Trivalent rare earth activated SrCaAl$_2$O$_5$ phosphor for white light-emitting diode

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ABSTRACT

Eu$^{3+}$, Dy$^{3+}$ activated SrCaAl$_2$O$_5$ phosphor were synthesized by the combustion method at 550°C. The prepared phosphor characterized by X-ray diffraction and photoluminescence measurements. The photoluminescence study of Eu$^{3+}$ doped phosphor shows that the intensity of electric dipole transition ($^2D_0$→$^2F_2$) at 615 nm dominates over that of magnetic dipole transition ($^2D_0$→$^2F_1$) at 596 nm under 395 nm excitation. The PL emission spectrum of Dy$^{3+}$ ion at 350 nm excitation gives an emission band at 484 nm (blue) and 575 nm (yellow). The optimum concentration of both the dopant having highest luminescence intensity is found to be 0.5 mole%. The obtained PL results indicated that prepared phosphor is suitable as near UV excited white light-emitting diodes. Copyright © 2013 VBRI press.

Keywords: Combustion synthesis; photoluminescence; phosphor; solid state lighting.

Introduction

In recent years, the development of tricolor phosphors suitable for near-ultraviolet (UV) excitation have been attracting more attention for fabricating white LED because they have a huge number of important applications in backlight of the liquid crystal display (LCD), consumer electronics, automobile light and traffic signals [1-4]. In recent years, large number of work has been done on Eu$^{3+}$ doped phosphors because it is one of the most promising red-orange phosphors for white LEDs and solid state lighting [5-7]. Due to the $^5D_{0}→^7F_{2}$ transition with in europium, phosphors shows intense red luminescence at around 615 nm wavelength having excitation band at around 395 nm [8, 9]. Dy$^{3+}$ ion which has been studied extensively because it gives two dominant emission bands in the blue region (470–500 nm) and yellow region (560–600 nm), which is useful for solid state lighting applications [10-12]. It is very well known that the trivalent dysprosium can be used as a luminescent center because it can emit yellow and blue lights corresponding to the $^4F_{9/2}→^4H_{15/2}$ and $^4F_{9/2}→^4H_{13/2}$ transitions. Especially, Dy$^{3+}$, Eu$^{3+}$ doped phosphors have played an important role in developing white LEDs. Recently some researchers have been reported new luminescent materials applied in white light emission diodes (LEDs) [13-17]. The search for stable, inorganic rare earth based red, blue, yellow phosphors with high absorption in the near UV/blue spectral region is therefore an attractive research task. In this paper we present and discuss the photoluminescence properties of the trivalent rare earth doped SrCaAl$_2$O$_5$ phosphors. In this work, trivalent rare earth activated Eu,
Dy doped SrCaAl$_2$O$_5$ phosphor were synthesized by low-cast conventional combustion method.

**Experimental**

**Materials**

The phosphor SrCaAl$_2$O$_5$: RE (RE=Eu, Dy) with varying concentration of Eu, Dy were prepared by the combustion method. All the starting materials employed in the experiment are of Merck-analytical grade. The starting materials are Ca(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Al(NO$_3$)$_3$.9H$_2$O, Eu$_2$O$_3$, Dy$_2$O$_3$ and Urea (NH$_2$CONH$_2$, Merk) was used as fuel.

The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Ka radiation) at a scanning step of 0.010, continue time 20s, in the 20 range from 10$^0$ to 80$^0$. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RFPC5301 Spectrofluorophotometer. The same amount of sample 2 gm was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

**Combustion method**

For the preparation of SrCaAl$_2$O$_5$: RE (RE=Eu, Dy) phosphors, all starting materials used were of Merck-analytical grade. The starting materials are calcium nitrate, strontium nitrate, aluminium nitrate, europium oxide, dysprosium oxide and Urea was used as fuel.

Europium oxide and dysprosium oxide are converted into nitrate form by mixing of appropriate amount of dilute nitric acid. All the mixtures were mixed according to stoichiometric ratio. For these stoichiometric compositions of the metal nitrates as oxidizers and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which serve as a numerical coefficient so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. Weighted quantities of each nitrates and urea are added to it and the mixture is crushed together for ½ hour to form a thick paste. The resulting paste is transferred into a vertical furnace maintained at 550°C. Flame temperature as high at 1600°C converts the vapour phase into mixed aluminates. The flame persists for about 30 seconds. The final product obtained is in the fluffy form, which is used for the further investigations.

**Results and discussion**

**XRD phase analysis**

In order to explore the crystal phase structure, the XRD phase analysis was adopted. The typical XRD patterns of SrCaAl$_2$O$_5$ phosphor are shown in Fig. 1. For the obtained phase, it is carefully observed that there are no peaks of raw materials. It is found that the main phase does not agree to any JCPDS available. The standard JCPD file of SrCaAl$_2$O$_5$ material is not available. Consequently, we speculate that the obtained unknown phase is likely to be a new phase. With respect to this point, a further study is still being carried on.

