Chapter-4

Structural and optical properties of some rare earth doped Ba$_2$YAlO$_5$ nanophosphors
SECTION-4.1

4.1.1 Introduction

Solid State lighting (SSL) system is evolved as to bring lighting revolution for booming the Nation’s national economy and energy security. At global context, the SSL devices are thought to be the part of green and clean technology sectors as these are featured with lower energy utilization, mercury free content, low maintenance required, digitally controllable and longer life of product [1-2]. The SSL products are proved to be more efficient than incandescent and fluorescent lighting [3-4]. The SSL specifically the light emitting diodes (LEDs) have replaced the traditional lighting systems owing to its great luminous efficacy, durability and reproducibility [5-7]. At present, the white light is generated at commercial level via yellow phosphor YAG:Ce$^{3+}$ coated over blue emitting LED chip but has some drawbacks like high correlated color temperature (>7000 K) and poor color rendering index because of deficit in red emitting component [7-8]. This deficiency can be overcome by combining all the three necessary white light component red, blue and green emitting phosphors coated over near ultraviolet excited chip to obtain the white light with improved optical performance [9-11]. So, being the essential component of WLEDs, the new red emitting phosphors are required, which possess good luminescence efficiency.

Luminescence features associated with these materials arise due to the doping of rare earth ion. Trivalent europium ion is considered to be one of the most efficient rare earth ions producing the emissions originating from the highly shielded 4f shell electrons irrespective of the crystal field surrounding the metal ion [12-16]. The Eu$^{3+}$ ion yield strong red emission originating from $^5D_0$ to various $^7F_j$ ($j = 0-4$) transition levels. It is possible to achieve the color tunable luminescent behavior arising from various $^5D_j$ levels ($j = 0,1,2$) to ground level of Eu$^{3+}$ ion producing chromatic color tuning from blue to red region by controlling the concentration of Eu$^{3+}$ ion in the host matrix [17].

Currently, the ternary aluminate host matrices are extensively probed as the luminescent material because of their stable crystallographic features, inherent electronic and optical properties. These aluminate matrices are far more stable, ecologically suitable and chemically safer/non-toxic than the fluoride and sulphide
host matrices [18-20]. In this series, highly crystalline \( \text{Ba}_2\text{YAlO}_5 \) is claimed as a worthy host matrix for application in tricolor based PC-WLEDs. \( \text{Ba}_2\text{YAlO}_5 \) is found to have similar prototype as perovskite structure \( \text{ABX}_3 \) having pseudo bcc bravais lattice. Barium ions occupy the A position, Y and Al ions are arranged orderly along B position and oxygen ions are arranged along X position with one oxygen ion vacancy [21]. As reported by Kovba et al., \( \text{Ba}_2\text{YAlO}_5 \) crystallize in monoclinic lattice with space group \( P2_1/1 \) having lattice parameters; \( a = 7.231(7) \, \text{Å}, b = 7.430(2) \, \text{Å}, c = 6.022(3) \, \text{Å}, \gamma = 117.23(6)^\circ \) and \( Z = 2 \) [22].

Among the various synthetic routes available for the synthesis of nanophosphors, a very economic solution combustion approach is employed to develop the product with maximum purity, homogeneity and crystallinity within nano domain [23-24]. In the present study, the systematic structural and photoluminescent investigation of solution combustion synthesized \( \text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5 \) nanophosphor including concentration controlled luminescent behavior with chromatic color tuning and concentration quenching phenomenon are explained in detail. To the best of author’s knowledge, no reports have been listed in literature regarding the luminescence analysis of \( \text{Ba}_2\text{YAlO}_5: \text{Eu} \) nanophosphor in Judd-Ofelt framework. The Judd-Ofelt analysis is also performed on the nano scaled \( \text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5 \) \( (x = 0.05) \) phosphor to better understand the luminescence behavior. The chromatic index in the red region and CCT (correlated color temperature) values advocates the applicability of \( \text{Eu}^{3+} \) doped nanophosphor for the tricolor based near ultraviolet excited PC-WLEDs.

