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A novel blue-greenish emitting phosphor $KAl_{1-x}PO_4F:Tb_x^{3+}$ $(0.1 \le x \le 1.0)$.

Akojwar Ashish[1], Naktode PK[2], Shinde KN[1*] and Kokode NS[2]

[1] N.S. Science and Arts College, Bhadrawati, Chandrapur- 442902, India
[2]N.H. College, *Bramhapuri*, Chandrapur-441206, India
Email: kartik_shinde@rediffmail.com

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ABSTRACT

The present paper reports synthesis and photoluminescence (PL) studies of the blue-greenish emitting phosphor $KAl_{1-x}PO_4F:Tb_x^{3+}$ $(0.1 \le x \le 1.0)$ were fabricated by combustion process at temperature 650⁰C. The received phosphor samples were characterized by using XRD, SEM, PL, CIE technique. The photoluminescence study shows blue-greenish emission at 490 nm and 544 nm when excited at 378 nm . The chromaticity coordinate of $KAlPO_4F:Tb^{3+}$ phosphor is (x =0.258, y =0.730) for green color. All the spectrum features indicate that $KAlPO_4F:Tb^{3+}$ might be a promising phosphor for lighting or w-LEDs.

Keywords: XRD, SEM, PL, CIE technique, photoluminescence (PL).

INTRODUCTION

Nowadays, white light emitting diode (w-LED) has drawn worldwide attention due to compactness, long lifetime, high efficiency, energy saving, and environmental friendliness. The most commercial approach to fabricate w-LED is combining a single yellow-emitting YAG with a blue LED chip [1, 2]. However, this kind of white light faces some disadvantages such as low color rendering index (Ra< 80) and high correlated color temperature (T_c > 4500 K). To solve this tough problem, another way is developed, which is combining the n-UV LEDs chip with three individual red, green, and blue-emitting phosphors [3, 4].

The w-LEDs synthesized in this way possess a sufficiently high CRI values and easily controlled emission color properties. Therefore, it is very essential to prepare a high efficient blue-greenish phosphor that can be efficiently excited in the n-UV range. The Tb^{3+} rare earth ions, an important lanthanide, are a renowned green emitting activator. The typical Tb^{3+} emission band consist in the blue and green regions corresponding to $^5D_3$–^7F_J and $^5D_4$–^7F_J transition, respectively. The Tb^{3+} doped luminescent materials, such as Gd_2O_2S:Tb^{3+} [5], K_3R $(PO_4)_2$(R = Y and Gd):Tb^{3+} [6], $Ca_9Lu(PO_4)_7$:Tb^{3+}, Mn^{2+} [7], and K_2YF_5:Tb^{3+}, Sm^{3+} [8], have been extensively investigated and commercially used because of their great optical performance. In addition, the color hue of phosphors doped with Tb^{3+} ions can also be easily varied to be red, green, blue, and even white via introducing additional dopants such as Ce^{3+}, Sm^{3+} and/or Tb^{3+} ions [9–11]. In general, phosphors are strongly affected by the different matrix structure. It is vital to select an optimal matrix. Recently, Phosphate compounds have been widely investigated owing to their considerable thermal stability and tetrahedral rigid three dimensional matrixes, which are believed to be ideal for charge stabilization [12,13]. Especially, Tb^{3+} doped phosphate phosphors exhibit efficient green emission and have been used in the display and lighting fields.[14–16]. Recently, for the first time we reported that $KAlPO_4Cl$:Eu^{3+} phosphor, prepared by the combustion synthesis exhibits a red emission under excitation of n-UV [17]. In this work, we attempt to extend the application of $KAlPO_4F$, i.e., green emission and to fabricate high-quality $KAlPO_4F$:Tb^{3+} phosphor powders using a simple and cost effective synthesis, e.g., the combustion synthesis. To the best of our knowledge, the effects of Tb^{3+} ions on the photoluminescence (PL) of KAl_{1-x} PO_4F: Tb_x^{3+} phosphors have not been reported previously. This phosphate could be considered an alternative green phosphor for n-UV excited LEDs.

