Influence of Li$^+$ doping on photoluminescence properties of Sr$_5$(PO$_4$)$_3$F:Eu^{3+}

K. N. Shinde* and S. J. Dhoble

Department of Physics, RTM Nagpur University, Nagpur 440033, India

*Corresponding author. Tel.: (+91) 9822239826; E-mail: kartik_shinde@rediffmail.com

ABSTRACT

In this article, the influence of lithium co-doped on Sr$_5$(PO$_4$)$_3$F:Eu^{3+} halophosphate based phosphor reported. The Sr$_5$(PO$_4$)$_3$F:Eu^{3+} and Sr$_5$(PO$_4$)$_3$F:Eu^{3+}, Li$^+$ phosphors were prepared by combustion synthesis route using urea as the fuel. The phosphors were characterized by X-ray diffraction (XRD) and photoluminescence (PL) techniques. The powders were annealed at 900°C and 1200°C and characterized by X-ray diffraction (XRD) which shows that the major crystalline phases from the as prepared or annealed powder samples were identical. The PL results show that the incorporation of Li$^+$ ions into the Sr$_5$ (PO$_4$)$_3$F:Eu^{3+} lattice could induce a remarkable improvement of the PL intensity in red region at 395 nm excitation wavelength. The highest emission intensity was observed with the compound of Eu$^{3+}_{0.5\ mol\%}$ and Li$^+_{0.5\ mol\%}$ co-doped Sr$_5$(PO$_4$)$_3$F, whose brightness was increased by a factor of more than 3.0 in comparison with that of the Sr$_5$(PO$_4$)$_3$F:Eu^{3+}. The 300–400 nm is Hg free excitation (Hg excitation is 85% 254 nm wavelength of light and 15% other wavelengths), which is characteristic of solid-state lighting phosphors. Hence PL emission in trivalent europium co-doped with lithium may be efficient photoluminescent materials for solid-state lighting phosphors as a red component. Copyright © 2010 VBRI press.

Keywords: Phosphor; solid state lighting; phosphate; photoluminescence.

K. N. Shinde is research student at the Department of Physics, RTM Nagpur University, Nagpur, India. He is working on phosphate based phosphor materials for lamp industry.

S. J. Dhoble is Professor at the Department of Physics, RTM Nagpur University, Nagpur, India. His current research interest is on the photoluminescent and thermoluminescent materials. He has published many research papers in various journals.

Introduction

Phosphate based inorganic compounds doped with rare earth ions form an important family of phosphors for solid state lighting applications. White light-emitting diodes (W-LEDs) offer benefits such as high luminous efficiency, low energy consumption, long lifetime, and environment friendly and so on. They are tipped to be the next generation solid state lighting, in the replacement of conventional incandescent and fluorescent lamps which are Hg pollutants, frangible and high energy consumption [**1, 2**]. In the recent years, research on the phosphors used for white LEDs has become a hot topic and gained maturity. A large number of papers have been published in the related journals about the successful synthesis and luminescence of rare earth phosphors with the orientation of exploring novel phosphors suitable for solid state lighting. As an important family of luminescent materials, orthophosphates have been paid intense attention because of their excellent properties, i.e., the large band gap and the high absorption of PO$_4^{3-}$ in VUV region, moderate phonon energy, the high thermal and chemical stability, and the exceptional optical damage threshold [**3–5**]. Phosphate is considered an excellent host for preparing phosphor due to its low sintering temperature and good stability. However, there are few reports on the research of phosphate system as host for a white phosphor.
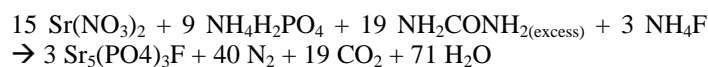
Recently, Dhoble and coworker reported some phosphate based phosphors Eu^{3+} and Dy^{3+} activated $Ca_3(PO_4)_2$ [6] and Dy^{3+} and Eu^{2+} ion in $M_5(PO_4)_3F$ (M = Ba, Sr, Ca) phosphors [7]. Also Ping Zhang et al. reported some new methods for the preparation of phosphate based phosphor, which are used in the commercial application [8].The novel red-emitting phosphors $Ca_{19}Zn_2(PO_4)_{14}:Eu^{3+}$ have been successfully synthesized by a modified solid-state reaction [9]. White light-emitting diodes (WLED) are attracting significant attention in recent years as a potential replacement for the incandescent and fluorescent light sources because of their high luminous efficiency, low cost synthesis, energy saving, long lifetime and environmental protection. A blue phosphor based on phosphate host matrix, $SrMg_2(PO_4)_2:Eu^{2+}$, was prepared by Wu et al. [10]. By introducing the Y^{3+} into $Sr_2P_2O_7:Eu^{3+}$, Pang et al. [11] successfully prepared**,** by the high-temperature solid state reaction method**,** a new phosphor with blue long-lasting emission.Eu^{3+}-doped triple phosphate $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) was synthesized by Haung et al. [12]. Nowadays, low temperature methods such as hydrothermal microwave [13], co-precipitation [14, 15], sol–gel [16, 17] and combustion [18] are used to prepare these phosphors. These methods are relatively cost-effective, quick and can be easily exploited to prepare phosphors with enhanced optical properties. Combustion synthesis often is referred to as self propagating high-temperature synthesis (SHS). Once initiated, it can proceed only by the energy released in highly exothermic reactions. The SHS process takes place within seconds; therefore, there is a negligible heat loss to possible gaseous products. The main advantages of the combustion method include high-purity product, energy and time savings, and a relatively simple one-step process [19].