4.1.2 Experimental

4.1.2.1 Materials and synthesis

A series of \( \text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5 \) \( (x = 0.25-10 \, \text{mol\%}) \) nanophosphors has been synthesized by urea assisted solution combustion. The process involves high purity metal nitrates as raw material such as \( \text{Ba(NO}_3\text{)}_2, \text{Y(NO}_3\text{)}_3.6\text{H}_2\text{O, Eu(NO}_3\text{)}_3.6\text{H}_2\text{O and Al(NO}_3\text{)}_3.6\text{H}_2\text{O} \). The stoichiometrically calculated amount of raw materials and organic fuel urea were mixed in minimum amount of deionized water in a 250 mL capacity beaker to obtain clear solution. The molar ratio of urea was calculated by analyzing the total oxidizing or reducing valencies in the balanced reaction [25]. The beaker was then placed into the preheated muffle furnace maintained at 500°C for few minutes. Urea gets oxidized by nitrate ions present in solution generating heat and
thus helps in production of stoichiometrically controlled oxide [26]. Within minutes the self sustained exothermic reaction may attain the temperature as high as 1600°C and proceed with dehydration, foaming and decomposition generating flammable gases that burn with flame generating desired solid [23-24]. The product was then taken out of furnace, cooled at room temperature, grounded to fine powdered form and sintered at different temperatures.

4.1.2.2 Material characterization

The qualitative structural analysis of $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ ($x = 0.25$-$10$ mol\%) nanophosphors was analyzed using high resolution Rigaku Ultima-IV X-ray powder diffractometer powered with Cu $K_\alpha$ radiation at 40 kV voltage and 40 mA tube current setting. Diffraction pattern was collected within 2θ range 10-80° with scan rate 2° min$^{-1}$. The morphological analysis was carried out by using Technai-G$^2$ transmission electron microscope (TEM) to confirm crystallite size as calculated by X-ray diffraction analysis. The photoluminescent features of the nanophosphors were examined by using Hitachi F-7000 fluorescence spectrophotometer assembled with Xe-lamp at scanning rate 1200 nm min$^{-1}$, 400 V PMT voltage set up and keeping excitation and emission slit width 2.5 nm. Judd-Ofelt analysis as well as chromaticity color coordinates was also examined. All the studies were examined at room temperature and atmospheric conditions.

4.1.3 Results and discussion

4.1.3.1 Structural properties

The qualitative phase analysis of the solution combustion synthesized sample has been carried out using X-ray diffraction analysis. The as-prepared sample at 500°C is allowed to undergo different heat treatment process with appropriate time setup to achieve single phased powder in nano domain. Fig.4.1.1 demonstrates the X-ray diffraction profile of $\text{Ba}_2\text{Y}_{0.95}\text{Eu}_{0.05}\text{AlO}_5$ sample sintered at 1225°C for 4 h in two slots along with the reference JCPDS card no. 37-0292. The inset of the figure shows the diffraction pattern of the sample sintered at different temperatures for 4 h. The inset figure depicts the unrequisite impurity phase indexed to $\text{Al}_2\text{Y}_4\text{O}_9$ phase, well matched with reference JCPDS card no. 83-0935. The sample sintered at 900°C as well as 1100°C is completely lacking any appearance of $\text{Ba}_2\text{YAlo}_5$ phase. Further
sintering of sample at 1225°C, result in formation of single pure Ba$_2$YAlO$_5$ phase. The diffraction pattern of sample sintered at 1225°C is very well accord to JCPDS card no. 37-0292. From the diffraction profile it is inferred that Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ crystallizes in monoclinic lattice with space group $P2_1/11$ inspite of substitution of some Y$^{3+}$ ion by Eu$^{3+}$ ion.

Fig.4.1.1 XRD profile of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ nanophosphor along with standard data of Ba$_2$YAlO$_5$ (JCPDS Card No. 37-0292). Inset showing effect of sintering temperature accompanying JCPDS Card No. 83-0935.

