



BLUE EMITTING PHOSPHOR FOR SOLID STATE LIGHTING

APPLICATION BY COMBUSTION SYNTHESIS: $\text{KCaBO}_3:\text{Ce}^{3+}$

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Abstract:

The intense blue emitting phosphor $\text{KCaBO}_3:\text{xCe}^{3+}$ is synthesized by solution combustion synthesis at comparatively lower temperature using urea as fuel. The method of synthesis is by simple, time saving and economical. X-ray power diffraction (XRD) analysis confirmed the formation of the said phosphor. Photoluminescence measurements showed that the phosphor exhibited intense emission at 427nm, corresponding to $5d \rightarrow ^2F_{7/2}$ transition of Ce^{3+} .

The excitation spectra monitored at 427nm shows peaks at 287nm and broad excitation band peaking at 360nm. The later lies in near ultraviolet (350-410nm) emission of UV LED. The phosphor $\text{KCaBO}_3:\text{xCe}^{3+}$ shows colour coordinates CIE 1931 as (0.14, 0.11) whereas the commercial blue phosphor BAM shows the colour coordinates as (0.14, 0.107), respectively. The SEM image recorded shows the particles with an irregular shape and the particle size ranging in 5-10 μm . The phosphor $\text{KCaBO}_3:\text{Ce}^{3+}$ can be a promising blue phosphor in solid state lighting application.

Keywords : : *photoluminescence, combustion synthesis, white LEDs*

1. Introduction

White LEDs are promising candidates to replace conventional incandescent and fluorescent lamps in the coming future due to their merits of a long operation life time, energy saving capabilities and high material stability and lack of pollutants [1]. White light emitting diodes are commercially used with the development of the InGaN blue LED chip and YAG- Ce^{3+} phosphor [2]. But the white light generated by this mechanism has higher color temperature due to lack of red light. Hence cannot be used in more extensive fields. Recently luminescent capacities

of GaN chip under the range of near UV (350-410nm) [3-4] has enhanced. Hence these chips coupled with red, green and blue phosphors have attracted much attention due to the advantages of color stability [4]. Thus the development of new phosphors with high quantum efficiencies for UVLED applications is highly desirable.

Alkaline earth borates are good host materials for the phosphors due to their inherent attributes of large electronic band gap, low synthesizing temperature, high chemical and physical stability, optical stability with good nonlinear characteristics. So are extensively used in phosphors as host material for LEDs.

Recently many rare earth doped borate phosphors such as NaSrBO₃:Ce³⁺ [5], Ba₂Ca(BO₃)₂:Ce [6], Ba₂LiB₅O₁₀:Eu²⁺ [7], KCaBO₃:Eu³⁺ [8], LiSrBO₃:Eu²⁺ [9], Sr₂Mg(BO₃)₂:Ce³⁺ [10] have been reported suitable for LED applications.

Rare earth lanthanide ion Ce³⁺ is with the simplest electronic configuration. It has a 4f¹5d⁰ ground state and a 4f⁰5d¹ excited state and therefore shows typical 4f-5d transitions.

The 4f-5d transitions are parity allowed. Hence shows a large absorption cross section and appear as intense bands in spectra. So the phosphors doped with Ce³⁺ absorb the excitation energy efficiently. Attributing to the extended radial wave functions of the 5d state the Ce³⁺ emission is host dependant [6]. So the position of its absorption and emission bands can be controlled by selecting a suitable host matrix. Excitation and emission at longer wavelengths have been observed for Ce³⁺ emission depending upon the host matrix [11]. This characteristic meets the LED applications and makes Ce³⁺ ion as appropriate activator in phosphor-converted LEDs.

In this paper we are reporting the luminescence of Ce³⁺ ion in KCaBO₃ matrix. The phosphor is synthesized by simple, time saving, economical method of solution combustion synthesis at comparatively lower temperature (550°C) using urea as fuel. This method is easy to

handle and requires no absolute control on the temperature. During the synthesis oxidizer and fuel will automatically decide the reaction temperature [12].

