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Effect of α/β ratio on color characteristics of $SrAl_2O_4$:αEu^{2+}, βDy^{3+}

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This study focuses on the color characteristics of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} which plays an important role in its potential practical applications, especially the luminescence properties of phosphors and dyeing property of luminous fiber which produces by using $SrAl_2O_4$:αEu^{2+}, βDy^{3+} as raw material. We present estimators for several ratios of α/β (0:0, 1:0, 2:0, 0:1, 1:1, 2:2, 1:2, 2:1) along with instrumental measurements of their color and luminescent properties. A summary of the main test results of the current versions was given. The X-ray diffraction, CIE Chromaticity Diagram, fluorescence spectrophotometer as well as the afterglow brightness tester as microcomputer thermo-luminescent dosimeter was applied to analyze performance of samples. A brief outline is also given of some phenomena aspects. Meanwhile a detailed physical description and a manual are available. The results suggest that a certain amount of α/β could promote forming of $SrAl_2O_4$ crystal phase from XRD analysis. Basically, the position as well as the width of emission spectra were the same, while the emission intensity increased with the addition of α/β, demonstrating that the luminescent center is Eu^{2+} in both formula and the intensity of fluorescence become weakened with the doping of Dy^{3+}. It's worth mentioning that the color of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} turned yellower with the ratio of α/β decreased.

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Keyword: $SrAl_2O_4$: αEu^{2+}, βDy^{3+}, Color character, Emission spectra, Afterglow properties

1. Introduction

Alkaline earth aluminates $SrAl_2O_4$: αEu^{2+}, βDy^{3+} is one of the most excellent material which have unexpectedly large field of applications, as its bright phosphorescence and long lasting phosphorescence properties. These kinds of materials have been widely used in night display material, safety protection, decorating material and traffic, etc. [1]. The Eu^{2+} as the luminous center has a broad emission peak of visible range from 450 nm to 570 nm and the location of the wave crest is just about 520 nm [2-3]. It is well known that light emitting of Eu^{2+} is a broadband emission generated by transition of electrons from $4f^65d^1 \rightarrow 4f$, and electrons of 4f level are shielded by the electronic shell of S and P [4-5]. Fig. 1 shows an entirely possibility model is proposed of $SrAl_2O_4$:αEu^{2+}, βDy^{3+} in light. The very short decay time and strong intensity of the luminescence (the step 2) is due to the excitation of ultraviolet as well as daylight (the step 1). It is also allowed nature of the electronic inter configurational transitions (the step 3) and the trap depth of the $SrAl_2O_4$:αEu^{2+}, βDy^{3+} can be effectively deepened by doping Dy^{3+} ion which affected the long afterglow (the step 4) with very long lifetime at the same characteristic green visible range as the photoluminescence [6-8]. The addition of H_3BO_3 affects the fusion of alkaline earth aluminates and rare earth when $SrAl_2O_4$:Eu^{2+}, Dy^{3+} was synthesized, thus further enhancing the synthesis technique and luminescent properties [9-10]. However, the factors which govern the color characteristics of $SrAl_2O_4$:αEu^{2+}, βDy^{3+} have yet to be fully defined.

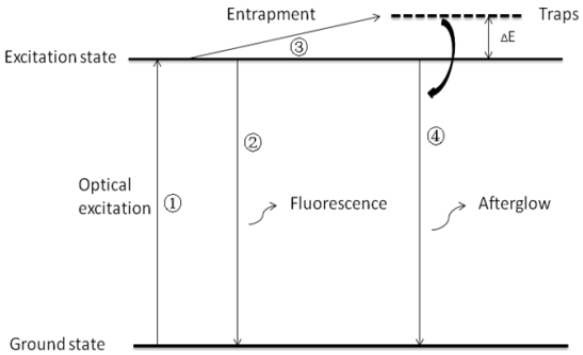

Fig. 1. The luminescent model of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} in optical excitation and persistent luminescence processes

It is complex to research the color characteristics of fluorescent material. We review the evidence for this attention of color character and discuss its implications for understanding the luminous performance and color character. In each case, the color character can be influenced by several factors such as the energy absorption, the intensity of fluorescence, the trapping levels even the times and the temperature [11-13]. There is thus a demand for better and more discussion of the color character. The search for color character of persistent luminescence materials would be greatly facilitated if the underlying mechanisms between luminance and color. In this study, $SrAl_2O_4$:αEu^{2+}, βDy^{3+} was synthesized by solid-state method with several different ratios of Eu^{2+} and Dy^{3+} [14-18].