METHODOLOGY

Synthesis:

Novel luminescent materials with improved properties are greatly in demand nowadays. Phosphate phosphors doped with rare earth ions have excellent thermal and charge stabilization [18, 19]. The $KAl_{1-x}PO_4F$: Tb_x^{3+}(x = $0.1 \leq x \leq 1.0$) phosphor were prepared through combustion synthesis. The starting material were taken as Potassium nitrate (KNO_3), aluminium nitrate [$Al(NO_3)_3.9H_2O$], di-ammonium hydrogen phosphate [$(NH_4)_2HPO_4$], Ammonium fluoride (NH_4F) and Terbium oxide (Tb_4O_7) . Terbium nitrate $Tb(NO_3)_3$ was prepared by dissolving Terbium oxide (Tb_4O_7) in nitric acid. All the reagents were of analytical grade from Merck with 99.99% purity were used without further purification. The correct amount of each excess urea [$CO(NH_2)_2$] were injected into the precursor solution or these compositions. The amount of metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. After stirring for about 20 min, precursor solution was transferred to a furnace preheated 650°C, The choice of host material and method of preparation are a crucial part of luminescence study. Luminescent properties can be significantly enhanced when phosphors are added to suitable activators and various method of preparation. The finest results presented in this manuscript are new, original and never published before. The phosphate phosphors doped with rare earth ions have excellent thermal and charge stabilization. The stoichiometric amount of redox mixture, when heated rapidly at 650^0C was boiled, underwent dehydration followed by decomposition generating combustible gases such as N_2, H_2O and oxygen. The volatile combustible gases ignite and burn with a flame and thus provide conditions suitable for the formation of phosphor lattice with dopants. Large amount so escaping gases dissipate heat and prevent the material from sintering and thus provide conditions for the formation of crystalline phase [20]. The porous products were obtained.

Measurements:

The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01^0, continue time 20 s, in the2θ range from 10-90^0.The morphology of the samples were investigated on scanning electron microscopy (SEM). The photoluminescence (PL) measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. All the measurements were conducted at room temperature.

RESULTS AND DISCUSSION

XRD of KAlPO$_4$F:Tb^{3+}phosphor powders:

Figure.1 shows the XRD pattern of KAlPO$_4$F materials prepared by combustion methods. The XRD patterns did not indicate presence of the starting constituents and other likely phases which are an indirect evidence for the formation of the desired compound. This result indicates that the final product was formed in crystalline and homogeneous form. The XRD spectrum of prepared compounds not matches the existing standards JCPDs file. However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds. These results imply that the prepared samples are not the simple physical mixtures of starting materials, but a new single-host KAlPO$_4$F:Tb^{3+}compound.

SEM of KAlPO$_4$F:Tb^{3+}phosphor powders:

Characterization of particles, surface morphology and size for micro crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared particles and composites. Fig. 2 shows the SEM images of KAlPO$_4$F:Tb^{3+} powder synthesized by combustion method. SEM images of prepared particles showed non uniform sizes and shapes of about 1-5µm. This is believed to arise from the non-uniform distribution of temperature and mass flow in the combustion flame. From these images, it is clear that some particles have rough surface with voids and pores. During the combustion process, a large amount of gaseous material is evolved and hence the combustion product is porous. Furthermore, cracks can also be seen on the surface. These features are expected in combustion derived product as combustion process is self-sustaining and self terminated. This shows that the combustion reactions of the mixtures took place well. The particles possess foamy like morphology formed from highly agglomerated crystallites. Hence it is suitable for solid state lighting (coating purpose). [21]

Photoluminescence of KAlPO$_4$F:Tb^{3+}phosphor powders:

The excitation and emission spectra of prepared KAl$_{1-x}$PO$_4$F:Tb$_x^{3+}$ (x = 0.1≤x≤ 1.0) were measured at room temperature and are shown in Fig. 3 (a) and (b), respectively. Fig. 3(a) shows the excitation spectrum of sample with varied Tb^{3+} doped concentration by monitoring the strongest 544 nm ($^5D_4$ -$^7F_5$) emission of Tb^{3+}. The emission spectra were recorded for all the phosphors exciting them with 378 nm wavelength as shown in the Fig. 3b. The emission spectra of terbium doped KAlPO$_4$F show blue emission in the region of 440-490 nm and green emission in 544-551 nm. It is well known that the $^5D_3$-^7F_J transition is responsible for the blue emission below 490 nm, while the green emission above 490 nm results from the $^5D_4$-^7F_J transition. The emission form the both levels $^5D_3$ and $^5D_4$ of Tb^{3+} have been observed. In fact, many Tb^{3+} activated materials show a blue emission from the $^5D_3$ level and a green emission from the $^5D_4$ level [22-24]. In this work the emission peaks at 440, 471, 490,544 and 551 nm are due to transitions from excited level $^5D_3$ and $^5D_4$ respectively. The emission peaks due to $^5D_3$ to $^7F_4$ and $^7F_3$ transition are observed at 440 and 471 nm respectively. Similarly, the emission peaks due to $^5D_4$ to $^7F_6$ and $^7F_5$ transitions are observed at 490 and 551 nm respectively [25]. Visible luminescence of Tb^{3+} is mainly due to the transitions from $^5D_3$ and $^5D_4$ to ^7F_J. Among these peaks, the green emission peak ($^5D_4$ - $^7F_5$) located at 544 nm is the most dominant, which is favorable for obtaining a phosphor with high color purity.

