Structural and optical properties of some rare earth doped $\text{BaY}_2\text{ZnO}_5$ nanophosphors
6.1.1 Introduction

In this present grooming era of nanotechnology, a class of rare earth doped nanophosphors allured the researchers owing to their use in plasma displays, field emission displays, opto-electronic devices, cathode ray tubes, solid state lasers and in development of white light emitting diodes [1]. Such types of nanophosphors are widely explored on grounds of their fascinating characteristics like pronounced luminescence efficiency, magnificent chemical stability and flexible emission colors accompanied by various activators [2-3]. Furthermore, it is also well known that the nanoscaling of the synthesized phosphor also reduces the non-radiative phenomenon and internal scattering which results in the enhancement of luminous efficacy. Moreover the nanoscaling imparts large surface to volume ratio which reinforces surface and interface effects. The phosphor converted white LEDs renders a benchmark in research area by virtue of low power consumption, ample stability, prolonged life time and ecologically beneficial thus replacing fluorescent lamps [4]. In order to fabricate white LEDs, one of the most feasible route consists of coating a near-ultraviolet LED chip with blue, green and red phosphor materials. Hence, being an essential component of PC-WLEDs, red or reddish orange nanophosphors are of great importance in SSL (Solid state lighting) engineering [5].

Luminescence is the utmost essential characteristic of rare earth doped inorganic nanomaterials originating from the ion intervening 4f electrons which are safely guarded from their chemical surrounding [6-9]. This results in a little influence of crystal field on energy levels yielding strong emission transition in visible range of spectrum with the activation in a suitable host matrix [10]. Among the various trivalent rare earth ions, Sm$^{3+}$ ion is one of the appealing activator owing to its efficient luminescence (strong orange emission) in visible region with ample application in optical devices. Nowadays, synthesis of single phased phosphors have attracted much attention by comprehending its utilization in phosphor converted WLEDs. In this series, BaY$_2$ZnO$_5$ is claimed as a worthy host matrix on account of its high thermal stability, high crystallinity, magnificent electronic and magnetic properties. BaY$_2$ZnO$_5$ crystallizes in orthorhombic crystal lattice with Pbnm (62) space group. The fundamental framework comprises of polyhedral units of YO$_7$.
BaO$_{11}$ and ZnO$_5$. In YO$_7$ polyhedra, Y resides in monocapped prismatic lattice coordinated by seven O atoms [11]. Ba atom in BaO$_{11}$ polyhedral unit resides in distorted 11-fold coordinated site while Zn resides in distorted tetragonal pyramidal lattice in ZnO$_5$ polyhedral unit.

Numerous strategies such as solid state method, hydrothermal process, sol-gel method and solution combustion approach have been exploited for the synthesis of nanoparticles with desired grain size. The conventional solid state method has disadvantages in form of sturdy mechanism of synthesis, very high processing temperature, long duration of time and sometimes decrease in luminescence properties by virtue of grinding process. We have implemented the solution combustion approach, a splendid tool for nanomaterials synthesis within short duration of time. Solution combustion is a very simple process with user friendly experimental set-up. The process involves heating of homogenous solution containing stoichiometric ratio of the oxidizers (metal nitrates) and the fuel (urea) in a preheated furnace maintained at 500°C. Within few minutes the self sustained highly exothermic reaction whose temperature may rise up to or more than 1600°C begins with frothing of liquid paste followed by ignition with flame yielding desired product expanded up to the top of the beaker [12]. The eruption of gases during the process helps in dissipation of large amount of energy as heat of combustion maintaining temperature of the system. The phosphor thus grown is single phased, homogenous, highly pure and crystalline in nature with high surface area at low temperature compared to conventional methods [13].

A few reports are available in literature regarding doping of BaY$_2$ZnO$_5$ host lattice with different rare earth ions such as Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Tm$^{3+}$ and Yb$^{3+}$ ions [11,14-24]. However, to the best of our knowledge no efforts have been made to explore the photoluminescence properties of Sm$^{3+}$ doped BaY$_2$ZnO$_5$ nanophosphor employing solution combustion process. Trivalent Sm$^{3+}$ ion with 4$f^5$ configuration is an excellent dopant providing greater radiation stability and high lumen output [25-26]. In view of this, Sm$^{3+}$ ion is selected as a dopant as it gives intense reddish orange emission attributed to its $^4$G$_{5/2}$→$^6$H$_j$ (j = 5/2, 7/2, 9/2, 11/2) transitions, which acts as a spectroscopic tool for investigating the local coordination environment around the central metal ion in mixed metal oxides. In the current work, the synthesis of single phased Sm$^{3+}$ doped BaY$_2$ZnO$_5$ nanophosphor by solution combustion process is
reported and its structural as well as photoluminescent properties are investigated. The Rietveld refinement study discloses that BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ exhibits single phase orthorhombic crystal lattice with *pbnm* space group. The luminescent properties were investigated as a function of temperature and varying concentration of Sm$^{3+}$ ion by excitation and emission spectra revealing ample application in NUV based phosphor converted white LEDs. Surface morphology and grain size were evaluated using transmission electron microscope (TEM) and X-ray diffraction studies.

### 6.1.2 Experimental

#### 6.1.2.1 Materials and synthesis

A series of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphors were synthesized by urea assisted solution combustion approach where $x$ vary from 0.005 to 0.07. High purity metal nitrates such as Ba(NO$_3$)$_2$, Y(NO$_3$)$_3$.6H$_2$O, Sm(NO$_3$)$_3$.6H$_2$O and Zn(NO$_3$)$_2$.6H$_2$O as starting materials were mixed in proper stoichiometric ratio along with calculated amount of the organic fuel urea in minimal amount of deionized water in a 250 mL capacity beaker. The mixture was continuously stirred in order to get a homogenous solution. The molar ratio of urea to the metal nitrates depends on total oxidizing and reducing valencies in the balanced reaction [27]. Urea as fuel is a necessary ingredient for the synthesis of highly uniform oxide with stoichiometric precision. In due course of reaction on being oxidized by nitrate ions urea acts as a fuel for the redox reaction. The beaker was then introduced into the preheated furnace maintained at 500°C for few minutes. The solution first faces dehydration and foaming accompanied by decomposition. The combustible gases produced in the way ignite and burn with flame resulting in formation of desired solid. The product was then taken out of furnace, cooled to room temperature and well crushed to powdered form. Fractions of the powder were sintered for 3 h at different temperatures from 700°C to 1100°C to analyze impact of temperature on luminescent behavior and configuration of nanophosphors.

#### 6.1.2.2 Material Characterization

The structural characteristics of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ as prepared and sintered at different temperatures were examined by Rigaku Ultima-IV X-ray powder diffractometer of high resolution using Cu K$_\alpha$ radiation operating at 40 kV voltage
setup and 40 mA tube current supply. The data was collected within diffraction angle 20 between 10 to 80° with scanning speed of 2° min⁻¹. The crystal phases of sample sintered at 1100°C (3 mol%) were inspected qualitatively and quantitatively employing Rietveld refinement technique by access to MAUD program for Rietveld refinement [28-31]. The morphological study of the Sm³⁺ activated nanophosphors was examined using Technai-G² transmission electron microscope (TEM). The photoluminescence spectra, decay curves and color coordinates were recorded using Hitachi F-7000 fluorescence spectrophotometer assembled with Xe-lamp. The excitation and emission slit width was set at 2.5 nm and PMT voltage of 400 V. The whole process was conducted at room temperature and atmospheric pressure.