In this research article, we have reported the effect of Li co-doped in the synthesis and photoluminescence characteristics in $Sr_5(PO_4)_3F:Eu^{3+}$ halophosphate based phosphor. The present phosphors are synthesized by the combustion synthesis. The XRD technique shows the crystalline nature of the prepared materials. PL emission spectrum of phosphors under Hg-free excitation shows a prominent and intense Eu^{3+} emission in the red region of the visible spectrum in the host lattice.

Experimental

Combustion synthesis route is a straight forward table top method of synthesis with considerable low processing temperatures besides the reduction in the preparation time. Li^+ co-doped in $Sr_5(PO_4)_3F:Eu^{3+}$ halophosphate based phosphors were prepared via combustion synthesis. The starting AR grade materials (99.99% purity) are taken strontium nitrate $(Sr(NO_3)_2)$, ammonium di-hydrogen phosphate $(NH_4H_2PO_4)$, ammonium fluoride (NH_4F), europium oxide (Eu_2O_3) , lithium nitrate $(LiNO_3)$ and urea (NH_2CONH_2) is used as fuel. In the present investigation, materials are prepared according to the chemical formula $Sr_{5-x}(PO_4)_3F:Eu_x$. The mixture of reagents is mixed to obtain a homogeneous solution. Eu^{3+} ions are introduced as $Eu(NO_3)_3$ solution by dissolving Eu_2O_3 into dil. HNO_3 solution. The molar ratio of rare earth ions are varied in $Sr_5(PO_4)_3F$ phosphor relative to Sr ions. Fuel urea is taken as excess than stoichiometric ratio for the complete combustion. After stirring for about 30 min, precursor

solution was transferred to a furnace preheated at 550-650°C and the porous products were obtained. The combustion reaction involves the exothermic decomposition of the metal nitrates and an organic compound (used as fuel) at relatively low temperature (575 K) generating sufficient heat to form the desired product. Since in this method samples are prepared through the solution route, better control over sample homogeneity and particle size would be obtained unlike in high temperature solid state reaction routes where the control on sample homogeneity and particle size is difficult. The stoichiometric amount of redox mixture when heated rapidly at ~600°C was boiled and undergoes dehydration followed by decomposition generating combustible gases such as oxides of N_2, H_2O and nascent oxygen. The volatile combustible gases ignite and burn with a flame and thus provide conditions for formation of phosphor lattice with dopants. The large amount of escaping gases dissipates heat and thereby prevents the material from sintering and thus provides conditions for formation of crystalline phase. Also, as the gases escape they leave voluminous, foaming and crystalline fine powder occupying the entire volume of the firing container and have no chance of forming agglomerations unlike in the other conventional processes. The combustion reaction roughly described as follow:

15 $Sr(NO_3)_2$ + 9 $NH_4H_2PO_4$ + 19 $NH_2CONH_{2(excess)}$ + 3 NH_4F
→ 3 $Sr_5(PO4)_3F$ + 40 N_2 + 19 CO_2 + 71 H_2O

Several complementary methods were used to characterize the prepared phosphor. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-K*a* radiation) at a scanning step of 0.01°, continue time 20s, in the 2θ range from 10 to 60°. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC Spectrofluorophotometer fitted with a sensitive photomultiplier tube. This spectrofluorophotometer provides corrected emission and excitation spectra in the 220–400 and 300–700 nm ranges, respectively at the room temperature. Samples of 2g were used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