Ba$_2$YAlO$_5$ is found to exist in similar phase prototype as perovskite structure with general stoichiometry ABX$_3$ or ABO$_3$ as X position is occupied by oxygen atoms or oxygen vacancy, B occupied by Y and Al while A occupied by Ba ions [21]. In ABO$_3$ phase prototype, BO$_6$ octahedra forms the network through corner sharing in which oxygen atoms coordinated in bridging position between adjacent B sites and in second environment by A cations present in dodecahedral interstices of oxygen sublattice as described by Kumar et al. in perovskite ceramic oxide Ba$_2$YZrO$_{6-d}$ [27]. In perovskite structure, A or B site of perovskite unit cell may get orderly or randomly substituted by the dopant rare earth ion which result in a complex perovskite structure [27]. But it is argued that the B site occupied by Y$^{3+}$ ion are expected to get substituted by dopant Eu$^{3+}$ ion because of closer ionic radii of both the trivalent ions (Y$^{3+}$ = 0.96 Å, Eu$^{3+}$ = 1.01 Å) and similar ionic valence [28-29]. Al$^{3+}$ ions and the A sites occupied by Ba$^{2+}$ ions are not substituted because of larger difference in ionic radii (Al$^{3+}$ = 0.53 Å and
Ba$^{2+} = 1.38$ Å) which may create larger defects in the monoclinic lattice [30-31]. Thus, Eu$^{3+}$ ions are expected to replace Y$^{3+}$ ions randomly as revealed by the similar diffraction pattern of the Eu$^{3+}$ doped powder with the undoped host lattice.

![XRD profile of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$](image)

**Fig.4.1.2** XRD profile of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x = 0.25$-10 mol%) nanophosphors along with standard data of Ba$_2$YAlO$_5$ (JCPDS Card No. 37-0292).

Moreover, the effect of Eu$^{3+}$ ion concentration on the monoclinic lattice crystallization of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ sample is also analyzed and highlighted in Fig.4.1.2 accompanying the reference JCPDS. It is found that the diffraction pattern of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x = 0.25$-10 mol%) is in well accordance with the JCPDS card no. 37-0292 irrespective of the Eu$^{3+}$ ion content; revealing that substitution of Y$^{3+}$ ion by Eu$^{3+}$ ion does not lead to any observable shifting in position of peaks. Additionally, the average crystallite size is estimated by utilizing Scherrer’s equation $D = \frac{0.941\lambda}{\beta \cos \theta}$ where $D$ denotes the average crystallite size, $\lambda$ is X-ray wavelength (0.1548 nm), $\theta$ is diffraction angle and $\beta$ is full width at half maximum (FWHM) of an observed peak. The average crystallite size of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x = 0.25$-10 mol%) sintered at 1225°C is measured to be 77.67, 76.17, 60.45, 77.58, 69.28, 79.17, 56.31 nm with corresponding FWHM as 0.112, 0.134, 0.145, 0.151, 0.123, 0.109, 0.154° respectively, as a function of Eu$^{3+}$ concentration.

### 4.1.3.2 Morphological characteristics

Fig.4.1.3(a) represents the TEM image of Ba$_2$Y$_{0.98}$Eu$_{0.05}$AlO$_5$ sample. The figure shows the more or less spherical shaped agglomerated particles with well defined
boundaries. The particle size analyzed from TEM analysis within the range 40-90 nm is in well accordance with that estimated from Scherrer’s equation. The nanosized particles have much enhanced electrical and optical properties than bulk materials because of larger surface area than volume, minimal internal scattering and non-radiative energy relaxation phenomenon [32-33].

Fig. 4.1.3 (a) TEM micrograph and (b) SAED pattern of Ba₂Y₀.₉₅Eu₀.₀₅Al₂O₅ powder sintered at 1225°C. The inset of (b) shows HR-TEM image.

The high resolution TEM (HR-TEM) image of Ba₂Y₀.₉₅Eu₀.₀₅Al₂O₅ sample is demonstrated in inset of Fig.4.1.3(b), which clearly displays the lattice fringes in the sample. The adjacent lattice fringes are found to have interplanar distance equal to
0.218 nm which is closely related with the d spacing of 22 plane of JCPDS card no. 37-0292. The selected area electron diffraction (SAED) pattern is shown in Fig.4.1.3(b). The ring pattern reveals the polycrystalline nature of the sample while the bright spots depicts that the different crystallites with related orientations agglomerate, which lead to limited set of orientations [27].

