

Preparation of Red-emitting Europium(III) doped $\text{SrAl}_2\text{B}_2\text{O}_7$ Phosphors and Investigation of Luminescent Properties

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Abstract. Red-emitting Europium(III) doped $\text{SrAl}_2\text{B}_2\text{O}_7$ phosphors have been prepared by precipitation method, and its luminescent properties under UV excitation have been investigated. The phosphors are characterized by x-ray diffraction (XRD) and photoluminescence spectra. The $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors can be obtained at 900°C by calcining precipitation precursor. These phosphors can be effectively excited by UV light at 394nm. In emission spectra, the strongest peak at 618 nm correlating to red emission is due to the electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} ions. The luminescent properties of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors with 8 mol% doping concentration of Eu^{3+} are optimal.

Introduction

Recently, the aluminoborates are regarded as the most promising phosphors host lattice which exhibit efficient energy transfer, high absorption in UV and thermodynamic stability [1, 2]. The aluminoborates phosphors were usually synthesized by conventional high temperature solid state reaction. The calcination temperature was over 1100°C for 4-5 h [3-5]. The phosphors agglomeration is severe, and the product need long time grinding to fit for following process. As a result, the crystal lattice of phosphor was destroyed and the luminescent intensity was decreased greatly. Spherical phosphor crystal with high luminance, high resolution and less dosage for coating can be achieved by precipitation method [6, 7]. The precipitation method is suitable for industrialized production besides solid state reaction method, and microcrystalline powder can be achieved at relatively lower temperature by this method.

In this paper, trivalent europium ions activated $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ red-emitting phosphors have been prepared by precipitation method, and its luminescent properties are investigated.

Experimental

The stoichiometric amounts of Eu_2O_3 was dissolved in dilute nitric acid solution (1:2 = v/v) to form aqueous solution. And then the amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and H_3BO_3 were added into aqueous solution. Under vigorous stirring, the mixture was added dropwise to urea aqueous solution at room temperature, the pH value of this solution was adjusted to be around 9 by adding ammonia. After continuous stirring for 1h, the precipitation was filtered, washed by distilled water. After drying at 70°C for 12 h, the resulting powder was then calcined in air at $850\text{--}1000^\circ\text{C}$ for 1-4 h to form the final powder sample.

The structure of phosphor powder was characterized by Rigaku D/max-2200 diffractometer type X-ray diffraction (XRD) employing $\text{Cu K}\alpha$ radiation at 40kV and 20 mA, a step size of 0.02° (2θ) was used with a scan speed of $8^\circ/\text{min}$. The luminescent properties were measured by a Hitachi F-7000 type fluorospectrophotometer (PMT Voltage: 500V, Scan speed: 1200 nm/min). All the measurements were performed at room temperature.

Results and discussion

Fig.1 shows the XRD patterns of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors calcined at 850- 1000°C for 3h. It can be seen in Fig. 1 that the major peaks assigned to $\text{SrAl}_2\text{B}_2\text{O}_7$ along with one impurity phase peak of EuBO_3 were observed from the sample calcined at 850°C. When the temperature was increased to 900°C or over, only the single phase of $\text{SrAl}_2\text{B}_2\text{O}_7$ was observed and the impurity phase EuBO_3 peaks disappeared.

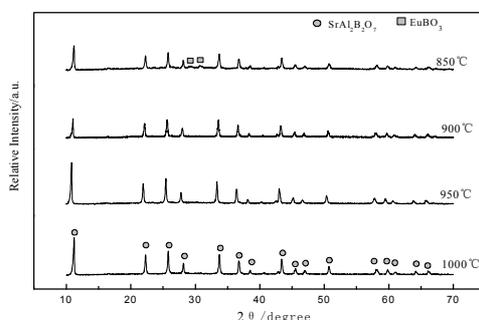


Fig.1 XRD spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ prepared at different temperature

Fig. 2 shows the excitation spectrum of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors monitored at 618 nm. The band at 260nm is assigned to the charge transfer transition between Eu^{3+} ions and neighboring O^{2-} ions. The strongest excitation peak at 394 nm is due to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of Eu^{3+} ions, the other peaks attributed to the various $f \rightarrow f$ transition of Eu^{3+} ions.