6.1.3 Results and discussion

6.1.3.1 Structural properties

The quantitative and qualitative phase analysis of the synthesized nanophosphors is carried out by employing Rietveld refinement method. The Rietveld refinement of the data of BaY₁.₉₄Sm₀.₀₆ZnO₅ nanophosphor sintered at 1100°C displaying observed (black dot line) and calculated (solid red line) X-ray Diffraction (λ = 0.1540562 nm) profiles along with their difference at bottom is shown in Fig.6.1.1.

Fig.6.1.1 Rietveld refinement of BaY₁.₉₄Sm₀.₀₆ZnO₅ sample sintered at 1100°C for three hours. χ = 2.44, R_wp (%) = 10.68, R_p (%) = 7.52, R_exp (%) = 4.37.

The Rietveld refinement data of sample demonstrates that BaY₁.₉₄Sm₀.₀₆ZnO₅ nanophosphor crystallizes in single phase orthorhombic structure having space group
*Pbnm* (62) with almost zero impurity. The lattice parameters are found to be $a = 7.0735 \text{ Å}, b = 12.3342 \text{ Å}, c = 5.7107 \text{ Å}, \alpha = \beta = \gamma = 90^\circ$, $V = 498.2 \text{ Å}^3$ and $Z = 4$ and the refinement finally converged to $R_p = 7.52\%$, $R_{wp} = 10.68\%$ and $\chi^2 = 5.95$ [32-33]. The crystal structure data of $\text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5$ and standard host are tabulated in Table 6.1.1 for comparative study.

**Table 6.1.1 Comparison of crystal structure data of $\text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5$ nanophosphors with standard $\text{BaY}_2\text{ZnO}_5$**

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\text{BaY}_2\text{ZnO}_5$ (Standard)</th>
<th>$\text{BaY}<em>{1.94}\text{Sm}</em>{0.06}\text{ZnO}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>460.52</td>
<td>464.15</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td><em>Pbnm</em></td>
<td><em>Pbnm</em></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>7.068(3)</td>
<td>7.0735</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.324(4)</td>
<td>12.3341</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.706(2)</td>
<td>5.7107</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma$ (degree)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>497.0</td>
<td>498.2</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>6.2</td>
<td>6.1881</td>
</tr>
</tbody>
</table>

In $\text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5$ nanophosphor, $Y^{3+}$ ions are substituted by $\text{Sm}^{3+}$ ions randomly supported by the fact that the insertion of $\text{Sm}^{3+}$ ions leads to increase in unit cell volume from 497 Å$^3$ to 498.2 Å$^3$ due to larger ionic radius of $\text{Sm}^{3+}$ than $Y^{3+}$ ion. The decrease in density of the unit cell is observed from 6.2 to 6.1881 g/cm$^3$ due to increase in cell volume. The crystal structure of $\text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5$ nanophosphors sintered at 1100°C is displayed in inset (a) of Fig.6.1.1 which shows the sharing of same coordination environment between both trivalent $\text{Sm}$ and $Y$ ions. In this lattice, $\text{Sm}$ or $Y$ resides in $Cs$ symmetry sites forming $\text{MO}_7$ ($M = Y, \text{Sm}$) monocapped trigonal prismatic structure with $\text{M}_2\text{O}_{11}$ basic structural unit connected through edges along $b$-axis [34] as demonstrated in inset (b) of Fig.6.1.1. As valencies and ionic radii of $\text{Sm}^{3+}$ (1.02 Å) and $Y^{3+}$ (0.96 Å) are comparable and has no charge compensation issue so, $\text{Sm}^{3+}$ ions can easily substitute $Y^{3+}$ ions from its lattice site without any point defect.

The XRD profile of $\text{Sm}^{3+}$ doped $\text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5$ as prepared and sintered at different temperatures for 3 h along with reference file (JCPDS card No. 49-0516) is depicted in Fig.6.1.2. It reveals that all the well resolved peaks at 1100°C can be
indexed to pure orthorhombic crystal phase, accords to JCPDS card No. 49-0516. Some extra peaks are also resolved in XRD pattern of as prepared and sample sintered at 800°C and 900°C. The additional peaks in as-prepared sample corresponds to undecomposed Ba(NO₃)₂ which accords to JCPDS card No. 04-0773 marked as ● are present besides doped BaY₂ZnO₅ phase.

Fig.6.1.2 XRD profile of BaY₁.₉₄Sm₀.₀₆ZnO₅ powder sintered at different temperatures along with standard data of BaY₂ZnO₅ (JCPDS No. 49-0516).

At sintering temperature 800°C few low intensity peaks designated by ♦ and * can be attributed to Y₂O₃ and BaY₂O₄ phases (accords to JCPDS card No. 88-2162 and 82-2319, respectively) also coexist in the spectrum whereas unreacted Ba(NO₃)₂ peaks disappeared completely. On further sintering at 900°C, peaks corresponding to BaY₂O₄ phase weaken in intensity while peaks corresponding to BaY₂ZnO₅ phase strengthen. At 1000°C, the additional diffraction peaks get fully vanished while the characteristic peaks of Sm³⁺ doped BaY₂ZnO₅ phase appear in spectrum giving clear insight that the dopant gets very well incorporated into host lattice. Further at 1100°C all the peaks intensify and pure single phased BaY₂ZnO₅ with orthorhombic crystal lattice having Pbnm (62) space group is obtained.

The crystallite size is calculated using Debye Scherrer’s equation, \( D = \frac{0.941\lambda}{\beta \cos\theta} \), where D is the average crystallite size, \( \lambda \) is the X-ray wavelength (0.1548 nm), \( \theta \) and \( \beta \) are the diffraction angle and full width at half-maximum (FWHM, in radian) of an observed peak, respectively [35]. The calculated crystallite size accompanying
FWHM and phase for various mol% of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphors sintered at different temperatures is given in Table 6.1.2.

**Table 6.1.2** FWHM ($\beta$) and crystallite size (D) of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ at different mol% calculated using Scherrer’s equation

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>x = 0.005</th>
<th>x = 0.01</th>
<th>x = 0.03</th>
<th>x = 0.05</th>
<th>x = 0.07</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>$\beta$ (°)</td>
<td>D (nm)</td>
<td>$\beta$ (°)</td>
<td>D (nm)</td>
<td>$\beta$ (°)</td>
</tr>
<tr>
<td>BaY$_2$O$_4$</td>
<td>0.144(60.52)</td>
<td>0.118(74.15)</td>
<td>0.102(86.61)</td>
<td>0.099(89.23)</td>
<td>0.138(61.76)</td>
</tr>
<tr>
<td>BaY$_2$ZnO$_5$</td>
<td>0.102(86.61)</td>
<td>-</td>
<td>0.099(89.23)</td>
<td>-</td>
<td>0.138(62.00)</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>0.099(89.23)</td>
<td>-</td>
<td>0.094(91.42)</td>
<td>-</td>
<td>0.136(63.32)</td>
</tr>
</tbody>
</table>

The FWHM of the most prominent peak of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ nanophosphor decreases with increasing sintering temperature as 0.164°, 0.099°, 0.091° and 0.090° at temperatures 800-1100°C, respectively.