2. Experimental

2.1. Phosphor materials preparation

Al_2O_3, $SrCO_3$, Eu_2O_3, Dy_2O_3 and H_3BO_3 of analytical reagent grade as the starting materials were mixed and milled by the ratio in a mortar. After preliminary mill these raw materials were dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30min and mechanical mixing for 30 min in order to get the homogeneous mixture. The samples were heated by adding H_3BO_3 (the ratio of H_3BO_3 was 8%mol relative to $SrAl_2O_4$:αEu^{2+}, βDy^{3+}) to a high temperature of 1400°C for 3h in a reducing atmosphere to $SrAl_2O_4$:αEu^{2+}, $\beta Dy3^{+}$. According to stoichiometric amount, the ratio of $SrCO_3$: Al_2O_3 was 0.95:1mol. % and α/β (the ratio was 0:0, 1:0, 2:0, 0:1, 1:1, 2:2, 1:2, 2:1) were the mole number of Eu^{2+} and Dy^{3+}, respectively. Finally, the sintered products were milled and sieved to get the desired samples.

2.2. Instrumental measurements

The conventional emission luminescence spectra of all the samples were obtained at room temperature with an excitation wavelength of 265 nm and 365 nm using a fluorescence spectrophotometer (F-4600 FL Spectrophotometer) with the Xe flash lamp as an excitation source; the slit was 1-5 nm in width; the excitation wavelength was from 200 to 900 nm and the ratio of scanning was 2400 nm/min. The X-ray diffraction was measured using Bruker D8 Advance made in Germany at room temperature; the scanning range of samples was from 10° to 90°and the speed of scanning were 4°/min. Afterglow decay curves were obtained using PR-305 afterglow brightness exciting the samples at 1000lx for 15 min; chromaticity coordinates and reflectivity were tested using Macbeth color-Eye 7000A color measuring and matching instrument made in the USA. Before all the testing, samples should be kept in darkness for 20h to rule out the existence of the afterglow of error.

3. Results and discussion

3.1. Fluorescence spectra of $SrAl_2O_4$: αEu^{2+}, βDy^{3+}

The emission spectra of rare earth co-doping strontium aluminates were obtained at room temperature excited at 265 nm and 365 nm respectively. From Fig. 2 it can be found that the intensity of fluorescence becomes weakened gradually with the increase of the ratio of Dy^{3+}. While the emission band excited by 265 nm is not fitted to Gaussian profile and the shoulder peak at 520 nm can be observed. The luminescent center is still Eu^{2+} from the emission spectra excited by 365 nm (Fig. 3) but the strong lattice vibrations of $SrAl_2O_4$:αEu^{2+}, $\beta Dy3^{+}$ under 265 nm UV-emission result in the presence of a strong crest at 540 nm.

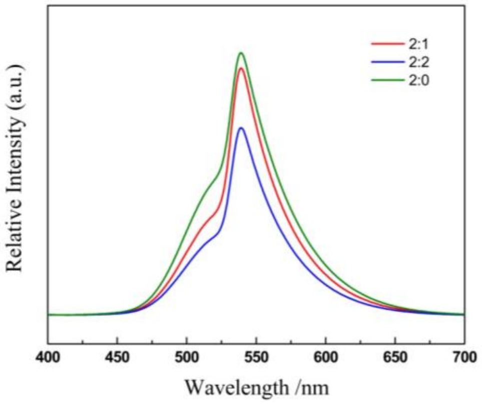

Fig. 2. The emission spectra of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} with different ratios of α/β excited by 265nm

In another word, this red shift could be appeared when $SrAl_2O_4$:αEu^{2+}, βDy^{3+} excited by the high frequency ultraviolet ray. For the Eu^{2+} ion, the electrons in 4f can get transition at seven positions under the ultraviolet. A possible explanation is that the transition of electrons from the valence band to the conduction band liberated the luminous energy which tends to low frequency and high intensity when the material was excited by frequency ultraviolet.