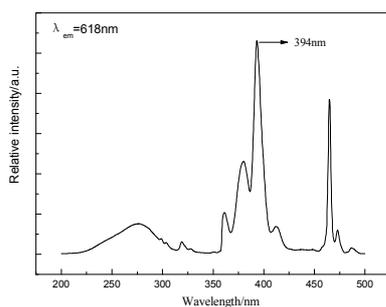


Fig.2 Excitation spectrum of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$

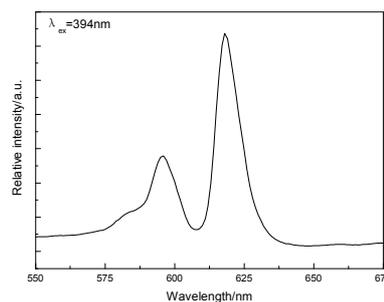


Fig.3 Emission spectrum of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$

Fig.3 shows the emission spectrum of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphor pumped by 394nm light sources. The emission spectrum is composed of two characteristic transitions of Eu^{3+} ions: one at 596 nm is ascribed to the magnetic dipole transition ($\text{Eu}^{3+}: {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$); another at 618 nm is the electric dipole transition ($\text{Eu}^{3+}: {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$), which is hypersensitive to local surrounding around Eu^{3+} ions. So, the electric dipole transition of Eu^{3+} ions dominates the photoluminescence processes in our spectral experiments. Here, Eu^{3+} ions are also regarded as a nanoprobe to find out local structure information of host lattice.

Fig. 4 shows the emission spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors prepared at different temperature. It can be seen in Fig. 4 that the luminescent intensities of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors increase with the calcination temperature; the luminescent intensity can reach up to the maximum at 950°C; and the luminescent intensity decreases beyond 950°C.

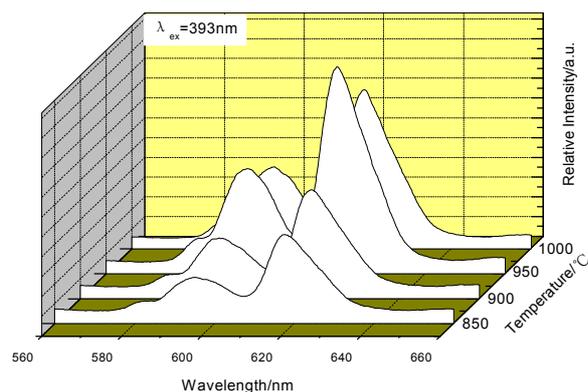


Fig. 4 Emission spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors prepared at different temperature

The XRD spectra of the phosphors $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x \leq 0.12$) are shown in Fig.5.

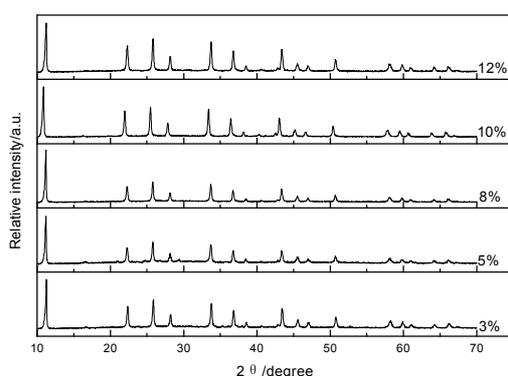


Fig. 5 XRD spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ with different Eu^{3+} doping molar ratios

It shows from Fig.5 that all peaks of XRD patterns can be attributed to the pure phase $\text{SrAl}_2\text{B}_2\text{O}_7$, and no other impurity phase peaks were observed. Moreover, peaks of rare earth oxide phase can not be found. The structure of samples with different doping concentration of Eu^{3+} ions were the same, the position and intensity of peaks are not obviously changed. It can be deduced that Sr^{2+} ions in $\text{SrAl}_2\text{B}_2\text{O}_7$ are replaced by Eu^{3+} ions. The calculating unit cell parameters a and c of $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x \leq 0.12$) are shown in table 1.

