Luminescence Investigation of Trivalent Dy and Tb doped KAlPO₄Cl Phosphor for Solid State Lighting

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Abstract- From the photoluminescence data found that in case of Dy³⁺ for excitation of 351 nm got the emission at 575 nm and incase of Tb³⁺ for the excitation of 380 nm we got the emission at 546 nm, chromaticity coordinates of the prepared phosphor are C_x=0.026 and C_y=0.412 for Dy³⁺ and C_x=0.271and C_y=0.719 for Tb³⁺ ion. The present study suggests that the KAlPO₄:Cl: Dy³⁺ and Tb³⁺ phosphor is a outstanding material as a yellow-orange and green component for phosphor- converted white light-emitting diodes (LEDs). Prepared compound were further characterized by SEM, XRD and PL.

Key Words: Solid state lighting, Photoluminescence, XRD, SEM.

1. INTRODUCTION

Now a day’s progress in the preparation of rare earth activated environmental suitable phosphor for a lighting industry with the outstanding luminous absorption, efficiency, very less expensive in addition to longer existence constitutes with significant challenges. Analysis of rare-earth ions activated with phosphors material carried out due to their potential application in present lighting industries applications and display areas. It is distinguished that host material activated with rare earth ions shows emission. For the next generation lighting industry applications and display devices LED used as a very important source due to their outstanding eco-friendly, energy consumption properties [1]. In recent years, researches on phosphors have attracted much attention due to their significant use in solid-state lighting such as white lighting emitting diodes (WLEDs) fabricated with blue or near-UVC chips. There are a number of phosphors suitable for blue or near-UVC excitation, such as sulfides, aluminates, orthosilicates, molybdates, phosphate and oxynitrides/nitrides [2]. At present, a blue LED chip combined with YₓAl₁₋ₓO₁:Ce³⁺ (YAG) phosphor is a common way to generate white-lighting. However, due to the lack of a red light component, white light generated by this method usually possess poor color rendering. Moreover, YAG phosphor shows a poor thermal stability under high temperature produced during the WLEDs [3]. Thus, it is needed to develop a phosphor which owns either higher thermal stability or small thermal quenching. Recently, phosphate materials of the ABPO₄ (A = alkaline metals, B = alkaline earth metals) were reported as an important family of luminescent host materials under UV excitation because of their excellent thermal stability [4-5]. Typically, ABPO₄ based phosphors prepared by a solid-state reaction using conventional sintering furnace requires a high temperature to achieve a complete reaction [6-7]. It was known that the sintering treatment is an important parameter for producing the phosphors. Phosphate has attracted renewed interest because of their potential use in a great variety of optical devices. Moreover, phosphate glasses are easy to prepare and show interesting physical and chemical properties, which make them attractive as hosts for luminescent ions [8]. Phosphate material has been widely studied because of their strong absorption properties close to UV region, higher thermal constancy, and chemical strength. Phosphate based phosphor material has vast significance for a broad study due to their wide applications in illumination and display devices [9]. We tried to prepare and develop new host materials and activators with high performance for solid state lighting such as Eu³⁺-activated MₓAlP₀ₓ₀ (M= Sr/Ba/Mg) [10], Naₓ(XPO₄)ₓF (X =Mg, Ca, Sr) [11], NaₓZnₓPO₄₋ₓ [12], KₓAl₂(PO₄)ₓ [13], NaCaPO₄ [14], and (Gdₓ,Y₁₋ₓ)₀.₉₄Eu₀.₀₆PO₄ [15] and studies generally concerned for the preparation of material for solid state lighting. Presently, there are two most important approaches for generation of white light out of which one has had large scale commercial success, while second one has some of restricted lighting application due to it is poor in the red emission, resulting in a low CRI index [16-17]. With the purpose of improving the quality of white light, the second options to get white light combines a near ultraviolet (NUV) LED chip with RGB phosphors results in a high color rendering index and better-quality color consistency as the white light is generate only by the phosphors [18]. Though, they require of wide and strong excitation bands in the NUV region makes this composite of small use in phosphor improved LEDs [19]. So, it is extremely advantageous to build up new methods and materials for phosphor improved LEDs. In this work, KAlPO₄Cl consider as the host material and photoluminescence properties i.e. the emission and excitation spectra of Dy³⁺ and Tb³⁺ dopand studied. We prepare KAlPO₄Cl: Dy³⁺ and Tb³⁺ phosphor, i.e., yellow-orange and green emission phosphor with the help of combustion synthesis method. To the best of our knowledge, the effects of Dy³⁺ and Tb³⁺ ions on the photoluminescence (PL) of KAlPO₄Cl: Dy³⁺ and Tb³⁺ phosphors have not been studied.