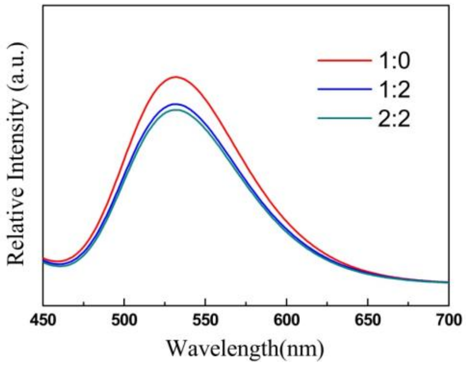

Fig. 3. The emission spectra of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} with different ratios of α/β excited by 365 nm

The emission spectra of samples were fitted to the Gaussian profile when they were excited by 365 nm. It is noteworthy that the curve of 1:2 is coinciding approximately with the ratio of 2:2. Unlike the sample of 1:0, which have a stronger intensity of emission, both of their intensity is weaker indicating that the same amount of Dy^{3+} has the same fluorescent intensity. For the reason, the samples of 1:2 and 2:2 have roughly equal active traps, then the amount of electrons was caught by the hole trap with the same depth under an instantaneous excitation of UV. From the energetics standpoint, the samples having the same molar ratio of Dy^{3+} have an equivalent capacity of stored energy.

It can be seen from Fig. 2 and Fig. 3 the molar ratio of α/β have hardly influence the position of emission spectra, just do the effect on the intensity of fluorescence. It is as the doped Dy^{3+} disturbed the process of excited electron transitions of Eu^{2+} ions from the excited state returning to ground [14]. Generally, bound electrons will be excited to singlet state at room temperature and then go back to ground state with the emission of fluorescence. While the generation of hole traps by doping Dy^{3+} bounded the electrons that were in the triplet state.

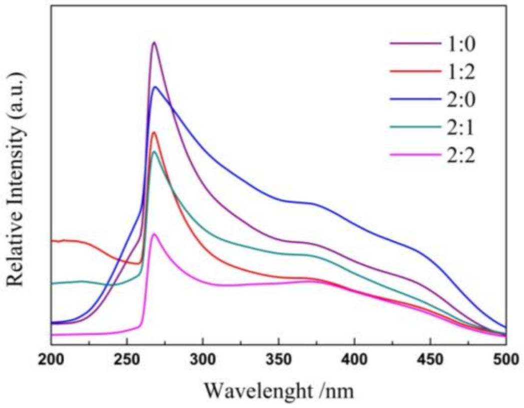

Fig. 4. The excitation spectra of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} with different ratios of α/β

Fig. 4 exhibit the excitation spectra rare earth co-doping strontium aluminates samples with 1:0, 1:2, 2:0, 2:1 and 2:2. From Fig. 4 it can be summarized that the UV absorptivity at 365 nm gets lower gradually with the content of Dy^{3+} increasing. According to the principle of conservation of energy, the batter absorptivity may generate batter fluorescence. It also could be found that the form of the wave of 1:0 and 1:2 are very similar, so do the samples of 2:0 and 2:1. It could be because the content of Eu^{2+} plays a decisive role in the form of the wave. Viewed in toto, these results indicate that the intensity of emission increased with the ratio of α/β increased.