Fig. 2 shows the excitation spectra of the SrCaAl$_2$O$_5$:Eu$^{3+}$ phosphors by monitoring the emission wavelength at 615 nm. The excitation lines appeared at longer wavelengths correspond to the characteristic f→f transitions of Eu$^{3+}$ ion. These lines are assigned as follows $^5$F$_0$$\rightarrow$$^7$D$_1$ (363 nm), $^5$F$_0$$\rightarrow$$^7$G$_4$ (381nm) and the main excitation line $^5$F$_0$$\rightarrow$$^7$L$_6$ (395 nm). As seen in Fig. 2, the intensity of the transition at 395 nm is the highest in the excitation spectra.

![Fig. 1. XRD of SrCaAl$_2$O$_5$ host.](image)

![Fig. 2. Excitation spectra of SrCaAl$_2$O$_5$: Eu$^{3+}$ under emission 615 nm.](image)

Fig. 3 represents the emission spectra upon direct excitation the $^5$F$_0$$→$$^7$L$_6$ transition of Eu$^{3+}$ at 395nm, which is excitation of the white light emitting diode. The luminescence spectrum of SrCaAl$_2$O$_5$: Eu$^{3+}$ is to some extent influenced by surrounding ligands of the host aluminates material because the transitions of Eu$^{3+}$ involve only a rearrangement of electrons within the inner 4f subshell [18]. There are five main sharp emission peaks at near 582nm, 589nm, 596nm, 615nm and 621 nm, among which the intensity of 615 nm line is the highest. The strongest doublet peak located at 615nm and 621nm contribute the red emission due to the hypersensitive $^5$D$_0$$→$$^5$F$_2$, $^5$D$_0$$→$$^5$F$_3$ electric dipole transition. Orange-reddish emissions peaked
at 582 nm, 589 nm and 596 nm which are mainly from the \( ^5D_0 \rightarrow ^7F_1 \) magnetic dipole transitions of Eu\(^{3+} \) ions. Upon excitation with 395 nm UV irradiation, the emission spectra are described by the well known \( ^5D_0 \rightarrow ^7F_1 \) (\( J = 1, 2, 3 \)) emission lines of the Eu\(^{3+} \) ions with the strong emission for \( J = 2 \) at 615 nm, which allows that the Eu\(^{3+} \) occupies a center of asymmetry in the host lattice [19, 20]. It is well known that the \( ^5D_0 \rightarrow ^7F_2 \) red emission of Eu\(^{3+} \) ions, which is due to hypersensitive transitions with \( \Delta \lambda = 2 \), which is strongly influenced by the outside surroundings.

![Figure 3: Emission spectra of SrCaAl\(_2\)O\(_5\): Eu\(^{3+} \) under excitation 395 nm.](image)

As shown in Fig. 3, the transition \( ^5D_0 \rightarrow ^7F_2 \) is much stronger than the transition \( ^5D_0 \rightarrow ^7F_1 \) which suggests that the Eu\(^{3+} \) located in a distorted (or asymmetric) cation environment, this is favorable to improve the color purity of the red phosphor. Most of the f–f transitions of the trivalent lanthanides are little affected by the environment. A few, however, are sensitive to the environment and become more intense. Such transitions have been called hypersensitive transitions and the intensity can vary by orders of magnitude, depending on the local environment [19, 21]. One of the interesting results of this work is that the excitation spectrum of the Eu\(^{3+} \) doped SrCaAl\(_2\)O\(_5\) phosphor could be strongly excited by the near-UV light, which has potential as a near-UV LED converted phosphor in solid state lighting technology [22-23].

**Photo-luminescence properties of SrCaAl\(_2\)O\(_5\): Dy\(^{3+} \) phosphor**

Fig. 4 shows an excitation spectrum of SrCaAl\(_2\)O\(_5\); Dy\(^{3+} \) phosphor, excitation bands observed in the range from 300 to 400 nm which are due to 4f–4f transitions of Dy\(^{3+} \) ion. The excitation spectra for the emission at 575 nm consist of a series of line spectra in 300–400 nm with the strongest one at 350 nm and some lines observed at 325, 365 and 385 nm, which are ascribed to the transitions from the ground state to excitation states in the \( 4f^8 \) configuration of Dy\(^{3+} \). The low-symmetry location of Dy\(^{3+} \) ions in the present phosphor results in the predominate emission of \( 4F_{9/2} \rightarrow 4H_{13/2} \) transition. The position of the emission peak is not influenced by the Dy\(^{3+} \) concentration but the luminescence intensity changes a lot. It is well known that the color of the trivalent dysprosium luminescence is close to white color. The whiteness mainly comes from the
mixture of the Dy\textsuperscript{3+} emissions in blue (484 nm) and in yellow (575 nm) regions. PL results show the excitation peak at 350 nm, which is away from Hg excitation and is useful for solid state lighting.