The influence of Tb^{3+} ion concentration on the PL intensity of phosphors KAl$_{1-x}$PO$_4$F: Tb$_x$ (x = 0.1mol%, 0.3mol%, 0.5mol% and 1mol %) is shown in Fig.3 (b). The emission intensity of the dominant peak located at 544 nm increases with the increasing of Tb^{3+} ion concentration and reaches the maximum when the molar fraction is 0.5mol%, then it decreases because of the concentration quenching shown in fig 4. The main emission band, located at 544 nm, gives rise to the well known intense green luminescence of Tb^{3+}, which indicates that it could be an excellent green phosphor applicant for solid state lighting.

Chromatic properties:

The chromaticity CIE diagram presented in Fig.5 The CIE chromaticity coordinate of KAlPO$_4$F:Tb^{3+}phosphor was calculated using a tristimulus value colorimetry system (X, Y, Z) as suggested in the CIE 1931(International Commission on Illumination) The chromatic coordinates (x, y) were calculate using the color calculator program radiant imaging [27]. The chromatic coordinates were calculated by using the intensity corrected emission spectra at the excitation of 378 nm. The chromaticity coordinates (x, y) of the as-prepared samples KAl$_{1-x}$PO$_4$F:Tb$_x^{3+}$ (x = 0.1≤ x ≤ 1.0) are measured and plotted in Fig. 5. With the incensement of Tb^{3+} doped content, the color hue shifts form blue (0.045, 0.294) to green (0.258, 0.730). These co-ordinates are very near to standard values of green. Hence this phosphor having excellent color tenability to green. The concentration quenching of Tb^{3+} ion $^5D_3$-^7F_J transition lead to the blue-greenish emitting phosphors. It means the KAlPO$_4$F: Tb^{3+} phosphor could be a good blue-greenish emitting phosphor applicant for creating white light in phosphor-converted solid state lighting, after combining with a UV-LED and RGB phosphor.