2. Experimental

The phosphors $\text{KCaBO}_3:\text{xCe}^{3+}$ doped with different molar concentration of Ce^{3+} ($\text{x} = 0.01, 0.02, 0.03$) were prepared by modified solution combustion synthesis [11] method. The synthesis is based on the exothermic reaction between the fuel (urea) and oxidizer (ammonium nitrate). The constituent raw materials (AR grade) potassium nitrate, calcium nitrate, cerium chloride, ammonium nitrate, urea and boric acid (as boron source) were weighed in stoichiometric proportion and dissolved in minimum amount of water and fired at 550°C . The solution boils and undergoes dehydration followed by decomposition with evolution of gases N_2, CO_2 etc. The mixture then forth's and swells forming foam that ruptures with a flame on ignition of combustible gases and glows to incandescence. During incandescence the foam further swells to the capacity of container. The whole process completes in few minutes. Following the combustion resulting fine powder was annealed in reducing atmosphere provided by half burned charcoal at 850°C for two hours and quenched to room temperature. The voluminous product obtained was ground with an agate mortar.

The phosphor powder obtained was subjected to XRD analysis using an X'Pert PRO advanced automatic diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) operated at 40kV and 30mA. The XRD data was collected in a 2θ range from 10° to 80° . The measurements of photoluminescence (PL) over the range of 370 to 550nm and photoluminescence excitation spectra (PLE) over 200–400 nm excitation range were carried out on Hitachi-F7000 fluorescence spectrophotometer at room temperature. The spectral resolution of both excitation and

emission spectra, width of the monochromator slits(1nm), as well the measurement conditions such as PMT detector sensitivity and scan speed were kept consistent from sample to sample in measurements.

The SEM image was recorded for surface morphology. The colour chromaticity coordinates were obtained according to Commission International de l'Eclairage (CIE) using Radiant Imaging colour calculator.

3. Result and discussion

3.1XRD analysis

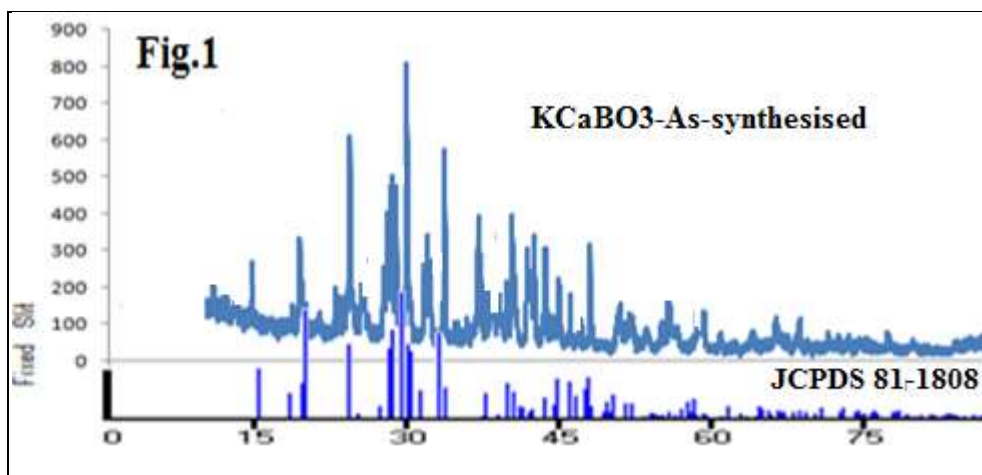


Fig. 1. The powder XRD pattern of KCaBO_3

KCaBO_3 shows monoclinic structure with Space group of $P21/c$ (analogous to LiBaBO_3 ; JCPDS card no. 81-1808). The reported lattice parameters of KCaBO_3 are $a=6.587(\text{\AA})$, $b = 7.119(\text{\AA})$, $c =7.779 (\text{\AA})$ and $\text{Beta} = 118.41(\text{\AA})$ where as Cell volume= 364.779\AA^3 with number of and cations in the unit cell (Z) are 4 [8].

The acceptable percentage difference in ionic radii between doped and substituted ions must not exceed 30% [13].The calculations of the radius percentage difference (D_r) between the doped ions and possible substituted ions are based on the formula:

$$Dr = \frac{Rm(CN) - Rd(CN)}{Rm(CN)}$$

Where CN -co-ordination number, $Rm(CN)$ -Radius of host cations and

$Rd(CN)$ - Radius of dopant ion

Thus it is clear that the Ce^{3+} ionic radius ($r = 1.19 \text{ \AA}$, $CN = 9$) is closest to that of Ca^{2+} ($r = 1.18 \text{ \AA}$, $CN = 9$). Hence, it is believed that the Ca^{2+} sites are replaced by Ce^{3+} in this lattice. [14]