![XRD profile of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$](image)

Fig.6.1.3 XRD profile of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ (x = 0.005–0.07) along with standard data of BaY$_2$ZnO$_5$ (JCPDS No. 49-0516).
This decrease in line width is possibly due to enhancement in crystallinity [36-37] with increasing temperature. The average crystallite size of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ nanophosphor is found to be 52.21, 86.63, 95.44 and 95.15 of as prepared and sample sintered at 800-1100°C, respectively by indexing the most prominent peak. This increase in particle size with temperature is because of fast crystal settlement due to greater movement of atomic particles [4]. Fig.6.1.3 displays the XRD profile of BaY$_{2(1-x)}$Sm$_2$ZnO$_5$ where x = 0.5-7 mol% sintered at 1100°C along with standard data (JCPDS card No. 49-0516). The effect of Sm$^{3+}$ ion concentration on BaY$_2$ZnO$_5$ host lattice seems to be negligible as the XRD pattern remains unaltered without any reshuffling of diffraction peaks at different Sm$^{3+}$ ion concentration i.e. 0.5- 7 mol%.

6.1.3.2 Morphological characteristics

Surface morphological study of Sm$^{3+}$ doped BaY$_2$ZnO$_5$ nanophosphors have been investigated by TEM analysis. TEM micrograph of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ nanoparticles sintered at 1100°C displayed in Fig.6.1.4 shows the average particle size in the range 80-90 nm which is in close relation with that determined from Scherrer’s equation.

Fig.6.1.4 TEM micrograph of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ powder sintered at 1100°C.

The sample exhibit semi spherical shaped particles without any agglomeration. The narrow size distribution of particles, increase in crystallinity with sintering temperature and removal of additional phases enhanced the photoluminescent properties of Sm$^{3+}$ doped BaY$_2$ZnO$_5$ nanophosphors.
6.1.3.3 Optical properties

On rooting emission wavelength at 610 nm, the photoluminescence excitation spectrum of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ nanophosphor sintered at 1100°C is demonstrated in Fig.6.1.5. The photoluminescence excitation (PLE) studies have been carried out in solid state at room temperature.

The spectrum comprise of a broad band in UV region ranging from 200 to 260 nm with maxima at 241 nm and some sharp peaks in the region between 350-550 nm which are the characteristic f-f transition of Sm$^{3+}$ ions from ground state to excited state. The peak at 241 nm is the charge transfer band attributed to host absorption and electron transition from O$^2-$ (2p orbital) to the empty 4f orbital of Sm$^{3+}$ ion [38]. The characteristic f-f transition peaks with maximum intensity peak at 411 nm is ascribed as $^6$H$_{5/2}$→$^4$K$_{11/2}$ transition and other peaks at 350, 366, 382, 395, 423, 469, 482 and 493 nm are attributed to the transition from ground state $^6$H$_{5/2}$ to $^3$H$_{7/2}$, $^4$F$_{9/2}$, $^4$D$_{5/2}$, $^4$P$_{11/2}$, $^6$P$_{5/2}$+$^4$M$_{19/2}$, $^4$F$_{5/2}$+$^4$I$_{13/2}$, $^4$G$_{7/2}$, $^4$I$_{11/2}$ + $^4$M$_{15/2}$ excited states respectively [39-40]. The maximum intensity peak at 411 nm wavelength reveals that such type of nanophosphors can be successfully excited by NUV LEDs [38].

Fig.6.1.6 depicts the PL emission spectra of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ as-prepared and sample sintered at different temperatures from 800°C to 1100°C on monitoring $\lambda_{ex}$ = 411 nm. The emission spectra comprise of a prominent peak at 610 nm ($^4$G$_{5/2}$→$^6$H$_{7/2}$),
which is partly magnetic dipole and partly forced electric dipole [41]. Another lower intensity peak originating from magnetic dipole transition is observed at 570 nm corresponding to $^4G_{5/2} \rightarrow ^4H_{5/2}$ transition and is independent of symmetry around luminescent center. Magnetic dipole transition obey selection rule $\Delta j = 0, \pm 1$ where $j$ is total angular momentum [10].

![Fig.6.1.6 PL emission spectra of BaY$_{1.94}$Sm$_{0.06}$ZnO$_5$ nanophosphor at different sintering temperatures on monitoring $\lambda_{ex} = 411$ nm.](image)

A hypersensitive peak of very low intensity is also visible in emission spectrum at 661 nm ascribed to electric dipole allowed $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition. This transition is symmetry dependent and its intensity decreases with increasing local symmetry. The ratio of electric to magnetic dipole intensity displays the symmetry of Sm$^{3+}$ ion in host lattice, greater ratio leads to more distortion. Here the ratio comes out to be 0.246. The smaller ratio suggests that Sm$^{3+}$ ions are properly embedded in the host lattice ruling out any distortion in the chemical environment [42]. The schematic energy level diagram portraying the energy transfer mechanism involving radiative and non-radiative transitions leading to down conversion process has been depicted in Fig.6.1.7.

Further it is obvious from Fig.6.1.6 that intensity of all the peaks enhances with increase in sintering temperature from 500 to 1100°C under same dopant concentration. The possible reason behind this boost in intensity is increase in crystallinity of nanophosphors and magnified grain size by post heat treatment process as supported by XRD profile Fig.6.1.2.
Fig.6.1.7 Energy level diagram for Sm$^{3+}$ doped BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphor sintered at 1100°C.

This increase in crystallinity yields more homogenous allocation of Sm$^{3+}$ ions in the lattice and also helps in reduction of non-radiative cross relaxation between adjacent ions [4, 43] because of amplified particle size, consequently luminescence intensity increases with gradual increase in sintering temperature.

Fig.6.1.8 PL emission spectra of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphors ($x = 0.5$-$7$ mol%) sintered at 1100°C on monitoring $\lambda_{ex} = 411$ nm.
The photoluminescent emission behavior of \( \text{BaY}_{2(1-x)}\text{Sm}_2\text{ZnO}_5 \) \((x = 0.5-7 \text{ mol%})\) powder as a function of trivalent samarium ion concentration is illustrated in Fig.6.1.8. The variance of emission intensity with various concentration of dopant ion in \( \text{BaY}_{2(1-x)}\text{Sm}_2\text{ZnO}_5 \) \((x = 0.5-7 \text{ mol%})\) sintered at 1100°C is shown by Fig.6.1.9. The figure depicts the increase in luminous intensity with increase in concentration up to 3 mol% thereupon decreases swiftly entitled as concentration quenching. Once the quenching concentration is attained, further increase in dopant concentration results in decrease in luminous intensity. The feasible ground of this quenching is that over doping brings the dopants closer which leads to increased possibility of non-radiative energy transfers from one to other luminescent center. Thus luminescence intensity decreases thereafter.