3.2. X-RD analyzes

Form Fig. 5 it can be found that when the α/β ratio is 2:2, 2:0, 1:1 and 0:1, all the patterns show the sharp peaks at 19.9°, 20.1°, 28.4°, 29.3°, 29.9°, 34.8°, 35.1° 2θ has a great agreement with the standard cord of $SrAl_2O_4$ indicating that the content of Eu^{2+} and Dy^{3+} do not destroy the crystal lattice of $SrAl_2O_4$. It also could be seen that the ratio of α/β has no effect on the form of the crystal lattice. When the ratio of α/β is 0:0, it can be observed that the sharp peaks at 31.9°, 45.8°, 56.9°, 66.8°2θ are shown. It could be inferred that there is not only $SrAl_2O_4$ but also $Sr_3Al_2O_6$ existence. In another word the sample of 0:0 is mixture of $SrAl_2O_4$ and $Sr_3Al_2O_6$. The Sr-rich phase would be synthesized when the sample of 0:0 was prepared.

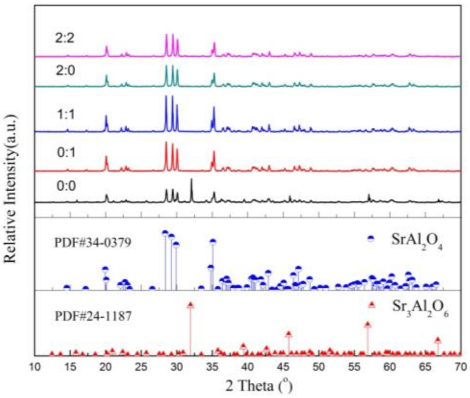

Fig. 5. The x-ray diffraction pattern of $SrAl_2O_4$: αEu^{2+}, βDy^{3+}, and the standard card of $SrAl_2O_4$ and $Sr_3Al_2O_6$

Taken together with our previous in X-RD analysis indicating that the co-doping of Eu^{2+} and Dy^{3+} is advantageous to generate the crystal lattice of $SrAl_2O_4$. The Sr-rich phase of $Sr_3Al_2O_6$ was synthesized without doping rare earth, because of the heterogeneous system on the micro level. The co-doping of rare earth could play a role in forming the phase structure of $SrAl_2O_4$. The specific parameters of crystal lattice were given in Table 1.

Table 1. The cell refinement of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} luminescence materials and $Sr_3Al_2O_6$

Composition	Crystal Form			Crystal Size		
	Crystal System	Bravais Lattice	Space group (Number)	a	b	c
$SrAl_2O_4$: αEu^{2+}, βDy^{3+}	Monoclinic	Primitive	P2/M(10)	8.4424	8.822	5.1607
$Sr_3Al_2O_6$	Cubic	Primitive	Pa-3(205)	15.844	15.844	15.844

3.3. Afterglow properties

In the case of the persistent luminescence of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, the bound electrons can be released from the traps at near room temperature. In the general, when the ratio of α/β is appropriate, the electrons and traps which are provided by Eu^{2+} and Dy^{3+} ion are distributed evenly in the matrix and the distance between the different charge carriers is rather long. While the content of rare earth beyond a certain number, it will bring about thick hole traps leading large trap potential force which make the electrons cannot get transition.

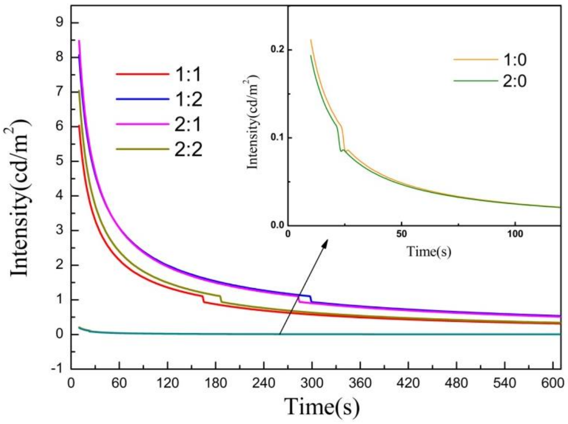

Fig. 6. Afterglow curves of $SrAl_2O_4$ co-doping different ratios of Eu^{2+} /Dy^{3+}

Fig. 6 shows the afterglow properties of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} with different ratios of Eu^{2+} and Dy^{3+} using the instrument of PR-305 afterglow brightness. It could be seen that the afterglow brightness of 1:1 decays below 1cd/m^2 first, and the sample of 1:2 at the last position. It reveals that the sample of 1:2 has the longest afterglow and the others decay successively. Also, it could be seen the sample of 2:1 has the strongest initial brightness and 1:2, 2:2 and 1:1 follow by.