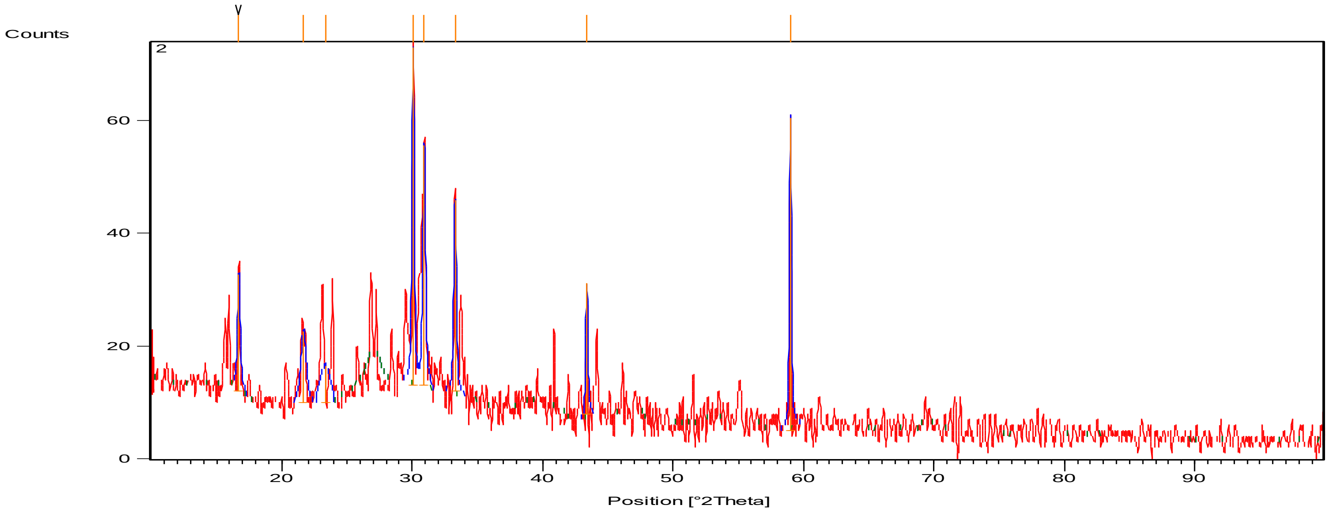

Fig. 1 X-ray diffraction (XRD) patterns of KAlPO$_4$F:Tb host prepared by combustion methods

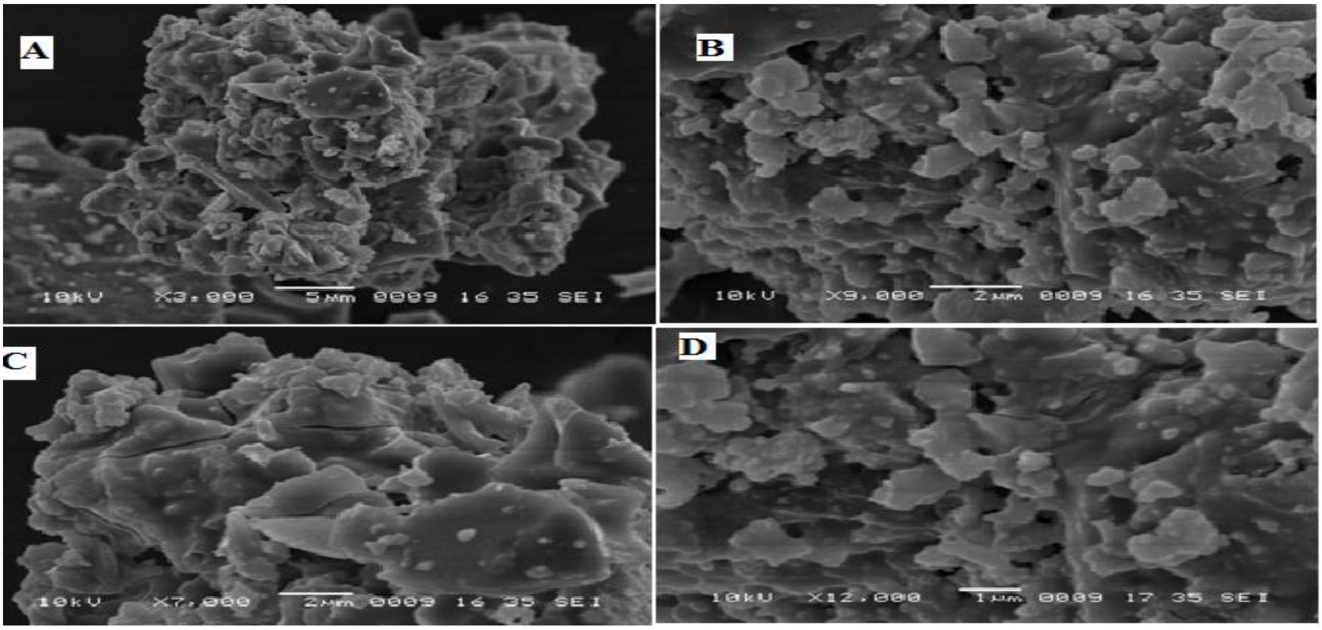

Fig. 2 SEM image of KAlPO$_4$F:Tb^{3+} phosphor at different magnifications.