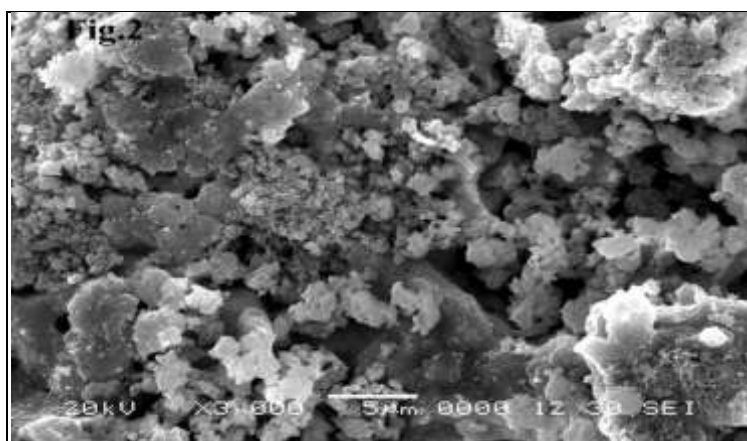


Fig.2 SEM image of $KCaBO_3$

Fig.2 represents the SEM image showing surface morphology of as-synthesised $KCaBO_3: Ce^{3+}$ phosphor. It shows the particles with an irregular shape and the particle size ranging in $5-10 \mu\text{m}$.

3.2 Photoluminescence

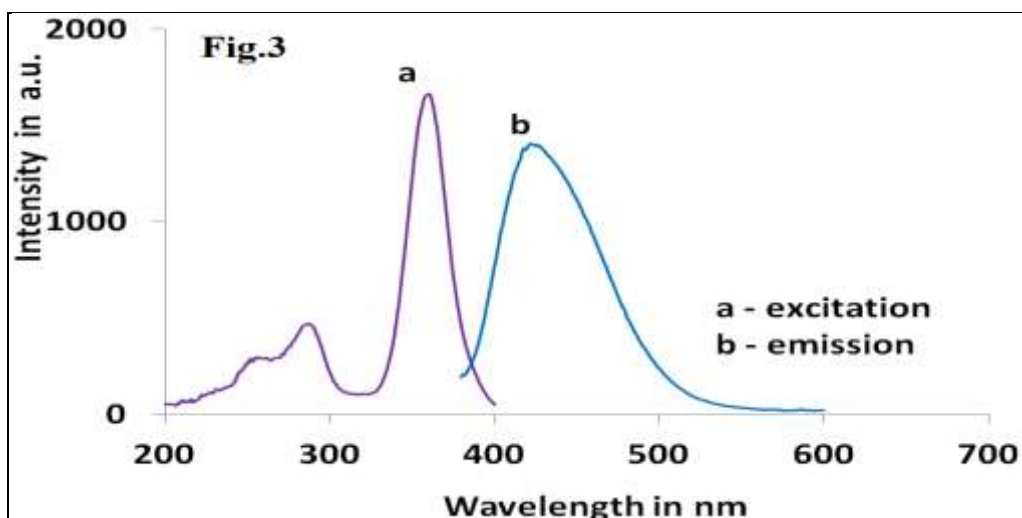


Fig.3 The photoluminescence excitation and emission spectrum of $\text{KCaBO}_3:\text{xCe}^{3+}$

Fig. 3 shows the photoluminescence excitation and emission spectrum of $\text{KCaBO}_3:\text{xCe}$ for ($x=0.02$). The excitation spectrum monitored at 427nm shows small excitation peak at 287nm and broad excitation band peaking at 360nm. The emission spectrum exhibits intense blue emission at 427nm when excited with 365nm wavelength.