Form the inset picture, it could be found that the initial brightness of 1:0 is higher than 2:0. This is because that the sample of 2:0 which has more luminescence center could emit luminous energy faster than 1:0 during foregoing 10s.

These observations collectively demonstrate that the samples with more Eu^{2+} glow well in emission and the samples which have more Dy^{3+} have the persistent ability to emit. However, it is a certain amount of unit cell centre, the cell point which could be replaced by rare earth ion is limited. When the co-doping ions are more then unit cell centres, redundantly replace will happy. Therefore, the concentration quenching would be happening, when the total content of Eu^{2+} and Dy^{3+} exceed 3mol just as the sample of 2:2. To some extent, with the increasing of Dy^{3+}, the persistence is enhanced. The initial brightness is controlled by content of Eu^{2+}. The samples doping more Eu^{2+} could emitting energy better.

3.4. Influence of the ratios of α: β on color characters of $SrAl_2O_4$: αEu^{2+}, βDy^{3+}

The curves of 0:0 and 0:1 are smooth relatively from Fig. 7 indicating that most of the light generated by D65 light source was reflected and the reflected light was close to white light. It is important to note that the samples of 2:0 and 1:0 show an obvious wave crest at 520 nm and the relative intensity of both are above the 100% from 490 nm to 590 nm. Aside from the ratio of 2:0 and 1:0, the rest samples have a smooth wave crest only and all these are below 100%.

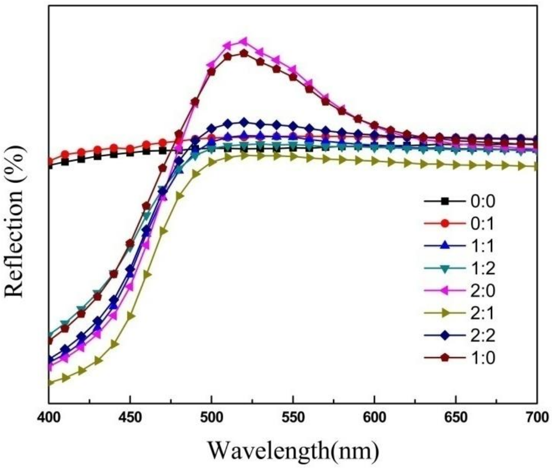

Fig. 7. The reflectivity curve of $SrAl_2O_4$: αEu^{2+}, βDy^{3+} with different ratios

It could be summarized that the samples only doping Eu^{2+} emit fluorescence hybridizing in the reflected light, therefore the samples with the ratios of 2:0 and 1:0 have a higher wave crest above the others. Because the samples of $SrAl_2O_4$: Dy^{3+} as well as the mixture of $SrAl_2O_4$ and $Sr_3Al_2O_6$ were synthesized without the luminescent center, it absorbs hardly the light from 400 nm to 700 nm. The wave bands from 400 to 450 were absorbed by the samples which have the existence of Eu^{2+}.

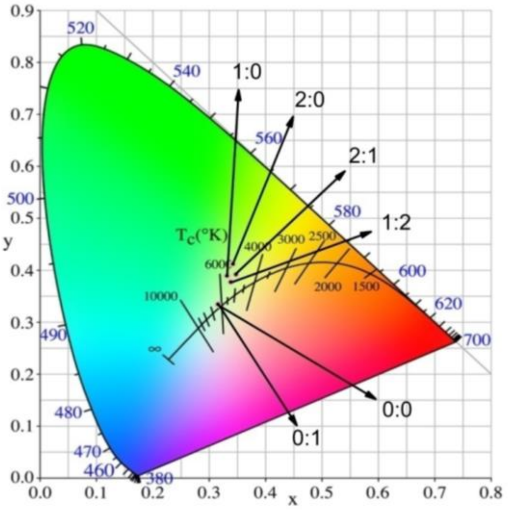

Fig. ***Error! Bookmark not defined.****. CIE 1931 x y Chromaticity Diagram of* *$SrAl_2O_4$: αEu^{2+}, βDy^{3+}*

