Synthesis and Characterization of Eu$^{2+}$ activated KNa$_3$Al$_4$Si$_4$O$_{16}$ phosphor

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Abstract
This work presents Eu$^{2+}$ doped KNa$_3$Al$_4$Si$_4$O$_{16}$ phosphor synthesized by combustion synthesis method. X-ray diffraction pattern (XRD) and photoluminescence spectra were used to characterize the structure and luminescence properties of the as-synthesized phosphors. From the excitation and emission curve it can be seen that the phosphor can be efficiently excited by the ultraviolet/visible light, it emits the light in the region from 400nm to 600nm. The broad emission band of Eu$^{2+}$ ions is observed due to 5d–4f transition of rare earth ions.

Keywords: Blue Phosphor: CS: WLEDs

1. Introduction:
Research on rare-earth (RE) ions activated inorganic phosphors have been widely carried out due to their potential applications in modern lighting and display field due to the abundant emission colors based on their 4f–4f or 5d–4f transitions due to their strong emission.[1, 2] Eu$^{2+}$ isostifened as activator because of the intense broad excitation and emission bands obtained from the dipole allowed 4f–5d electronic transitions. In different hosts, the emission wavelength of Eu$^{2+}$ ions changes from n-UV to red region according to the selection of the host.[3]. Research on next generation of solid-state illumination devices, white LEDs has become a hot cake now a days because of their durability, low energy consumption, long lifetime and less pollution features as compared to the incandescent and fluorescent lamps.[4–7]. White LEDs can be made by basically two ways. [8, 9]. The first approach is by combining blue LED chip and yellow phosphors (such as YAG: Ce$^{3+}$).[10]. But this combination has low color rendering index due to the absence of red component. In order to achieve warm white light, the second method involved to obtain white LEDs is by using tri-colored phosphors (red, green and blue) excited by a near ultraviolet (near-UV, around 350–420nm) chip. Aluminosilicates based phosphor have been paid more attention as an optical and luminescent materials due to their high luminous efficiency, water resistant property, excellent durability, low cost, good physical and chemical stability. Now a days, aluminosilicates compounds have been extensively studied as host lattices for phosphors activated by Ce$^{3+}$, Eu$^{2+}$ and Tb$^{3+}$. However, to the best of our knowledge, very few aluminosilicates phosphors have been reported. Here Eu$^{2+}$ activated KNa$_3$Al$_4$Si$_4$O$_{16}$ phosphors have been reported and its photoluminescence properties have been discussed. Thus, the presented phosphor would offer good candidature for solid state lighting.

2. Synthesis procedure:
Combustion synthesis is simple, less time consuming and inexpensive method. This route yields highly pure and homogeneous single phase compound as a result of high temperature generation during the combustion reaction. Thus it is fast and effective method to synthesize phosphors by varying the dopants and starting materials. A series of KNa$_3$Al$_4$Si$_4$O$_{16}$ phosphors was prepared via combustion route at 550°C. The starting materials for the preparation of KNa$_3$Al$_4$Si$_4$O$_{16}$ phosphors were used as KNO$_3$ (Merck’s 99.9%), NaNO$_3$(Merck’s 99.9%), Al(NO$_3$)$_3$·9H$_2$O (Merck’s 99.9%), SiO$_2$(A.R.), urea NH$_2$CONH$_2$ (Merck’s 99.9%), (NH$_4$)$_2$Ce(NO$_3$)$_6$. In this method metal nitrates were used as oxidizers, and urea (NH$_2$CONH$_2$) was used as fuel for combustion. The weight of all the ingredient used above was calculated using the concept of propellant chemistry. All the precursors were mixed together in mortar pestle and were crushed up to form a homogeneous solution. While crushing, small amount of dilute nitric acid was added to the mixture to maintain the homogeneity of the solution. After crushing for about 15 min, precursor solution was transferred to the silica crucible and it was then placed into a vertical muffle furnace preheated at 550°C. During the
exothermic reaction between metal nitrates and organic fuel complexes at low temperature, sufficient heat gets generated to form the highly fluffy and porous crystalline materials which were then fully ground for the characterization.

KNa₃Al₅Si₄O₁₆ phosphor is analyzed using scanning electron microscopy (SEM). SEM is a versatile tool to give structural information over a wide range of magnification, the study of texture, topography and surface features of the prepared phosphors. Fig. 3 shows the SEM images of KNa₃Al₅Si₄O₁₆ phosphor. From Fig. 3, it is observed that KNa₃Al₅Si₄O₁₆ phosphor particles are agglomerated with irregular morphology with partial size under 1-3µm. Thus from the result it is inferred that by using combustion method there is an increase in process flexibility and it has accelerated the reaction by the presence of urea as a combustible fuel.