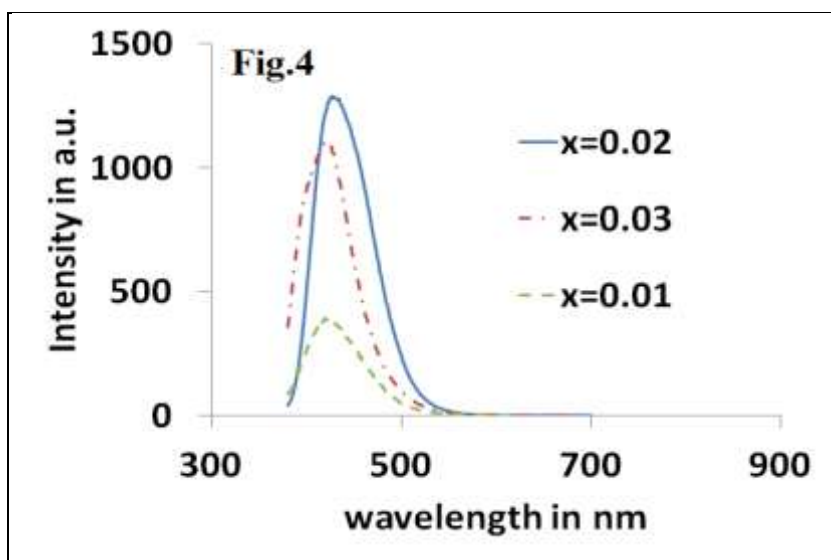


Fig.4. Emission spectra of $\text{KCaBO}_3:\text{xCe}^{3+}$ for different 'x' values with excitation wavelength of 365nm

Fig. 4 represents the emission spectra of KCaBO_3 doped with different Ce^{3+} concentrations for the excitation wavelength 365nm. All of the emission spectra exhibit the similar profile with different relative intensities. The emission intensity increases initially with the increase of Ce^{3+} concentration and reaches to the maximum at $x=0.02$, then decreases due to the internal concentration quenching.

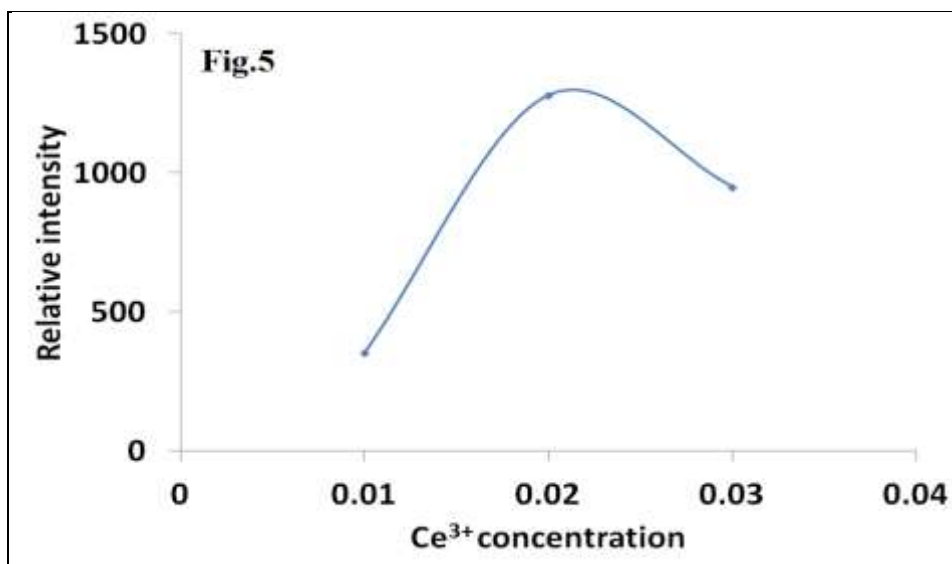


Fig.5. Dependence of relative intensity of emission on Ce^{3+} doping concentration

Fig.5 shows the dependence of the peak intensity of the emission centred at 427nm on Ce^{3+} doping concentration (x) in $\text{KCaBO}_3:x\text{Ce}^{3+}$. The optimum intensity of emission is at $x=0.02$ after that intensity drops due to internal concentration quenching.

The concentration quenching mechanism is generally associated with energy transfer. Non-radiative energy transfer process from one Ce^{3+} ion to another Ce^{3+} ion can be described by three different methods: (1) exchange interaction (2) radiation reabsorption and (3) multipolar interaction.

While discussing the mechanism of energy transfer in phosphors, Blasse [15] suggested that if the activator is introduced solely on one



crystallographic site (here Ca^{2+} site), the critical energy transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume. In order to further discuss the mechanism of energy transfer between the activators in KCaBO_3 host, the critical energy transfer distance (R_c) can be calculated by the following equation:

$$R_c \approx 2 \left(\frac{3V}{4\pi\chi_c N} \right)^{\frac{1}{3}}$$

Where x_c the critical concentration, N is the number of cation sites in the unit cell, and V is the volume of the unit cell. So in this case, $V=364.779 \text{ \AA}^3$, $N=4$ and the critical doping concentration of Ce^{3+} in the KCaBO_3 host is found to be 0.02. Thus, the R_c of Ce^{3+} in $\text{KCaBO}_3:\text{Ce}^{3+}$ phosphor is determined to be 20.57 \AA . Since R_c is not less than 5 \AA exchange interaction is not responsible for non-radiative energy transfer process from one Ce^{3+} ion to another Ce^{3+} ion in this host. The mechanism of radiation reabsorption is the primary method only if the fluorescence spectra of the excitation and emission have obvious overlap. Thus, in view of the emission and excitation spectra of $\text{KCaBO}_3:\text{Ce}^{3+}$ (Fig3), the radiation reabsorption is unlikely to occur. As a result, the energy transfer process of Ce^{3+} in KCaBO_3 phosphor would be due to multipolar interaction. Further it can be proved to be because of quadrupole-quadrupole interaction.