Results and discussion

XRD and photoluminescence properties of $Sr_5(PO_4)_3F:Eu^{3+}$

Fig.1 shows the XRD patterns of the as-prepared, 900°C and 1200°C annealed powder samples of $Sr_5(PO_4)_3F:Eu_{1\,mol\%}$. A small quantity of the doped ions in the crystal does not change the crystal purity. The patterns were compared with those of the standard JCPDs data file number No. 017-0609 and it is well match. The patterns did not show any super lattice peaks and the full width at the half maxima varied only in a small range. It is independent of the fluoride content purity formed in the materials, which indicates the absence of cluster of F ions. The bond length between divalent host metal ion and fluoride i.e. Sr^{2+} ± F in $Sr_5(PO_4)_3F$ is smaller than the sum of the ionic radii between individual host metal and F ion in case of

coordination number being seven [20]. Polarization of the Sr^{2+} divalent metal ions in the triangles by the small F ions could play the role in reducing effective radius in the direction towards the F^- ion showing more effective photoluminescence properties.
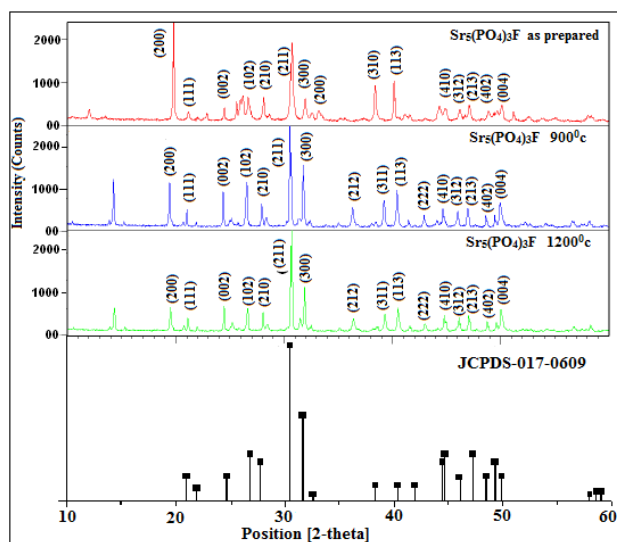

Fig. 1. XRD patterns of $Sr_5(PO_4)_3F$ host lattice as prepared, 900°C and 1200°C heating.

The XRD pattern did not show presence of the constituents and other likely phases which is a direct evidence for the formation of the desired compound. These results show that the final product was formed in crystalline and homogeneous form.
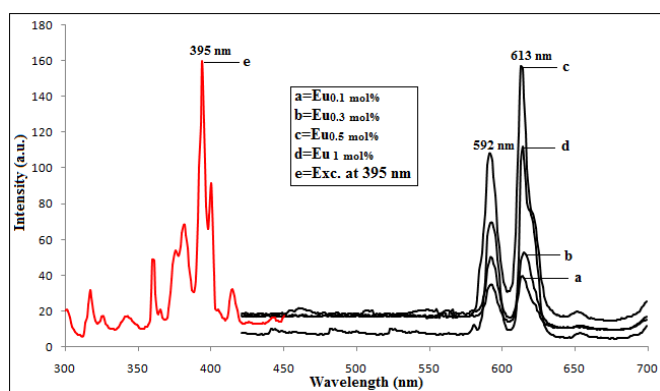

Fig. 2. PL excitation and emission of $Sr_5(PO_4)_3F:Eu^{3+}$ monitored at 613 nm.