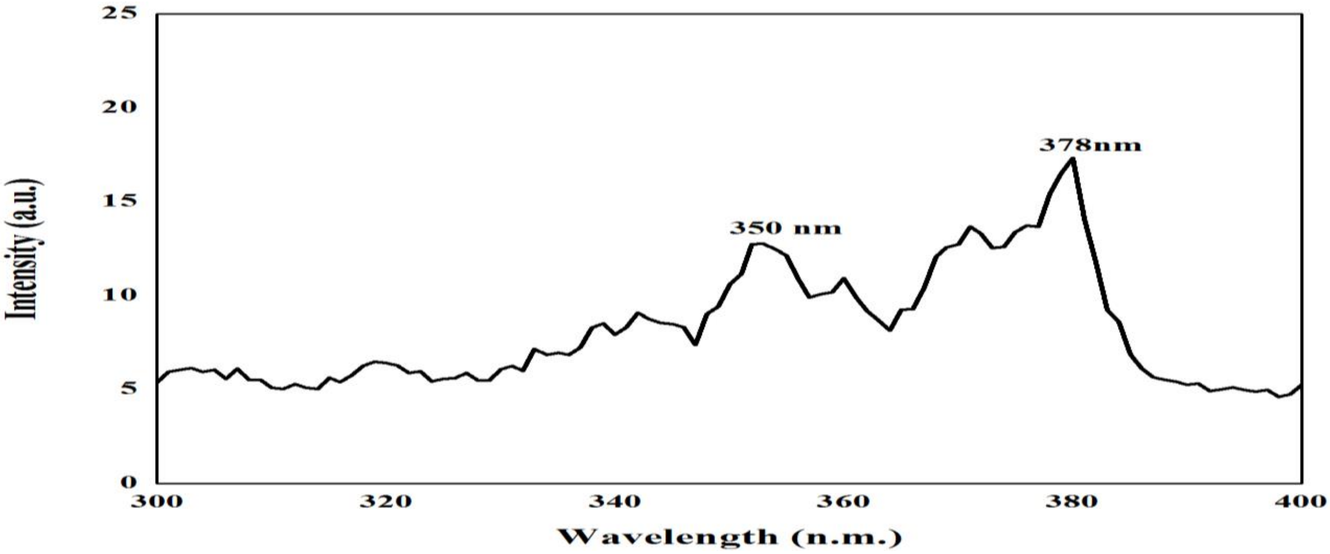

Fig 3(a) Excitation spectrum of KAlPO$_4$F:Tb^{3+} phosphor (λ_{emi} = 544 nm)

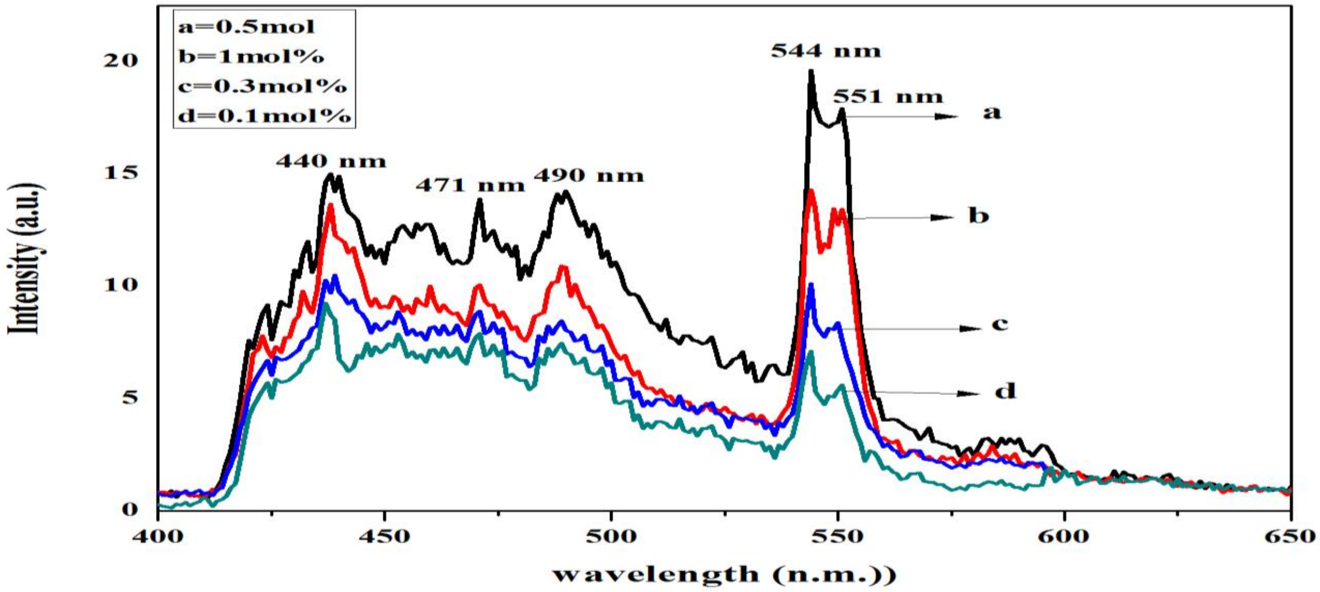

Fig 3(b) Emission spectra of KAl$_{1-x}$PO4F: Tb$_x^{3+}$ (0.1 ≤ x ≤ 1.0) phosphor powder when excited at 378 nm.