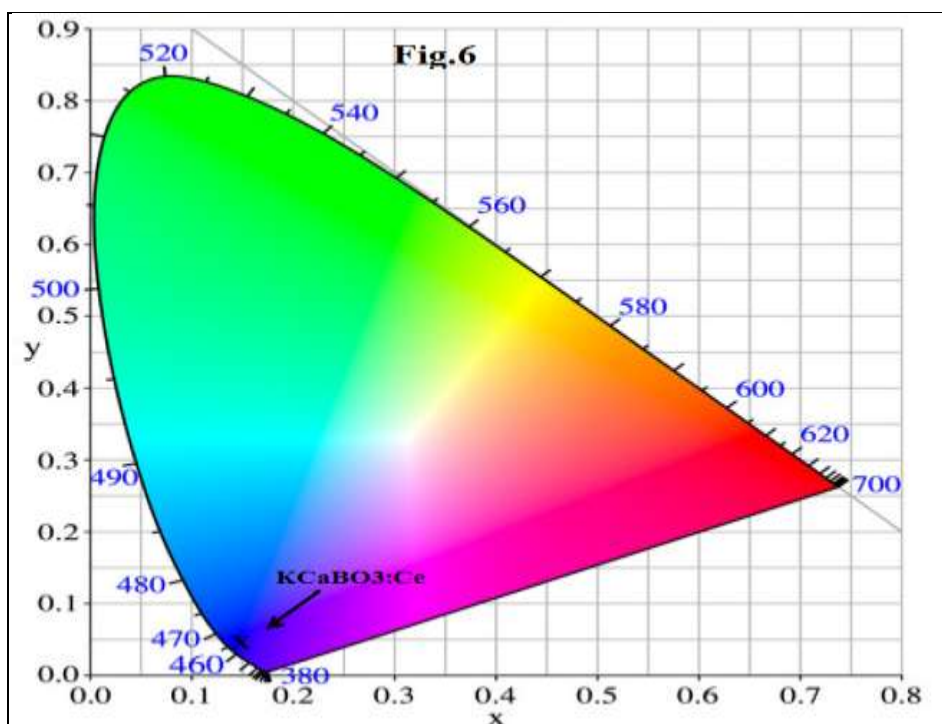


Fig.6.CIE colour coordinates of the phosphor $\text{KCaBO}_3:\text{xCe}^{3+}$

Fig.6 Shows CIE colour coordinates of the phosphor $\text{KCaBO}_3:\text{xCe}^{3+}$. The colour coordinates CIE 1931 for the as-synthesised phosphor are (0.14, 0.11) where as the commercial blue phosphor $\text{BAM}:\text{Eu}^{2+}$ shows the colour co-ordinates as (0.14, 0.107) indicating that as-synthesised phosphor is suitable blue emitting phosphor for solid state lighting.

Conclusion:

The blue emitting phosphor $\text{KCaBO}_3:\text{xCe}^{3+}$ is prepared by simple, time saving, economical method of solution combustion synthesis at comparatively lower temperature using urea as fuel. X-ray power diffraction (XRD) analysis confirmed the formation of the said phosphor. Photoluminescence measurements showed that the phosphor exhibited emission peak at 427nm, corresponding to $5d \rightarrow ^2F_{7/2}$ transition of Ce^{3+} .



The excitation spectra monitored at 427nm shows small peaks at 287nm and broad excitation band peaking at 360nm. The later lies in near ultraviolet (350-410nm) emission of UV LED.

The PL spectrum at various doping concentration of Ce^{3+} shows maximum emission intensity at $x=0.02$ after that concentration quenching is observed. The phosphor $KCaBO_3: 0.02Ce^{3+}$ shows color coordinates CIE 1931 as (0.14, 0.11) for optimum emission intensity. It is thus a potential candidate as blue emitting phosphor for solid state lighting using nUV chip.

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