The PL spectra of $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors are shown in **Fig. 2**. Narrow emission peaks are expected due to the shielding effect of 4f electrons by 5s and 5p electrons in the outer shells of the Eu^{3+} activator. The strongest emission peak located at 613 nm is assigned to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions, and the peak at 592 is related to $^5D_0 \rightarrow {}^7F_1$ transition when excited at 395 nm wavelength. In fig.2 it is clearly seen that broad band with a maximum intensity at 395 nm (stronger excitation band). The excitation 395 nm caused by the f→f transitions from ^7F_J of Eu^{3+} to excited levels, that is to say, the transition $^7F_0 \rightarrow {}^5L_6$ of Eu^{3+} attribute to the 395 nm. The 300–400 nm is Hg free excitation (Hg excitation is 85% 254 nm wavelength of light and 15% other wavelengths), which is characteristic of solid-state lighting phosphors. It is known that $^5D_0 \rightarrow {}^7F_1$ transition is mainly a magnetic dipole transition, while $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ transitions are electric dipole transitions [21]. Between these two emission bands the 613 nm is main line corresponding to the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} whereas other corresponds to the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ of Eu^{3+} ion which is less prominent. These two peaks are obtained due to the splinting of Eu^{3+} ion emission. The multiphoton relaxation derived from the vibration of phosphate groups, which can bridge the gaps between the lowest $^5D_0$ level of Eu^{3+} and the higher energy levels ($^5D_1$, $^5D_2$) effectively so there is no emission from the higher energy levels of Eu^{3+} ion can be detected.

Effect of Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$

Fig. 3 shows PL excitation and emission of Li^+ co-doped in $Sr_5(PO_4)_3F:Eu^{3+}$. Co-doping with Li^+ ion leads to an increase of the quantum yields because Li^+ substitution in the lattice led to a decrease in interstitial oxygen and hence increase in hole concentration. It is showed that the decrease in interstitial oxygen led to a decrease in the competitive absorption and hence yielded a higher quantum yield. The results show that the location of the excitation and emission spectrum $Sr_5(PO_4)_3F:Eu^{3+}$ phosphor was not influenced by Li^+ ion. However, the excitation and emission spectrum intensities were greatly influenced by Li^+ ion and the emission peak intensities were all enhanced (see **Fig. 3**). Under the condition of the same Li^+ concentration, the emission peak intensities of $Sr_5(PO_4)_3F:Eu^{3+}$ phosphor were shows that the accretion effect of doping Li^+ is the best. The effect of Li^+ concentration on the emission peak intensity of $Sr_5(PO_4)_3F:Eu^{3+}$ phosphor was studied. The results show that the emission peak intensity first increased with the increasing Li^+ concentration, then decreased, and reached the maximum value at 0.5 mol% Li^+ and the maximum value is about three times as much as the Li^+ undoped one.

Normally, the luminescence property of phosphor is known to be strongly affected by the concentration of the activator. The optimal concentration of Eu^{3+} seems to be different with the preparation method. Usually, low doping gives weak luminescence but excess doping perhaps causes quenching of luminescence [22]. In our case, $Sr_5(PO_4)_3F:Eu^{3+}$ and Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors the maximum intensity of emission is observed at $Eu^{3+}_{0.5\ mol\%}$ and $Li^+_{0.5\ mol\%}$ co-doped (see **Fig. 4**). The excitation spectrum shows around 393 nm peak is the characteristic of the LED lighting and emission in the red region of the spectrum shows the Eu^{3+} doped Li co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors may be candidate of warm white LED lighting as a red phosphor.
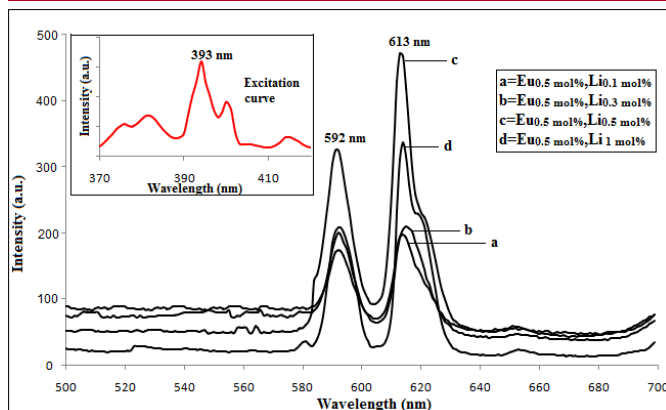
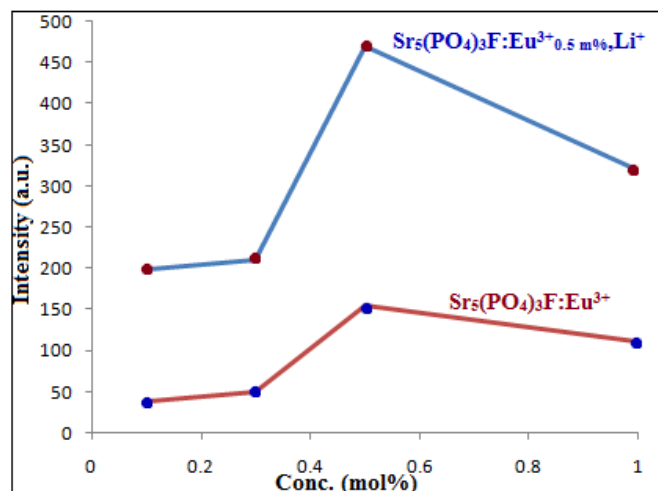**Fig. 3.** PL excitation and emission of $Sr_5(PO_4)_3F:Eu^{3+}$, Li^+ monitored at 613 nm.