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Phosphors are improved with concentration of Dy$^{3+}$ and Tb$^{3+}$ ion. This phosphate phosphor could be considered a good promising yellow-orange and green emitting phosphor for solid state lighting.

2. EXPERIMENTAL

2.1 Sample Preparation

For the preparation of KAIP04Cl: Dy$^{3+}$ and Tb$^{3+}$ phosphor by using combustion method. The starting materials all from AR grade (99.99% purity) taken as Potassium nitrate (KNO$_3$), Aluminium nitrate (Al(NO$_3$)$_3$9H$_2$O), Di-ammonium hydrogen phosphate (NH$_4$H$_2$(PO$_4$)), Ammonium chloride (NH$_4$Cl), Dysprosium oxide (Dy$_2$O$_3$), terbium oxide (Tb$_2$O$_3$) and Urea (NH$_4$CONH$_2$) was used as fuel for combustion. The compositions of the metal nitrates (oxidizers) and urea (fuel) were considered using the total oxidizing and reducing valences of the components. The mixture of all the compounds was mixed together for obtaining a homogeneous solution. Dy$^{3+}$ and Tb$^{3+}$ ion was introduce in the form of Dy(NO$_3$)$_3$ and Tb(NO$_3$)$_3$ solution by dissolving Dy$_2$O$_3$ and Tb$_2$O$_3$ into HNO$_3$ solution separately. While doping with KAIP04Cl, variation in molar ratio of Dy$^{3+}$ and Tb$^{3+}$ from 0.1 to 1 m% and 0.1 to 5 m%. Combustion synthesis method done with the dissolution of metal nitrate along with fuel (urea) with heating at approximately $\sim$550 °C. Within a few minutes, the solution boiled, ignited and produced a self propagating flame. The products obtained by the combustion synthesis process were fluffy masses and these were crushed into a fine powder to obtain the KAIP04Cl: Dy$^{3+}$ and Tb$^{3+}$ powders. For analysis of phase purity and crystalline nature of prepared pure host using XRD analysis method was used. A PAN-analytical diffractometer (Cu–Kα radiation) at a scanning step of 0.01°, continue time of 20 s and in the 2θ range 10–90°; and particle size with the help of SEM. The photoluminescence measurements i.e. excitation and emission were recorded on a Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2 g) was used for each measurement at room temperature using a spectral slit width of 1.5 nm.

3. RESULTS AND DISCUSSION

3.1 XRD phase analysis

Fig. 1 shows the XRD patterns of the KAIP04Cl phosphor prepared at $\sim$550 °C temperature using combustion synthesis method. There is no JCPDS data available for comparison of this particular composition so on the basis of previous work done by shinde et al [20]. To analyze the phase and purity of the prepared compound XRD phase analysis method was used and from the result obtained we concluded that the prepared host compound is in exactly matched with the JCPDS data source file no. XRD structure analyzed that Dy$^{3+}$ and Tb$^{3+}$ had no significant influence on the crystal structure of host materials and was completely dissolved into the host lattice without forming any Dy$^{3+}$ and Tb$^{3+}$ containing compounds.

3.2 SEM Analysis

As shown in Fig. 2, size and morphology of the KAIP04Cl: Dy$^{3+}$ phosphor powders were examined by scanning electron microscopy (SEM). The KAIP04Cl: Dy$^{3+}$ phosphor powders prepared at 550°C have approximately narrow size and irregular shape in the range of 1-2 µm. Particularly the particles obtained by combustion method are irregular in shape but well-defined grain boundaries. Though, an elevated degree of agglomeration of the particles takes place. It was found that there were agglomerates or clusters of many particles. The morphology of particles looks like foamy due to highly agglomerated crystallites [21]. Moreover, an average crystallite size is in sub-micrometer range of KAIP04Cl: Dy$^{3+}$ phosphors, which is appropriate for the solid state lighting (coating purpose) [22].