3.1 X-ray diffraction and SEM

The phase purity and the crystalline nature of the as prepared phosphor was checked by powder X-ray diffraction (XRD). Powder diffractogram of KNa₃Al₅Si₄O₁₆ phosphors prepared by combustion synthesis has been shown in Fig. 1. X-ray diffraction pattern was recorded using Cu-kα(1.54060 nm) radiation with Step Size 20 deg. 0.0190, scan step time (s) 31.8152, and measurement temperature (1C) 25.00. It is well agreed with standard JCPDS file no. 741718. Surface morphology of the combustion synthesized powder particle of KNa₃Al₅Si₄O₁₆ phosphor is analyzed using scanning electron microscopy (SEM). SEM is a versatile tool to give structural information over a wide range of magnification, the study of texture, topography and surface features of the prepared phosphors. Fig. 3 shows the SEM images of KNa₃Al₅Si₄O₁₆ phosphor. From Fig. 3, it is observed that KNa₃Al₅Si₄O₁₆ phosphor particles are agglomerated with irregular morphology with partial size under 1-3µm. Thus from the result it is inferred that by using combustion method there is an increase in process flexibility and it has accelerated the reaction by the presence of urea as a combustible fuel.

3.2 PL Characterization

Eu²⁺ luminescence spectroscopy

The excitation and emission spectra of KNa₃Al₅Si₄O₁₆ : Eu²⁺ phosphor is shown in Fig. 3.

From the excitation and emission spectra it can be seen that, under excitation of 357 nm, the emission spectrum is a broad band spreading over 400 nm to 600 nm due to the 4f⁷→ 4f⁶5d¹(8S₇/₂) transition of Eu²⁺ ions as shown in Fig. 4.
The $4f^6 \rightarrow 4f^6 5d$ transition of Eu$^{2+}$ strongly depends on the host lattice because the outermost 5d orbit is very sensitive to the crystal-field surrounding. Eu$^{2+}$ emission can vary from UV to red region depending on the host lattice, the size of the cation, and the strength of the crystal field [11]. From the emission curve it can be found that the broad band shows two peaks, one centred at 449nm in the blue region and the other highest intensity peak at 531nm in the green region. Gaussian fit of the emission spectra in to two peaks for 0.1mole % concentration of Eu$^{2+}$ has been shown in Fig.5. With 351 nm UV light excitation, the Eu$^{2+}$ ions are excited to the higher $4f^6$ energy level. After a non-radiative process, the excited Eu$^{2+}$ ions fall back to the lower energy region of $4f^6$ state and then emit green light while falling back to the $4f^7$ ground state[12]. Also from emission spectra, it can be seen that the broad band emission is slightly asymmetric due to the superposition of two emission bands of the same initial state (the lowest 5d1 crystal-field level) but different final states, i.e., $\frac{7}{2}$ and $\frac{5}{2}$ multiple of $4f_1$, as a result of spin-orbit interaction. The concentration of Eu$^{2+}$ ions is increased from 0.05 mol% to 1 mol %, then emission intensity maximum found at 0.1 mol % and further increase in concentration of dopent it decreases, which may be assigned due to the non radiative energy transfer between Eu$^{2+}$ ions at different sites of the host. The role Eu$^{2+}$ concentration in searching of optimal composition of phosphor is very crucial and important. Therefore, the variation of PL intensity with different Eu$^{2+}$ concentrations for KNa$_3$Al$_4$Si$_4$O$_{16}$ :Eu$^{2+}$ phosphor has been graphically shown in Fig.6. The positions of the emission peak are not influenced by the Eu$^{2+}$ concentration. The luminescence intensity increases with Eu$^{2+}$ doping increasing until a maximum intensity at x = 0.1 is attained, and then it decreases because of conventional concentration quenching process.
4. Conclusion:
Thus, a novel KNa$_3$Al$_4$Si$_4$O$_{16}$ : Eu$^{2+}$ phosphor was successfully synthesized by combustion method for the first time. Phosphor shows efficient green emission under nearer to UV excitation wavelength. Synthesized phosphor is characterized by XRD, SEM, analysis. Good crystalline nature of the phosphor is confirmed by XRD pattern. Thus, the observed broad band emission in KNa$_3$Al$_4$Si$_4$O$_{16}$ : Eu$^{2+}$ phosphor shows that it may be used for display and solid state lighting applications.

References