Fig. 4. Variation in the PL intensity as function of the Eu^{3+} and Li^+ ion concentrations.

A sample model illustrating the excitation and emission process in $Sr_5(PO_4)_3F:Eu^{3+}$ and Li co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ is shown in **Fig. 5**. In $Sr_5(PO_4)_3F:Eu^{3+}$ and Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ the excitation (around 393 nm) takes place as a sharp excitation lines at longer wavelengths corresponding to the characteristic f-f transitions absorption of Eu^{3+}. The lines in the spectrum can be assigned to $^7F_0 \rightarrow ^5L_6$ (393 nm) which means this phosphor is well matched with the emission wavelengths of both near-UV-LEDs and blue-LEDs. Then the excitation energy relaxes to the $^5D_0$ energy level of Eu^{3+}, where the radiative transitions to ground state ($^7F_1$, $^7F_2$) occur, resulting in $^5D_0 \rightarrow ^7F_1$ (592 nm) and $^5D_0 \rightarrow ^7F_2$ (613 nm) emission, as shown in Fig.5. The Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ phosphor particles can be excited by more photons than the $Sr_5(PO_4)_3F:Eu^{3+}$ phosphor under the same excitation conditions, and more photons will emit in the former than in the latter. Thus, it is understandable that the Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors have higher photoluminescence intensity than that of the $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors. **Fig. 5** represent the schematic energy level of the Eu^{3+} ion diagram showing the states involved in the luminescence process and the transition probabilities and how Li^+-doping can improve the PL intensity of the $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors. The high

contributions of the red ($^5D_0 \rightarrow ^7F_2$) emissions and the low intensity of the orange ($^5D_0 \rightarrow ^7F_1$) emission results in high colour purities that is adequate for solid state lighting applications. The Li^+ co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ is promising phosphor of solid-state lighting because of its effective excitation around 393 nm.

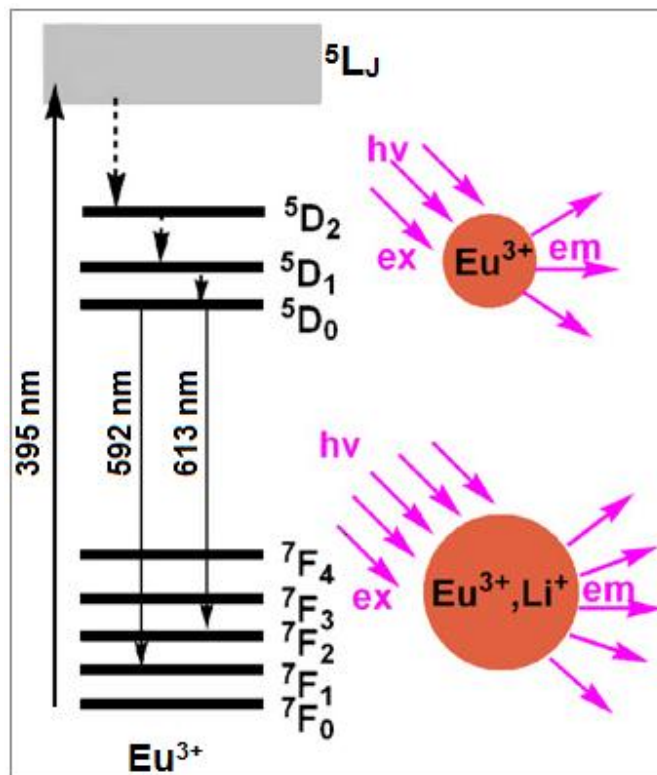**Fig. 5.** A simple model illustrating excitation and emission process in $Sr_5(PO_4)_3F:Eu^{3+}$ and how Li^+-doping can improve the PL intensity of the $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors.

