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Trivalent rare earth activated SrCaAl₂O₅ phosphor for white light-emtting diode

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ABSTRACT

Eu³⁺, Dy³⁺ activated SrCaAl₂O₅ 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 Eu³⁺ doped phosphor shows that the intensity of electric dipole transition (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) at 615 nm dominates over that of magnetic dipole transition (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) at 596 nm under 395nm excitation. The PL emission spectrum of Dy³⁺ ion at 350nm 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.

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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 Eu³⁺ 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 ${}^{5}D_{0}$ — ${}^{7}F_{2}$ transition with in europium, phosphors shows intense red luminescence at around 615nm wavelength having excitations band at around 395 nm [8, 9]. Dy³⁺ 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 ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transitions. Especially, Dy³⁺, Eu³⁺ 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 SrCaAl2O5 phosphors. In this work, trivalent rare earth activated Eu, Dy doped $SrCaAl_2O_5$ phosphor were synthesized by low-cast conventional combustion method.

Experimental

Materials

The phosphor SrCaAl₂O₅: 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(NO₃)₂ , Sr(NO₃)₂ , Al(NO₃)₃ .9H₂O, Eu₂O₃, Dy₂O₃ and Urea (NH₂CONH₂, 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-K α radiation) at a scanning step of 0.010, continue time 20s, in the 2 θ range from 10^o to 80^o. 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 SrCaAl₂O₅: RE (RE=Eu,Dy) phosphors, all starting materials used were of Merckanalytical 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 in to nitrate form by mixing of appropriate amount of dilute nitric acid. All the mixtures were mixed according to stochometric 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 1/2 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 $SrCaAl_2O_5$ 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 JCPDs file of $SrCaAl_2O_5$ 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.

Photoluminescence properties of SrCaAl2O5:Eu3+ phosphor

Fig. 2 shows the excitation spectra of the SrCaAl₂O₅:Eu³⁺ phosphors by monitoring the emission wavelength at 615 nm. The excitation lines appeared at longer wavelengths correspond to the characteristic f \rightarrow f transitions of Eu³⁺ ion. These lines are assigned as follows $^{7}F_{0}\rightarrow^{5}D_{4}$ (363 nm), $^{7}F_{0}\rightarrow^{5}G_{4}$ (381nm) and the main excitation line $^{7}F_{0}\rightarrow^{5}L_{6}$ (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 SrCaAl₂O₅ host.

Fig. 2. Excitation spectra of SrCaAl₂O₅: Eu³⁺ under emission 615 nm.

Fig. 3 represents the emission spectra upon direct excitation the ${}^{7}F_{0}$ → ${}^{5}L_{6}$ transition of Eu³⁺ at 395nm, which is excitation of the white light emitting diode. The luminescence spectrum of SrCaAl₂O₅: Eu³⁺ is to some extent influenced by surrounding ligands of the host aluminates material because the transitions of Eu³⁺ 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 ${}^{5}D_{0}$ → ${}^{7}F_{2}$, ${}^{5}D_{0}$ → ${}^{7}F_{3}$ electric dipole transition. Orange-reddish emissions peaked

at 582nm, 589nm and 596 nm which are mainly from the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transitions of Eu³⁺ ions. Upon excitation with 395nm UV irradiation, the emission spectra are described by the well known ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1, 2, 3) emission lines of the Eu³⁺ ions with the strong emission for J= 2 at 615 nm, which allows that the Eu³⁺ occupies a center of asymmetry in the host lattice [**19**, **20**]. It is well known that the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ red emission of Eu³⁺ ions, which is due to hypersensitive transitions with $\Delta J = 2$, which is strongly influenced by the outside surroundings.

Fig. 3. Emission spectra of SrCaAl₂O₅: Eu³⁺ under excitation 395 nm, where (a) Eu=0.1 mole % (b) Eu=0.2 mole % (c) Eu=0.5 mole % (d) Eu=1 mole %.

As shown in **Fig. 3**, the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is much stronger than the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ which suggests that the Eu³⁺ 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 Eu³⁺ doped SrCaAl₂O₅ 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 SrCaAl2O5: Dy3+ phosphor

Fig. 4 shows an excitation spectrum of SrCaAl₂O₅; Dy³⁺ phosphor, excitation bands observed in the range from 300 to 400 nm which are due to $4f \rightarrow 4f$ transitions of Dy³⁺ ion. The excitation spectra for the emission at 575 nm consist of a series of line spectra in 300–400nm 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 $4f^9$ configuration of Dy³⁺.

Fig. 5 shows emission spectrum taken under excitation at 350 nm. The emission spectrum was measured in the 400–650 nm range. Both the excitation and the emission

spectra comprise the characteristic lines of Dy³⁺ with in 4f⁹ configuration [24]. PL emission peaks are observed at blue and yellow regions of the spectrum due to Dy³⁺ ion. Two emission bands centered at 484 and 575 nm were observed, originating from two different origins. The blue (484 nm) and yellow (575 nm) emission bands are typical emissions of Dy³⁺ corresponding to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{6}H_{13/2}$ transitions, respectively. It is well known that Dy³⁺ emission around 484 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$) is of electric dipole origin [25]. It is well known that the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ hypersensitive transition belongs to a forced electric dipole transition and this is predominant only when Dy³⁺ ions are located at low-symmetry sites with no inversion centers.

Fig. 4. Excitation spectra of SrCaAl₂O₅: Dy³⁺ under emission 575 nm.

Fig. 5. Emission spectra of SrCaAl₂O₅:Dy³⁺ phosphors under excitation 350 nm, where (a) Dy=0.1 mole % (b) Dy =0.2 mole % (c) Dy =0.5 mole % (d) Dy =1 mole %.

The low-symmetry location of Dy^{3+} ions in the present phosphor results in the predominate emission of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ 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^{3+} emissions in blue (484 nm) and in yellow (575nm) 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^{3+} and Dy^{3+} ion concentration on $SrCaAl_2O_5$ phosphor

Research Article

The emission intensity dependence on the Eu³⁺ and Dy³⁺ ion concentration is shown in **Fig. 6**. In order to optimize the luminescence properties of Eu³⁺, Dy³⁺ ion in SrCaAl₂O₅ phosphor, the relationship between emission intensity and concentration of Eu³⁺, Dy³⁺ ion is shown in **Fig. 6**.

Fig. 6. Variation in the PL intensity as function of the $Eu^{\rm 3+}$ and $Dy^{\rm 3+}$ ion concentration in SrCaAl_2O5 phosphor

From Fig. 6, it is clearly observed that with the increase in concentrations of Eu³⁺ and Dy³⁺, 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 Eu³⁺ and Dy³⁺ ions, which was corresponding to the quench of the emission intensity of Eu^{3+} and Dy^{3+} [26-27]. Lower doping concentrations and excessive doping lead to weak luminescence and concentration quenching of the Eu³⁺ and Dy³⁺ 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^{3+} and Dy^{3+} doped $SrCaAl_2O_5$ phosphor were prepared by the combustion method. The PL spectroscopic characterizations of the prepared phosphors were done using excitation and emission spectra. In Eu^{3+} doped phosphor, the strongest excitation lines appeared at 395nm. Upon excitation with near UV light, the phosphor showed strong red-emission lines at 615 nm correspond to the forced electric dipole ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} . In Dy^{3+} doped phosphor two emission bands are present having excitation 350 nm,

which corresponds to the transitions of ${}^{4}F_{9/2} \rightarrow {}^{6}H1_{15/2}$ (blue) and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow). When the concentration of both the doping where 0.5 mole % in SrCaAl₂O₅ 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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