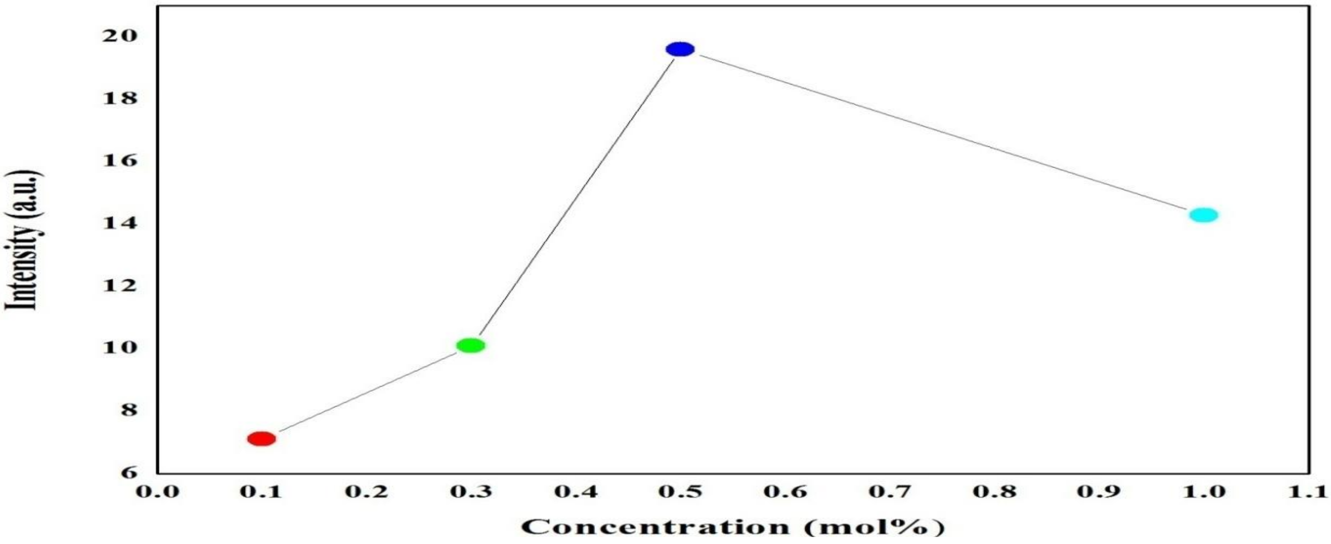

Fig.4 maximum PL intensity of KAlPO$_4$F:Tb^{3+} with varying concentration

CONCLUSION

Terbium doped $KAlPO_4F$ powder phosphors were successfully synthesized by using a combustion method. The combustion processing provides a convenient and fast approach to doping with rare earth ions, to modify the properties of the powders. SEM indicates the final product is irregular in shape with particles size of about 1-5µm. This sub-micrometer range of $KAlPO_4F:Tb^{3+}$ phosphate phosphors are appropriate for the solid state lighting (coating purpose). The strongest excitation peak appeared at 378 nm both the blue emission $^5D_3$ -^7F_J and the green emission $^5D_4$ -^7F_J observed in the emission spectrum of $KAlPO_4F$ with different doped concentration of Tb^{3+}. The emission from the $^5D_4$-^7F_J transition of Tb^{3+}increases with increasing Tb^{3+} concentration. The CIE chromaticity coordinate of $KAlPO_4F:Tb^{3+}$ phosphor excited at 378 nm is (x = 0.045, y = 0.294) for blue and (x = 0.258, y = 0.730) for green color. Thus From the result, it is concluded that the $KAlPO_4F:Tb^{3+}$ compound prepared by combustion synthesis along with blue-greenish color is a vital phosphor for the solid state lighting applications.

Conflicts of interest: The authors stated that no conflicts of interest.

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