![Fig.6.1.9 Emission Intensity of \( \text{BaY}_{2(1-x)}\text{Sm}_2\text{ZnO}_5 \) nanophosphors as a function of concentration of \( \text{Sm}^{3+} \) ion contents sintered at 1100°C.](image)

Non-radiative energy relaxation process of \( \text{Sm}^{3+} \) ions may occur via three possible routes; exchange interaction, radiation reabsorption and multipole-multipole interaction. Later depends on the critical distance \( (R_c) \) between neighboring \( \text{Sm}^{3+} \) ions which can be calculated by utilizing equation (6.1.1) as:

\[
R_c = 2 \left[ \frac{3V}{4\pi x_c N} \right]^{1/3}
\]

(6.1.1)

Where \( N \) corresponds to the host cations in the unit cell, \( x_c \) is the critical concentration of dopant ion and \( V \) is the volume of unit cell [44]. From the crystal structure data of \( \text{BaY}_{1.94}\text{Sm}_{0.06}\text{ZnO}_5 \) nanophosphors, \( N = 8, x_c = 0.03 \) and \( V = 498.2 \text{ Å}^3 \), the value of \( R_c \)
is found to be 15.82 Å. Radiation reabsorption for energy relaxation mechanism is discarded because of large critical distance and further the PL spectrum is devoid of any overlapping between excitation and emission spectra, so exchange interaction route is also over ruled. Therefore, the relaxation process must be followed by multipole-multipole interaction pathway directed by the Dexter’s theory [45]. The multipolar interactions between the dopant ions in host lattice can be determined by utilizing equation (6.1.2) as:

\[
\frac{I}{x} = K\left[1 + \beta(x) Q^{1/3}\right]^{-1}
\]  

(6.1.2)

Where \(x\) corresponds to concentration of dopant ion greater than critical concentration, \(Q\) is multipolar interaction constant whose value varies as 6, 8, 10 for dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively while \(K\) and \(\beta\) are the constants for the given host under similar conditions of excitation. The slope of the curve plotted between \(\log(I/x)\) and \(\log(x)\) is found to be -2.1895 yielding \(Q\) value 6.5685 \(\approx\) 6 (Fig.6.1.10). Hence dipole-dipole interactions are the primary reason behind the occurrence of concentration quenching in trivalent samarium doped \(\text{BaY}_2\text{ZnO}_5\) nanophosphors.

![Fig.6.1.10 Plot of log (I/x) against log(x) in \(\text{BaY}_{2(1-x)}\text{Sm}_x\text{ZnO}_5\) nanophosphors.](image)

For \(\text{BaY}_{2(1-x)}\text{Sm}_x\text{ZnO}_5\) nanophosphors (\(x = 0.5\)-7 mol%), the decay of emission intensity at 610 nm as a function of time is depicted in Fig.6.1.11. The decay curves follow single exponential function as:
\[ I = I_0 \exp(-t/\tau) \quad (6.1.3) \]

where \( \tau \) is radiative decay time, \( I \) and \( I_0 \) are luminescence intensities at time \( t \) and 0, respectively. The life time values (ms) for \( \text{BaY}_2(1-x)\text{Sm}_2x\text{ZnO}_5 \) nanophosphors calculated from mono exponential fits are tabulated in Table 6.1.3.

![Decay curves of the \( ^4G_{5/2} \rightarrow ^6H_{7/2} \) transition at 610 nm for \( \text{Sm}^{3+} \) doped \( \text{BaY}_2(1-x)\text{Sm}_2x\text{ZnO}_5 \) nanophosphors with different concentration.](image)

The mono exponential essence of decay curve implies the existence of uniform allocation of trivalent samarium ions in the host crystal lattice without any kind of agglomeration [46].

**Table 6.1.3 CIE coordinates and lifetime of \( \text{BaY}_2(1-x)\text{Sm}_2x\text{ZnO}_5 \) with different mol\% of \( \text{Sm}^{3+} \) ions sintered at 1100°C on monitoring 411 nm excitation wavelength**

<table>
<thead>
<tr>
<th>( \text{BaY}_2(1-x)\text{Sm}_2x\text{ZnO}_5 ) (mol%)</th>
<th>CIE Coordinates ((x, y))</th>
<th>Lifetime (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5617, 0.4362</td>
<td>0.888</td>
</tr>
<tr>
<td>1</td>
<td>0.5659, 0.4320</td>
<td>0.806</td>
</tr>
<tr>
<td>3</td>
<td>0.5632, 0.4344</td>
<td>0.690</td>
</tr>
<tr>
<td>5</td>
<td>0.5720, 0.4256</td>
<td>0.570</td>
</tr>
<tr>
<td>7</td>
<td>0.5685, 0.4281</td>
<td>0.552</td>
</tr>
</tbody>
</table>
Fig. 6.1.12 CIE chromaticity diagram for different concentration of Sm$^{3+}$ ion for BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphors ($x = 0.5, 5, 7$ mol%) sintered at 1100°C on monitoring $\lambda_{ex} = 411$ nm.

The emission color of BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ doped with various concentration of Sm$^{3+}$ ions sintered at 1100°C on rooting 411 nm excitation wavelength is examined. All the color coordinates lie in orange-red region affirmed by Commission International De l’Eclairage (CIE 1931) chromaticity diagram. The value of color coordinates ($x, y$) evaluated using corresponding emission spectra are tabulated in Table 3. The coordinates shifts slightly from orange ($x = 0.5617, 0.4362$) to reddish orange ($x = 0.5720, 0.4256$) with increasing dopant concentration from $x = 0.5$ to 7 mol% as depicted in Fig. 6.1.12. All the color coordinates for the nanophosphor lie in orange-red region marking their suitability for near ultraviolet excited phosphor converted white light emitting diodes [49–50].
SECTION-6.2

6.2.1 Introduction

From last few decades, the scientific community is witnessing a boom in the sector of nanotechnology. The nanoscaling imparts these materials with magnificent electronic, optical and structural properties with much enhanced features than the bulk materials [51-52]. Due to these enhanced properties these nanomaterials are widely explored in the display devices like plasma display panels (PDPs), field emission displays and one of the most fascinating research areas that are mercury free solid state lighting system consisting light emitting diodes accompanying suitable phosphors [53-57]. In order to develop lighting systems with high color rendering index (CRI), improved color temperature and high luminescence efficiency the UV LEDs establish a platform specifically near ultraviolet (NUV- 300< λ <400 nm) excited, phosphor converted white light emitting diodes; designed by combination of red, blue and green phosphors coating a near UV excited LED chip [58]. In this regard, green emitting phosphors proves as an efficient component of RGB tricolor based lighting materials for the production of white light.

Moreover, these nanophosphors doped with rare earth ion marks as the thrust domain of research, owing to its remarkable characteristics like high lumen output, good color rendering index, high thermal stability and magnificent quantum efficiency involved with its unique optical behavior [59-63]. The intra configurational 4f shell electrons in RE$^{3+}$ ions, which are shielded from the outer crystal field by 5s$^2$ and 5p$^6$ electrons, are solely responsible for the electronic transitions from various states yielding luminescence characteristic to these nanophosphors. Among the various RE$^{3+}$ ions, Er$^{3+}$ doped nanophosphors are widely explored because of green emitting luminescent properties and hence utilized as essential green component of the PC-WLEDs [64-66]. These Er$^{3+}$ doped materials makes a good choice in lighting materials on ground of its unique photoluminescent characteristics in the range 380-760 nm which fall in the visible domain of electromagnetic spectrum. Moreover, the capability to absorb in the longer wavelength region marks the utility of Er$^{3+}$ ion in the field of laser [67].