**Effect of activators Eu\textsuperscript{3+} and Dy\textsuperscript{3+} ion concentration on SrCaAl\textsubscript{2}O\textsubscript{3} phosphor**

The emission intensity dependence on the Eu\textsuperscript{3+} and Dy\textsuperscript{3+} ion concentration is shown in Fig. 6. In order to optimize the luminescence properties of Eu\textsuperscript{3+}, Dy\textsuperscript{3+} ion in SrCaAl\textsubscript{2}O\textsubscript{3} phosphor, the relationship between emission intensity and concentration of Eu\textsuperscript{3+}, Dy\textsuperscript{3+} ion is shown in Fig. 6.

From Fig. 6, it is clearly observed that with the increase in concentrations of Eu\textsuperscript{3+} and Dy\textsuperscript{3+}, the intensities of the emission lines are enhanced significantly and reaching a maximum at a concentration of 0.5 mole % and then decrease due to concentration quenching. Concentration quenching is caused by the migration of excitation energy between the emission ions or energy migration to quenching centers where the excitation energy is lost by non-radioactive transition. It is clearly observed from Fig. 6, the highest emission intensity peak is observed at a concentration of 0.5 mole % for both the dopant and then intensity decreases gradually owing to the energy transfer between the neighboring Eu\textsuperscript{3+} and Dy\textsuperscript{3+} ions, which was corresponding to the quench of the emission intensity of Eu\textsuperscript{3+} and Dy\textsuperscript{3+} [26-27]. Lower doping concentrations and excessive doping lead to weak luminescence and concentration quenching of the Eu\textsuperscript{3+} and Dy\textsuperscript{3+} emission, respectively. The concentration quenching of both the dopant is mainly caused by cross-relaxation, i.e. energy transfers from one ion to another neighbor ion by transition that match in energy.

**Conclusion**

In the present work, the novel Eu\textsuperscript{3+} and Dy\textsuperscript{3+} doped SrCaAl\textsubscript{2}O\textsubscript{3} phosphor were prepared by the combustion method. The PL spectroscopic characterizations of the prepared phosphors were done using excitation and emission spectra. In Eu\textsuperscript{3+} doped phosphor, the strongest excitation bands appeared at 395 nm. Upon excitation with near ultraviolet light, the phosphor showed strong red-emission lines at 615 nm correspond to the forced electric dipole transition of Eu\textsuperscript{3+} \( ^{5}D_{0} \rightarrow ^{7}F_{2} \). In Dy\textsuperscript{3+} doped phosphor two emission bands are present having excitation 350 nm, which corresponds to the transitions of \( ^{5}F_{2} \rightarrow ^{9}H_{15/2} \) (blue) and \( ^{5}F_{2} \rightarrow ^{9}H_{13/2} \) (yellow). When the concentration of both the doping where 0.5 mole % in SrCaAl\textsubscript{2}O\textsubscript{3} phosphors have the strongest PL emission intensity observed due to concentration quenching. Thus, it is expected from PL emission the prepared phosphors may be efficient photo luminescent materials for solid-state lighting and could be the promising red phosphors for white LEDs.

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**References**

1. M.G. Craford, Commerical, Light Emitting Diode Technology, Kluwer Academic Publishers, Orrecht, 1996.
2. N. Nakamura, G. Fasol, *The Blue Laser Diodes*, Springer, Berlin, 1997.
3. Kim, J.S.; Jeon, P.E.; Choi, J.C.; Park, H.L.; Mho, S.I.; Kim, G.C.; Appl. Phys. Lett. 2004, 84, 2931.
4. Doble, N.S.; Pawade, V.B.; Doble, S.J.; Adv. Mat. Lett. 2011, 2(5), 327-330.
5. Doble, K.N.; Doble, S.J.; Adv. Mat. Lett. 2013, 4(3), 207.
6. Wang, S.F.; Rao, K.K.; Wang, Y.R.; Hsu, Y.F.; Chen, S.H.; Lu, Y.C.; J. Amer Ceram Soc. 2009, 8, 1732.
7. Rao, C.A.; Rao, P.; Nannapaneni, V.; Murthy, K. V. R.; Adv. Mat. Lett. 2013, 4(3), 207.
8. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2013, 4(3), 207.
9. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 29, 527.
10. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 1, 322.
11. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
12. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
13. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
14. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
15. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
16. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
17. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
18. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
19. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
20. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
21. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
22. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
23. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
24. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
25. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
26. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
27. Shinde, K.N.; Doble, S.J.; Adv. Mat. Lett. 2011, 2, 132.
26. Dexter, D.L.; Schulman, J. H.; J. Chem. Phys. 1954, 22, 1063. DOI: 10.1063/1.1740265

27. Yerpude, A.N.; Dhoble, S.J.; J. Lumin. 2012, 132, 2975. DOI: 10.1016/j.jlumin.2012.04.037

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