To directly address the role of α/β intuitively, we have now analyzed the expression of the CIE 1931 x y Chromaticity Diagram. The emission peak of Eu^{2+} ion is 520 nm, while the samples which are prepared to co-doping Eu^{2+} and Dy^{3+} are Yellow or Green Kind. The strontium aluminate and these samples doped Dy^{3+} have emerged white just have a little difference in whiteness. At the same time, it could be found that the samples which have the Eu^{2+} doping are turning yellow with the content of Dy^{3+} increasing.

Therefore, it can be concluded that strontium aluminate and Dy^{3+} co-doping strontium aluminate are white. The color of strontium aluminate mixing Eu^{2+} ion turn yellow with the addition of Dy^{3+}, and it is turning yellow with the ratio of Dy^{3+} increasing.

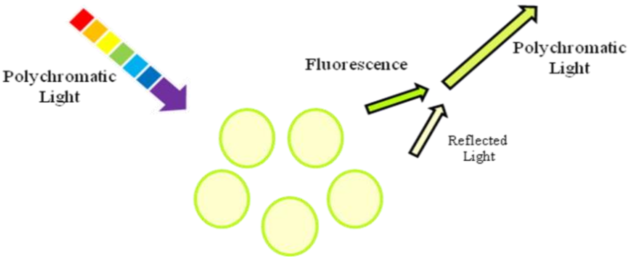

Fig. 8. The formation of color simulation of *$SrAl_2O_4$: αEu^{2+}, $\beta Dy^{3+\backslash}$*

The graphical representation of color formation of phosphor is shown in Fig. 9. From Fig. 9 it could be found obviously the light that was received by the eyes and instrumental was the two-component light which was comprised by fluorescence of $SrAl_2O_4$:αEu^{2+}, βDy^{3+} and reflected light from the nature. Thus, it can be seen easily the samples that have stronger intensity of fluorescence (the step ②in Fig. 1) will be greener. However, it is very hard to evaluate the absolute reflected light without the fluorescence for phosphor. The fluorescence intensity of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} with more Dy^{3+} doping is weaker than it is less. And it can be seen that the color with the ratio of 1:2 which have a weaker fluorescence intensity is yellow closely. So the reflected light approximates yellow, and that is why the samples turn yellow with the ratio of α/β decreased.

4. Conclusions

In order to investigate the influence of α/β ratio on color characteristics of $SrAl_2O_4$:αEu^{2+}, βDy^{3+} phosphors. $SrAl_2O_4$:αEu^{2+}, βDy^{3+} were fabricated by solid-state reaction and several ratios of rare earth strontium aluminate phosphors were prepared. Rare earth strontium aluminates were used as the rare-earth luminescent material and the material such as H_3BO_3 as a flux. From the analysis, we could get the conclusion that the color characteristics of $SrAl_2O_4$:αEu^{2+}, βDy^{3+} phosphors were different from one another as the α/β ratio changed. The emission spectra showed that the emission intensity increased with the addition of α/β ratio at first then decreased when the total over 3% mol. From afterglow decay results, it could be found that the sample without Dy^{3+} doping showed shorter persistent time. From the X-RD analysis indicating that the co-doping of Eu^{2+} and Dy^{3+} is conducive to generate the crystal form of $SrAl_2O_4$. From the measurements of color properties, it could be inferred that with the content of Dy^{3+} increased $SrAl_2O_4$:αEu^{2+}, βDy^{3+} turned yellower gradually. In conclusion, further research aspects held promise in this interesting scientific domain. It was possible to obtain regularity that was about the color of the emission and reflected light for the most kinds of phosphors.

Acknowledgements

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