid and slow. The initial afterglow intensity for chromatic luminous fibers was found to vary with different inorganic pigments and the highest afterglow intensity was observed in white luminous fiber.

The range of the excitation wavelength of chromatic luminous fiber was 340–460 nm, belonging to ultraviolet rays and visible light. The shapes of emission spectras for chromatic luminous fibers were similar to that of the fiber without any pigment. However, the emission peak of luminous fibers in white, yellow and green colors were located at around 510 nm, belonging to the typical yellow-green luminescence, and originating from 5d-4f transition of Eu^{2+} ions. Furthermore, blue luminous fiber showed obvious blue-shift phenomenon with the emission peak at 446.4 nm, while red luminous fiber could be tuned from yellow-green to orange-red easily by doping red inorganic pigment.

The emission colors of chromatic rare-earth fibers could be tuned from yellow-green to orange-red easily by doping different kinds of inorganic pigments, which can make the materials have potential applications in many areas.

Acknowledgements

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