Table 1 Unit cell parameters of $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$

| $x_{\text{Eu}^{3+}}$ (%) | a (nm) | c (nm) |
|--------------------------|----------|----------|
| 0 | 0.4915 | 4.7952 |
| 3 | 0.4911 | 4.7948 |
| 5 | 0.4909 | 4.7934 |
| 8 | 0.4906 | 4.7868 |
| 10 | 0.4892 | 4.7867 |
| 12 | 0.4886 | 4.7859 |

It can be seen from the Table 1, the unit cell parameters a and c are decreased as the increase of the molar fraction of Eu^{3+} ions doping ($x \leq 0.12$). The structure of $\text{SrAl}_2\text{B}_2\text{O}_7$ has been distorted when Sr^{2+} ions are replaced by Eu^{3+} ions, because the ionic radius of Eu^{3+} ions is smaller than Sr^{2+} ions.

The Emission spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ with different Eu^{3+} doping molar ratios are shown in Fig.6. The luminescent intensity of phosphors is enhanced as the increase of the molar fraction of Eu^{3+} and reaches a maximum at 8% (mol). The luminescent intensity of samples is decreased when the molar fraction of Eu^{3+} doping is over 8% concentration. With Eu^{3+} concentration increasing, the amount of

luminescent centers increase in $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ crystal so that the intensity of luminescent spectra at 618nm increases. Up to 8%, the increasing of Eu^{3+} ions causes the quenching of concentration.

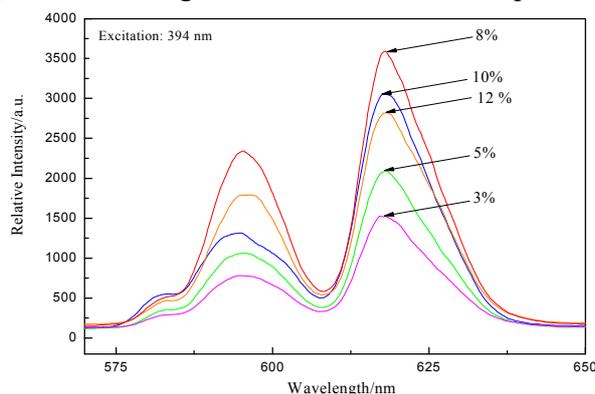


Fig. 6 Emission spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ with different Eu^{3+} doping molar ratios

Fig.7 shows the emission spectra of $\text{Sr}_{0.92}\text{Eu}_{0.08}\text{Al}_2\text{B}_2\text{O}_7$ phosphors at 950°C with different calcining times. As shown in Fig.5, the emission intensities of $\text{Sr}_{0.92}\text{Eu}_{0.08}\text{Al}_2\text{B}_2\text{O}_7$ phosphors increase with calcining times from 1 to 3h, and then decreased.

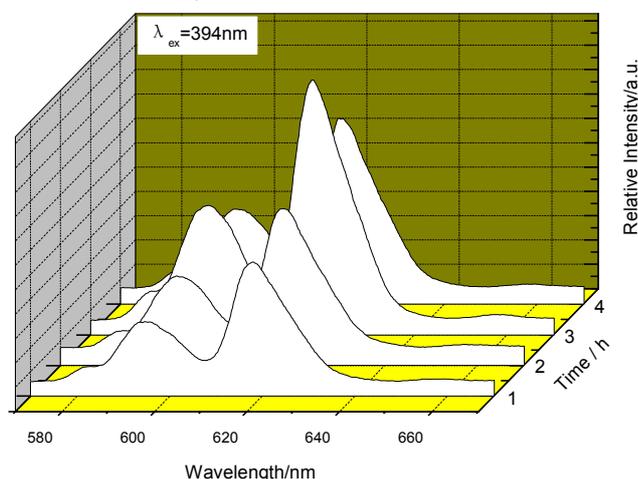


Fig. 7 Emission spectra of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ prepared for different time

Conclusion

The red-emitting phosphors $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ have been prepared by the precipitation method Using Urea as precipitating agent, and their emission abilities could be improved by optimizing the synthesizing conditions. It is found that $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ can be effectively excited by ultraviolet light 394 nm, and the strongest peak of emission spectrum at 618 nm correlating to red radiation was due to the forced electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of the doped Eu^{3+} ions. The luminescent properties of phosphor sample with 8 mol% doping concentration of Eu^{3+} were optimal. The phosphors of $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ prepared by the precipitation method have a great application prospect.

Acknowledgments

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