Chromatic properties

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates which recognize that the human visual system uses three primary colours: red, green, and blue [23, 24]. In general, the colour of any light source can be represented on the (x, y) coordinate in this colour space. The colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)). The chromatic coordinates (x, y), was calculated using the colour calculator program radiant imaging [25].The coordinates of the Eu doped and Li co-doped $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors of color orange (x ≈0.6747, y ≈0.3250) is showing in fig .6 by solid circle sign (•). The location of the colour coordinates of the Eu^{3+} doped and Li^+ co-doped $Sr_5(PO_4)_3F$ phosphate based phosphor on the CIE chromaticity diagram presented in **Fig. 6** indicates that the colour properties of the phosphor powder prepared by combustion method is approaching those required for field emission displays. The dominant wavelength is the single monochromatic wavelength that appears to have the same colour as the light source. The dominant wavelength can be determined by drawing a straight line from one of the CIE white illuminants (Cs (0.3101, 0.3162)), through the (x, y) coordinates to be measured, until the line intersects the

outer locus of points along the spectral edge of the 1931 CIE chromatic diagram.

All the results calculated from the emission spectra in **Fig. 2** and **3** are plotted in the Commission International de l'E´clairage (CIE) 1931 chromaticity diagram, as shown in **Fig. 6**. It indicates that present phosphors are close to the edge of CIE diagram, which indicates the high color purity of these phosphors. By connecting these two points as a triangle (included white light point (0.31, 0.32)) the intermediate compositions can generate warm white light with a particular ratio of this phosphor.
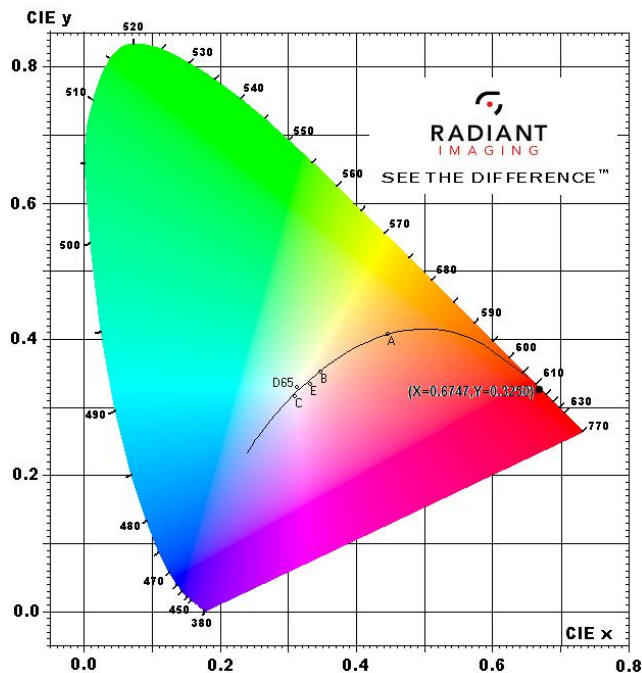

Fig. 6. CIE chromatic diagram showing the chromatic coordinates.

Conclusion

In present article, the Eu^{3+} doped and Li^+ co-doped $Sr_5(PO_4)_3F$ phosphate based phosphor phosphors were prepared by combustion synthesis, confirmed by XRD and their luminescent properties were investigated. The formation of homogeneous single phase lamp phosphors not only demonstrates the capability of the combustion process in the atomic level doping of impurity ions in the host lattices but also confirms the highly exothermic nature of combustion. The major advantages of the combustion process are improvement in processing time, energy saving and the fine particle nature of the combustion products. Under the excitation around 395 nm, the $Sr_5(PO_4)_3F:Eu^{3+}$ phosphors show the red/orange emission from Eu^{3+}. Due to the existence of an inversion symmetry for the sites occupied by Eu^{3+} in $Sr_5(PO_4)_3F$ host, the $^5D_0 \rightarrow ^7F_1$ transition of Eu^{3+} dominate their emission spectra. The luminescence intensity of $Sr_5(PO_4)_3F:Eu^{3+}$ was significantly enhanced by co-doped with Li^+, probably due to the charge compensation. The highest emission intensity was observed with the formula of $Sr_5(PO_4)_3F:Eu^{3+}_{0.5\ mol\%}$, $Li^+_{0.5\ mol\%}$, whose brightness was increased by a factor of more than three in comparison with that of $Sr_5(PO_4)_3F:Eu^{3+}$. This fundamental work might be important in developing new luminescent devices applicable for tricolor lamps, light emitting diodes and other fields.

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