In this series, erbium doped oxide host matrix BaY$_2$ZnO$_5$ finds potential applications for luminescent phosphors on grounds of its magnificent electronic and
magnetic properties, greater crystallinity, high thermal stability and high stability in air. As a consequence, BaY$_2$ZnO$_5$ is claimed as a worthy host material selection for the present study and its properties are investigated accordingly. The erbium doped oxide BaY$_2$ZnO$_5$ can be crystallized in orthorhombic crystal lattice with $Pbnm$ (62) space group. This orthorhombic lattice is composed of polyhedral units of BaO$_{11}$, ZnO$_5$ and YO$_7$ basic units. In BaO$_{11}$ unit Ba resides in distorted 11-fold coordination geometry, Zn occupies distorted tetragonal pyramidal lattice in ZnO$_5$ unit while Y coordinated by seven O atoms occupies monocapped prismatic lattice in YO$_7$ polyhedra [11].

Amongst the various techniques available for the synthesis of nanophosphors such as solid state method, sol-gel synthesis, hydrothermal process, microwave assisted synthesis and solution combustion synthesis; the solution combustion process is implemented in order to synthesize the single phased particles in nano regime. The solution combustion synthesis is user friendly process and has very easy experimental setup to handle. This process is triggered by the self governed exothermic reaction involving heating of stoichiometric ratio of metal nitrates and the oxidizer organic fuel (urea). Within a few minutes the reaction mixture may attain the temperature as high as 1600°C accompanied by dehydration, decomposition and generation of gases and finally leading to formation of desired product with narrow size distribution, greater homogeneity, high crystallinity and high chemical purity [12-13].

This process is economical one having merits in terms of energy saving, absorbs lesser time, cheaper, safe and simple handling with single step reaction. While the nanophosphors synthesized via conventional method, may sometimes deals with reduced luminescence features due to exhaustive grinding [20]. Also this process involves high sintering temperature with longer time duration. Some reports have been pinpointed in literature concerning doping of BaLn$_2$ZnO$_5$ (Ln = Y/Gd/La) host matrix [11, 14, 16-24, 68-69] however, to the best of author’s knowledge this is the first report to synthesize erbium doped BaY$_2$ZnO$_5$ nanophosphor via solution combustion method.

Herein, the synthesis, properties and suitability of BaY$_{2(1-x)}$Er$_x$ZnO$_5$ nanophosphors for the solid state lighting system in NUV excited PC-WLEDs are demonstrated. The author did not come across any report explaining the mechanism behind the concentration quenching phenomenon in Er$^{3+}$ doped BaY$_2$ZnO$_5$ host
matrix. The mechanism of concentration quenching has been illustrated appropriately in the present study. To better understand the cause of this phenomenon the critical distance ($R_c$) between the neighboring luminescent centres is calculated to analyze the non-radiative energy transformations.

6.2.2 Experimental

6.2.2.1 Materials and synthesis

A series of $\text{BaY}_{2(1-x)}\text{Er}_x\text{ZnO}_5$ ($x = 0.005-0.07$) nanophosphors were synthesized by urea assisted solution combustion approach. High purity metal nitrates such as $\text{Ba(NO}_3)_2$, $\text{Y(NO}_3)_3.6\text{H}_2\text{O}$, $\text{Er(NO}_3)_3.6\text{H}_2\text{O}$ and $\text{Zn(NO}_3)_2.6\text{H}_2\text{O}$ as raw materials were weighed according to the stoichiometric ratio. They were then mixed with calculated amount of the organic fuel urea in minimal amount of deionized water in a 250 mL capacity beaker with vigorous stirring to obtain a homogenous solution. The molar ratio of urea was taken according to the total oxidizing and reducing valencies in the balanced reaction [27]. Urea acts as a fuel for development of highly uniform stoichiometrically precised oxide which in turn gets oxidized by nitrate ions and supplies energy in due course of the exothermic reaction. The beaker was then referred into the preheated furnace maintained at 500°C for few minutes. The exothermic reaction initially suffered dehydration and foaming accompanied by decomposition. The flammable gases generated in the course of high energy exothermic reaction ignite and burn with flame yielding desired solid. The product was then taken out of furnace, cooled to room temperature and grounded to fine powdered form. The powder was transferred to desiccator for further characterization.

6.2.2.2 Material characterization

The structural analysis of $\text{BaY}_{2(1-x)}\text{Er}_x\text{ZnO}_5$ as-prepared and sintered at different temperatures was done using high resolution Rigaku Ultima-IV X-ray powder diffractometer operating with Cu $\text{K}_\alpha$ radiation at 40 kV voltage and 40 mA tube current. Diffraction pattern was recorded at scan speed of 2° min$^{-1}$ within 2θ range 10 to 80°. The qualitative and quantitative phase elucidation of samples was performed by using Rietveld refinement technique by GSAS (General Structure Analysis System) package for Rietveld refinement [70-72]. The morphological study of the Er$^{3+}$doped nanophosphors was carried out using Tecnai-$\text{G}^2$ transmission electron microscope (TEM) in order to confirm grain size as estimated by Scherrer’s equation.
using the X-ray diffraction analysis. The photoluminescent studies including excitation and emission spectra, decay curves and chromaticity color coordinates were carried out at PMT voltage of 400V, excitation and emission slit width 2.5 nm and scanning rate 1200 nm min$^{-1}$ by using Hitachi F-7000 fluorescence spectrophotometer assembled with Xe-lamp. All the above studies were conducted at room temperature and atmospheric conditions.

6.2.3 Results and discussion

6.2.3.1 Structural properties

The phase composition and crystallinity of the synthesized powder material is checked by assessing X-ray diffraction analysis. The quantitative and qualitative phase analysis of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ nano-crystalline sample sintered at 1300°C is processed by employing Rietveld refinement technique. Rietveld refinement performed over the XRD data of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ sample is illustrated in Fig.6.2.1 depicting the observed (black dot line) and calculated (solid red line) X-ray diffraction profile ($\lambda = 0.15405$ nm) accompanying their difference at the bottom of the figure.

![Rietveld refinement of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ with sample sintered at 1300°C for three hours. $\chi^2 = 1.89$, $R_{wp}$ (%) = 16.50, $R_p$ (%) = 13.10.](image)

The figure reveals that the sample crystallizes in orthorhombic lattice with Pbnm (62) space group. The unit cell parameters are found to be $a = 7.0699(3)$ Å, $b = 12.3351(5)$
Å, c = 5.7088(2) Å, V = 497.85(4) Å³, Z = 4 with the refinement finally converged to 
$R_p = 13.10\%$, $R_{wp} = 16.50\%$ and $\chi^2 = 1.89$. The three dimensional unit cell structure 
seen from 111 miller plane is shown in inset of Fig.6.2.1. The lattice parameters of 
$\text{BaY}_{1.92}\text{Er}_{0.08}\text{ZnO}_5$ and standard host matrix are presented in Table 6.2.1 for 
comparison.