3.3 Optical Properties of KAIP04Cl: Dy$^{3+}$ phosphors

Phosphor prepared with Dy$^{3+}$ ions plays an important role for solid state lighting applications. Due to this significance with the fact that it is extremely perceptive rare earth material, excellent thermal strength while in preparation with economical stability differentiate from others, so used rarely in solid state lighting industry applications. Emission spectrum fig 04 has sharp lines on account of f–f transition of Tb$^{3+}$ ions. The emission spectrum usually has major contribution from $^5D_4\rightarrow^7F_j$ (J= 6, 5, 4, 3) and peak due to $^5D_4\rightarrow^7F_{15/2}$ can also be seen. The nature of $^5D_4 \rightarrow^7F_j$ transitions is governed by the selection rule $\Delta l = \pm 1$ for electric dipole and $\Delta J = 0, \pm 2$ for magnetic dipole transitions respectively.
3.4 Optical Properties of KAlPO$_4$Cl: Tb$^{3+}$ phosphors  

Excitation spectrum of Tb$^{3+}$ singly doped sample, KAlPO$_4$Cl, is shown in Fig. 5 and the emission spectrum of KAlPO$_4$Cl:Tb$^{3+}$ is shown in Fig. 6, by observing the emission at 546 nm. When the emission wavelength is observed at 546 nm, Tb-activated phosphors constantly show strong $f-f$ transition band absorption in the region of 300–400 nm.

Emission spectra consist of numerous particular relatively narrow bands that are associated with some $4 f ightarrow 4 f$ electronic transitions in the activating terbium ions, characteristic blue and green emission peaks related to Tb$^{3+}$ intra $4 f$ transitions from the excited levels to lower levels, $^5D_{j} \rightarrow ^7F_{J} (J = 4, 5)$ and $^5D_{4} \rightarrow ^7F_{J} (J = 4, 5, 6)$ transitions, respectively are seen. Emission spectrum of Tb$^{3+}$ is strongly dependent on Tb$^{3+}$ concentration. Blue emissions at 419 and
439 nm, ascribed to the $^5D_3 \rightarrow ^7F_J$ ($J = 5, 4$) transitions occurring at wavelength below 485 nm, were observed at low Tb$^{3+}$ concentrations. These blue emissions are attributed to the transition from $^5D_3$ excited state to $^7F_J$ ground states [23]. Blue emission was normally found to disappear when Tb$^{3+}$ concentration is improved beyond the critical concentration for cross-relaxation to occur [24].

Green emission peaks are found at 546 nm and 589 nm, corresponding to the $^5D_4 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_4$ typical transitions of Tb$^{3+}$ in the host lattice. The strongest $^5D_4$ to $^7F_5$ transition due to its largest probability for both electric-dipole and magnetic-dipole induced transitions make the sample emit intense green light [25]. Photoluminescence (PL) results show that prepared phosphors possess the highest emission intensity. The energy-variation diagram of Tb$^{3+}$, activated with the prepared phosphors is shown in Fig. 5. The main emission band, located at 546 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.

Fig. 9 shows the Commission International de l'Eclairage (CIE) chromaticity coordinates of the KAlPO$_4$: Dy$^{3+}$ and Tb$^{3+}$ phosphor. The color purity was compare to the 1931 CIE regular Source C (illuminant Cs (0.3101, 0.3162)). The chromatic coordinates $(x, y)$ were calculated using the color calculator program radiant imaging [26]. The chromatic coordinates of the prepared phosphor are $C_x=0.026$ and $C_y=0.412$ for Dy$^{3+}$ and $C_x=0.271$and $C_y=0.719$ for Tb$^{3+}$ ion, which exactly fall into the yellow-orange and green region in the CIE 1931 chromaticity diagram. As seen in the PL spectra, the KAlPO$_4$: Dy$^{3+}$ and Tb$^{3+}$ phosphor have yellow-orange and green emission under the UV light. It means the KAlPO$_4$: Dy$^{3+}$ and Tb$^{3+}$ phosphor could be a good yellow-orange and green emitting phosphor applicant for creating white light in phosphor-converted solid state lighting, after combining with a UV LED and RGB phosphor.

4. CONCLUSIONS

In this work we have attempted to find an efficient yellow-orange and green emitting phosphor synthesized by using combustion method. For this we synthesized KAlPO$_4$:Cl: Dy$^{3+}$ and Tb$^{3+}$ compound activated with Dy$^{3+}$ and Tb$^{3+}$ for analysis of emission and excitation mechanism. For the excitation of 353 nm observed emission peak situated at 575 nm and in case of Tb$^{3+}$ excited with the 380nm giving emission of 546 nm. From the result concluded that the compound prepared is prominent candidates for UV-lighting along with yellow-orange and green phosphor for the solid state lighting applications.

REFERENCES


[15] K. N. Shinde, R. Singh, and S. J. Dhole, “Photoluminescence properties of (Gd, Y)0.94Eu0.06PO4 (0≤x≤1.0) phosphors,” J. Lumin., vol. 145, pp. 930-935, 2014.