**Table 6.2.1 Comparison of crystal structure data of $\text{BaY}_{1.92}\text{Er}_{0.08}\text{ZnO}_5$ nanophosphors with standard $\text{BaY}_2\text{ZnO}_5$**

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\text{BaY}_2\text{ZnO}_5$ (Standard)</th>
<th>$\text{BaY}<em>{1.92}\text{Er}</em>{0.08}\text{ZnO}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>460.52</td>
<td>466.79</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>$Pbnm$</td>
<td>$Pbnm$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>7.07020(7)</td>
<td>7.0699(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.33677(13)</td>
<td>12.3351(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.70908(6)</td>
<td>5.7088(2)</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma$ (degree)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>497.97</td>
<td>497.85(4)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Furthermore, the ionic radii of trivalent ions $Y^{3+}$ and $\text{Er}^{3+}$ ion are close enough 
(0.96 Å and 0.945 Å, respectively) with similar valencies, so $\text{Er}^{3+}$ ion can easily 
substitute $Y^{3+}$ ion in the orthorhombic crystal lattice leaving out any possibility of 
point defect in the lattice. In the orthorhombic crystal lattice $Y/\text{Er}$ acquires 
monocapped trigonal prismatic structure forming $Y_2O_{11}$ basic framework with every 
$Y_2O_{11}$ polyhedral unit joined with each other through edges making chain along b axis 
[35]. Both $Y/\text{Er}$ sites ($Y_1/\text{Er}_1$ and $Y_2/\text{Er}_2$) shares the same seven coordinated 
environment in the orthorhombic lattice. Moreover, the small change in unit cell volume from 497.97 Å³ to 497.85(4) Å³ is measured which further claims the 
substitution of $Y^{3+}$ ion by $\text{Er}^{3+}$ ion in the lattice.

Fig.6.2.2 illustrates the diffraction pattern of $\text{BaY}_{1.92}\text{Er}_{0.08}\text{ZnO}_5$ as-prepared 
sample and sintered at different temperatures accompanied by the standard data 
JCPDS card No. 49-0516. The well defined profile peaks at 1000°C and 1100°C 
temperatures are very well accord to the JCPDS confirming the completion of 
crystallization of the sample in single phased orthorhombic lattice. The XRD 
spectrum of as prepared sample and sintered at 800°C as well as 900°C is a mixture of
phases along with the required BaY$_2$ZnO$_5$ phase. In order to get single pure phased BaY$_2$ZnO$_5$ nanophosphors the as-prepared sample required further heat treatment and was sintered for 3 h at different temperatures. The as-prepared sample shows very poor phase purity because of presence of secondary phase corresponding to unreacted Ba(NO$_3$)$_2$ (JCPDS card No. 04-0773) marked by ● which get dissolved in the spectrum on further heat treatment of the sample. On sintering at 800°C, the spectrum carries additional peaks marked as ♦ and * corresponding to Y$_2$O$_3$ and BaY$_2$O$_4$ (JCPDS card No. 88-2162 and 82-2319, respectively) in addition to few peaks of BaY$_2$ZnO$_5$ phase with high line width giving insight of poor phase crystallinity of the sample. Even at 900°C the motive of single phase was not yet achieved and marked by presence of trace amount of secondary phase BaY$_2$O$_4$ although the other impurity phases like Ba(NO$_3$)$_2$ and Y$_2$O$_3$ are fully vanished from the spectrum.

![XRD profile of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ powder sintered at different temperatures along with standard data of BaY$_2$ZnO$_5$ (JCPDS No. 49-0516).](image)

**Fig.6.2.2** XRD profile of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ powder sintered at different temperatures along with standard data of BaY$_2$ZnO$_5$ (JCPDS No. 49-0516).

At 1000°C the sample is characterized by impurity free BaY$_2$ZnO$_5$ peaks that are well indexed to the orthorhombic crystal lattice having $Pbnm$ space group. On further sintering at 1100°C for 3 h, the characteristic BaY$_2$ZnO$_5$ peaks get intensified with decrease in full width half maximum (FWHM) of the most prominent peak at 29.58° arising from (131) plane. The increase in intensity as well as decrease in the line width adds to the improved crystallinity of the BaY$_2$ZnO$_5$ phase with increase in sintering temperature.
The effect of doping concentration on crystallization of BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ (x = 0.5-7 mol%, respectively) sintered at 1100°C along with JCPDS card No. 49-0516 is depicted in Fig.6.2.3. The figure illustrates the similar pattern of diffraction peaks accompanying different concentration of Er$^{3+}$ ion without any reshuffling in position of peaks; making clear that the small concentration of dopant ion (Er$^{3+}$) does not have any considerable impact on the crystal structure of BaY$_2$ZnO$_5$.

Fig.6.2.3 XRD profile of BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ (x = 0.005–0.07) along with standard data of BaY$_2$ZnO$_5$ (JCPDS No. 49-0516).

Debye Scherrer’s equation, $D = \frac{0.941 \lambda}{\beta \cos \theta}$ was utilized in order to calculate the crystallite size where D is the average grain size, $\lambda$ the X-ray wavelength used (0.1548 nm), $\theta$ and $\beta$ are the diffraction angle and full width at half-maximum (FWHM, in radian) of an observed peak, respectively [4]. The line width has a close relation with the crystallinity; decrease in line width increases the crystallinity factor. And also with increase in sintering temperature the FWHM of the most prominent peak decreases leading to increase in crystallite size.

FWHM of the most prominent peak at 29.58° of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ nanophosphor is found to be 0.212, 0.151, 0.136, 0.134 at 800-1100°C, respectively while the corresponding crystallite size is estimated to be 40.45, 56.98, 62.05, and 64.05 nm, respectively. This enhancement in crystallinity with increasing temperature occurs as a result of increase in kinetic energy of the atomic particles which speed up the crystal growth due to faster mobility of particles and accounts for the increase in particle size with increasing temperature [73]. The calculated crystallite size of BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$
(x = 0.5-7 mol%) powder along with FWHM and phase at different sintering temperature has been summarized in Table 6.2.2.

Table 6.2.2 FWHM (β) and crystallite size (D) of BaY_{2(1-x)}Er_{2x}ZnO_{5} at different mol% calculated using Scherrer’s equation

<table>
<thead>
<tr>
<th>Temperature</th>
<th>BaY_{2(1-x)}Er_{2x}ZnO_{5} Phase</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.005</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.189(45.21)</td>
<td>0.148(57.98)</td>
<td>0.134(64.15)</td>
<td>0.126(67.94)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.165(52.04)</td>
<td>0.175(50.14)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.180(46.70)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x = 0.01</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.207(41.35)</td>
<td>0.182(47.07)</td>
<td>0.140(61.30)</td>
<td>0.133(64.30)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.274(31.41)</td>
<td>0.208(49.64)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.199(42.21)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x = 0.03</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.239(35.74)</td>
<td>0.142(60.67)</td>
<td>0.139(61.90)</td>
<td>0.135(63.50)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.169(51.07)</td>
<td>0.153(57.06)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.361(24.03)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x = 0.04</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.212(40.45)</td>
<td>0.151(56.98)</td>
<td>0.136(62.05)</td>
<td>0.134(64.05)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.156(55.22)</td>
<td>0.152(56.25)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.220(39.46)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x = 0.05</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.185(46.15)</td>
<td>0.161(53.06)</td>
<td>0.135(63.53)</td>
<td>0.134(63.81)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.160(53.85)</td>
<td>0.179(48.50)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.261(33.18)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x = 0.07</td>
<td>BaY_{2}ZnO_{5}</td>
<td>0.211(42.03)</td>
<td>0.141(60.49)</td>
<td>0.138(61.97)</td>
<td>0.137(62.30)</td>
</tr>
<tr>
<td></td>
<td>BaY_{2}O_{4}</td>
<td>0.176(50.11)</td>
<td>0.159(55.14)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Y_{2}O_{3}</td>
<td>0.259(34.26)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

6.2.3.2 Morphological characteristics

The morphological investigation of BaY_{2(1-x)}Er_{2x}ZnO_{5} nanophosphor has been executed through transmission electron microscopy. Fig.6.2.4 represents the TEM micrograph of BaY_{1.02}Er_{0.08}ZnO_{5} sample which shows single particle with more or less spherical morphology. The randomly distributed non-agglomerated particles are observed with the average particle size in the range 40-70 nm which is in close agreement with that estimated from Scherrer’s equation. The nanoscaled particles possess larger surface area to volume ratio and reduced internal scattering than the bulk system which improves the luminous efficacy of the materials [74-75]. Additionally, the spherical shape and narrow size distribution of the nanoparticles further appeal in the development of nanophosphors with effective and desired properties for application in various fields.
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Although this HA band arising from the electron transition from oxygen 2p orbital to the vacant f orbital of Er$^{3+}$ is weak and appear as a very low intensity band in the spectrum [21] while the intra 4f transitions appear as very sharp lines in the spectrum associated with transition from ground state $^4$I$_{15/2}$ to various excited state of Er$^{3+}$ ion. The most prominent intensity peak appear in the spectrum at 380 nm ascribed to $^4$I$_{15/2}$$\rightarrow$$^4$G$_{11/2}$ transition while other peaks at 359, 367, 408, 446, 453, 491, and 522 nm are assigned to $^4$I$_{15/2}$$\rightarrow$$^4$G$_{7/2}$, $^4$I$_{15/2}$$\rightarrow$$^4$G$_{9/2}$, $^4$I$_{15/2}$$\rightarrow$$^2$G$_{9/2}$, $^4$I$_{15/2}$$\rightarrow$$^4$F$_{3/2}$, $^4$I$_{15/2}$$\rightarrow$$^4$F$_{5/2}$, $^4$I$_{15/2}$$\rightarrow$$^3$F$_{7/2}$ and $^4$I$_{15/2}$$\rightarrow$$^2$H$_{11/2}$ transition, respectively [76].

![Fig.6.2.6 PL emission spectra of BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ nanophosphor at different sintering temperatures on monitoring $\lambda_{ex}$ = 380 nm.](image)

On NUV irradiation at 380 nm, BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ nanophosphor sintered at different temperatures exhibits strong green emission is depicted in Fig.6.2.6. After efficiently excited to $^4$G$_{11/2}$ level of Er$^{3+}$ ion, through non-radiative emission populates different level, which then relaxes radiatively to the ground state. The normalized emission spectra comprise of three peaks with dominating green emissive peak at 549 nm arising from to $^4$S$_{3/2}$$\rightarrow$ $^4$I$_{15/2}$ transition [76]. The doublet nature of this transition can be explained in terms of Stark splitting. Another green emission occurs at 529 nm corresponding to $^2$H$_{11/2}$$\rightarrow$ $^4$I$_{15/2}$ transition.

A comparative lower intensity violet band appears at 409 nm wavelength arising from to $^2$H$_{9/2}$$\rightarrow$ $^4$I$_{15/2}$ transition [43]. The spectrum is devoid of a red emission band at 660 nm may be attributed to $^4$F$_{9}$$\rightarrow$ $^4$I$_{15/2}$ transition unveiling non-radiative emission.
from this transition level. All the spectral lines present in the spectrum are further split in two or three shoulder peaks. The energy transfer mechanism associated with radiative and non-radiative energy transition resulting down conversion process is illustrated through schematic energy level diagram in Fig.6.2.7.

![Energy level diagram for Er\(^{3+}\) doped BaY\(_{2(1-x)}\)Er\(_{2x}\)ZnO\(_5\) nanophosphors sintered at 1100°C.](image)

The emission or luminescence efficiency is affected by the crystallite size in the nano scale. The crystallite size increases with increase in sintering temperature giving indication of better crystallization possibly due to reduction of non-radiative recombination effects, quenching sites and surface effects leading to increase in luminescence efficiency [73]. This increase in crystallinity by heating process leads to more homogenous distribution of Er\(^{3+}\) in the host lattice [44]. And this is clear from the normalized spectra in Fig.6.2.6 which depicts that with increase in temperature the ratio of green to blue emission peaks increases. This observation shows the enhancement in green emission intensities of spectral lines of BaY\(_{1.92}\)Er\(_{0.08}\)ZnO\(_5\) nanophosphor as a function of sintering temperature with maximum intensity at 1100°C. The concentration dependent luminescent behavior of Er\(^{3+}\) doped BaY\(_2\)ZnO\(_5\) nanophosphor sintered at 1100°C is depicted in Fig.6.2.8. The variance of emission intensity as a function of Sm\(^{3+}\) ion is illustrated in Fig.6.2.9.

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Fig. 6.2.8 PL emission spectra of BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ nanophosphors ($x = 0.5$ - 7 mol%) sintered at 1100°C on monitoring $\lambda_{ex} = 380$ nm.

The normalized spectra reveal that at low concentration of Er$^{3+}$ ion the blue emission dominates in the spectra. But with increasing Er$^{3+}$ ion concentration the green to blue emission peak ratio increases.

Fig. 6.2.9 Emission Intensity of BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ nanophosphors as a function of concentration of Er$^{3+}$ ion contents sintered at 1100°C.

The relative green emission peak ratio increases as a function of Er$^{3+}$ concentration up to 4 mol% then decreases afterwards and is also reflected from the color coordinate
values discussed later. Further increase in dopant concentration beyond 4 mol% reduces the separation between the dopant ions which facilitates the non-radiative energy transformations among neighboring Er\(^{3+}\) ions leading to concentration quenching. Thus the luminescence intensity decreases with increase in doping beyond 4 mol%. To better understand the effect of doping in terms of concentration quenching phenomenon, the origin of non-radiative energy relaxations is expressed in a detailed manner.

The non-radiative energy transformations among neighboring Er\(^{3+}\) ions may occur by any of the one possible pathway namely exchange interaction, radiative reabsorption and multipolar interaction. These interactions can be explained on basis of the critical distance (R\(_c\)) among neighboring Er\(^{3+}\) ions estimated by equation (6.1.1). By considering, \(x_c = 0.04\), \(N = 8\) and \(V = 497.85 \text{ \AA}^3\) from crystal structure analysis; the critical distance for cross relaxation is found to be 14.38 \text{ Å}. The higher value of critical distance reveals that the exchange interactions for non-radiative energy transfer becomes ineffective because such type of relaxation operate when two dopant ions are 4 \text{ Å} far apart allowing effective overlapping of wave functions of both ions. The radiative reabsorption relaxation mechanism comes into play only when excitation and emission spectrum shows broad overlapping.

\[ \log \left( \frac{I}{x} \right) \text{ against } \log (x) \text{ in } \text{BaY}_2(1-x)\text{Er}_2x\text{ZnO}_5 \text{ nanophosphors.} \]

Thus the only plausible mechanism for non-radiative energy transfer between the Er\(^{3+}\) in BaY\(_2\)ZnO\(_3\) host lattice is credited to multipolar interactions. By taking the
consideration of Dexter’s theory [77], the multipolar interactions between the dopant ions can be expressed by exploiting the equation (6.1.2). Fig.6.2.10 represents the dependency of $I/x$ on $x$ over a logarithmic scale. The slope of the straight line is found to be -2.55795; resulting a Q value approximately equal to 8 (7.674). The result gives a clear insight of the energy transfer mechanism which is followed by dipole-quadrupole interactions, majorly responsible for concentration quenching.

The decay lifetime analysis of Er$^{3+}$ emission intensity at 549 nm further reflects the nearby environment of Er$^{3+}$ ion in the host lattice. The luminescence decay curves for BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ ($x = 0.5$-7 mol%) sintered at 1100°C at $\lambda_{ex} = 380$ nm has been depicted in Fig.6.2.11. The figure reveals the single exponential decay of lifetime derived by equation (6.1.3) as explained earlier in section-6.1 of this chapter.

![Fig.6.2.11 Decay curves of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at 549 nm for Er$^{3+}$ doped BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ nanophosphors with different concentration.](image)

The life time values (ms) derived from single exponential fits for BaY$_{2(1-x)}$Er$_{2x}$ZnO$_5$ nanophosphors has been listed in Table 6.2.3. The single exponential fit of decay curves gives indication of homogenous distribution of Er$^{3+}$ ion in the host lattice. The life time values decrease from 2.38 ms to 1.99 ms as concentration of Er$^{3+}$ ion increases from 0.5 to 7 mol% respectively, indicating increase in non-radiative energy transfer between the Er$^{3+}$ ions. The sharp decrease in life time values beyond 4 mol% can be accredited to concentration quenching because of predominance of non-radiative cross relaxation mechanism.
Table 6.2.3 lifetime and CIE coordinates of $\text{BaY}_2(1-x)\text{Er}_2x\text{ZnO}_5$ with different mol% of Er$^{3+}$ ions sintered at 1100°C on monitoring 380 nm $\lambda_{ex}$.

<table>
<thead>
<tr>
<th>$\text{BaY}_2(1-x)\text{Er}_2x\text{ZnO}_5$ (mol%)</th>
<th>Lifetime (ms)</th>
<th>CIE Coordinates ($x$, $y$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.5$</td>
<td>2.38</td>
<td>0.2851, 0.5163</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>2.33</td>
<td>0.2819, 0.5465</td>
</tr>
<tr>
<td>$x = 3$</td>
<td>2.28</td>
<td>0.2933, 0.5803</td>
</tr>
<tr>
<td>$x = 4$</td>
<td>2.18</td>
<td>0.2855, 0.6168</td>
</tr>
<tr>
<td>$x = 5$</td>
<td>2.02</td>
<td>0.2924, 0.6000</td>
</tr>
<tr>
<td>$x = 7$</td>
<td>1.99</td>
<td>0.2899, 0.5485</td>
</tr>
</tbody>
</table>

The emission color of $\text{BaY}_2(1-x)\text{Er}_2x\text{ZnO}_5$ nanophosphors ($x = 0.5$-7 mol%) sintered at 1100°C is analyzed and confirmed by Commission International De l’Eclairage (CIE 1931) chromaticity diagram as represented by Fig.6.2.12.

Fig.6.2.12 CIE chromaticity diagram for different concentration of Er$^{3+}$ doped $\text{BaY}_2(1-x)\text{Er}_2ZnO_5$ nanocrystals sintered at 1100°C on monitoring $\lambda_{ex} = 380$ nm.

All the color coordinates are examined using respective emission spectrum which lie in green region and are tabulated in Table 6.2.3 along with decay time of respective nanophosphor. $\text{BaY}_{1.92}\text{Er}_{0.08}\text{ZnO}_5$ sample synthesized via solution combustion method holds well comparable color coordinates (0.285, 0.616) with the European Broadcasting Unit (EBU, illuminant green = 0.29, 0.60) and other previously reported
green phosphors like BaY$_2$ZnO$_5$:Tb phosphor synthesized by conventional method (0.35, 0.55), ZnS:Cu,Al (0.284, 0.605), Y$_2$O$_3$:Tb (0.319, 0.597), Y$_2$O$_3$:Er (0.32, 0.62), and Zn$_2$SiO$_4$:Tb (0.287, 0.554) phosphors [4, 78-80]. The chromatic index in the green region proclaims the application of this green emitting nanophosphor in solid state lighting system.

**Conclusions**

In brief, BaY$_{2(1-x)}$M$_x$ZnO$_5$ where M = Sm$^{3+}$/Er$^{3+}$ single doped nanoparticles have been successfully synthesized via cost effective, single step urea assisted solution combustion process. Heat treatment is given to obtain the maximum crystallinity and phase purity. The Rietveld refinement study reveals that BaY$_{2(1-x)}$Sm$_x$ZnO$_5$ nanophosphors crystallizes in single phased orthorhombic lattice with space group $Pbnm$ at 1100°C. The cell volume increases due to the incorporation of Sm$^{3+}$ ion in the host lattice and resides in similar coordination environment as Y$^{3+}$ ion. Surface morphological studies reveal spherical shaped non-agglomerated loosely distributed particles in nano regime accountable for prominent luminescence in visible range of spectrum. Optical analysis reveal that these nanophosphor can be successfully excited at 411 nm and 380 nm wavelength yielding reddish-orange/green emission attributed to transition of Sm$^{3+}$/Er$^{3+}$ ion manifesting the suitability for implementation in near UV excited white LEDs.

The PL spectrum of BaY$_{2(1-x)}$Sm$_x$ZnO$_5$ (x = 0.5-7 mol%) exhibits dominant emission peak at 610 nm due to $^4{}G_{5/2}$$\rightarrow$$^6{}H_{7/2}$ transition of Sm$^{3+}$ ions when excited at 411 nm wavelength proclaiming the significant orange-red component for WLEDs. Dipole-dipole interactions among dopant ions are primarily responsible for concentration quenching through non-radiative energy relaxation beyond 3 mol%. Concentration dependent luminescence behavior of BaY$_{2(1-x)}$Er$_x$ZnO$_5$ (x = 0.5-7 mol%) reflects optimal composition as BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ for achieving the maximum luminescence. The critical distance measurement reveal that the dipole-quadrupole interactions among dopant ions are predominantly accountable for the concentration quenching which facilitate the non-radiative cross relaxation channel and responsible for the decline in the luminescence property beyond 4 mol%. CIE color coordinates reflecting orange-red and green emissions, respectively makes these nanophosphors a wonderful aspirant in NUV excited WLEDs regime.
References

33 R. Shpanchenko, E. Antipov, Moscow State Univ, Russia. ICDD Grant-in-Aid, 1999.