4.1.3.3 Optical properties

Europium doped Ba$_2$YAlO$_5$ nanophosphor is noticed to possess some remarkable photoluminescent properties showing low phonon nature of the host matrix on irradiation with near ultraviolet radiation. Fig.4.1.4 displays the photoluminescent excitation and emission spectrum of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ sample sintered at 1225°C on applying $\lambda_{em} = 625$ nm and $\lambda_{ex} = 394$ nm, respectively.

![Excitation and emission spectrum of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ nanophosphor sintered at 1225°C ($\lambda_{em} = 625$ nm and $\lambda_{ex} = 394$ nm, respectively).](image)

The excitation spectrum is composed of a strong high charge intensity band in the region 200-290 nm and $f$-$f$ transitions of Eu$^{3+}$ ion beyond 310 nm region. The broad peak at 258 nm is attributed to the feeding of charge from filled 2$p$ orbital of O$^{2-}$ to the vacant 4$f$ orbital of Eu$^{3+}$ ion [34]. Whereas the $f$-$f$ transitions positioned at 318, 360, 376, 384, 394 and 412 nm arises due to $^7F_0$$\rightarrow$$^5H_6$, $^7F_0$$\rightarrow$$^5D_4$, $^7F_0$$\rightarrow$$^5G_2$, $^7F_0$$\rightarrow$$^5G_3$, $^7F_0$$\rightarrow$$^5L_6$ and $^7F_0$$\rightarrow$$^5D_3$ transitions of Eu$^{3+}$ ion, respectively [35-38]. The sufficiently
intense excitation peak at 394 nm suggests that Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ nanophosphor can be efficiently pumped by NUV light and employed in PC-WLEDs.

The PL emission spectrum (green and red line) of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ sample is obtained by rooting $\lambda_{ex} = 394$ nm as displayed in Fig.4.1.4. The spectrum reveal the characteristic emission transitions of Eu$^{3+}$ ion arising from various $^5$D$_j$ levels to the $^7$F$_j$ ground levels [39-44]. The inset in the figure shows the expanded scale from 400 to 560 nm depicting the transitions from $^5$D$_j$ (j = 3,2,1) levels to the ground state $^7$F$_j$ (j = 0,1,2,3) levels corresponding to the transitions at 417, 427, 452, 468, 474, 498, 516, 530, 538 and 553 nm respectively. The transitions in the higher energy region reveal the low phonon nature of the host. In higher wavelength region, transitions from $^5$D$_0$$\rightarrow$$^7$F$_j$ (j = 0,1,2,3,4) levels correspond to the transitions at 578, 588, 625, 659 and 701 nm, respectively.

![Fig.4.1.5 Energy transfer mechanism for Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ (x = 0.25-10 mol%) nanophosphors sintered at 1225°C.](image)

Among these transitions the emission spectrum is dominated by $^5$D$_0$$\rightarrow$$^7$F$_2$ transition at 625 nm; responsible for red emission, it is electric dipole (ED) allowed and obeys the
selection rule $\Delta J = 2,4,6$. This transition is strongly influenced by the local crystal field present around the Eu$^{3+}$ ion [38].

Additionally, the crystal field may cause the Stark splitting of symmetry dependent $(2J+1)$ degenerate levels into a number of splitting lines. The doublet behavior of $^5D_0 \rightarrow ^7F_2$ transition arises due to the Stark splitting created by the electric field present [45-46]. The simplified energy level diagram demonstrating the down-conversion energy transfer (ET) mechanism through radiative and non-radiative routes is highlighted in Fig.4.1.5. It is clear from the figure that the CTB at 258 nm can directly feed the highest $^5H_6$ level of Eu$^{3+}$ ion through non-radiative decay. Secondly, the higher energy levels of Eu$^{3+}$ ion depopulate non-radiatively to increase the electronic population in lower energy excited levels of Eu$^{3+}$ ion.

![Energy Level Diagram](image)

**Fig.4.1.6** Excitation spectra of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ nanophosphor ($x = 0.25$-$10$ mol%) as a function of europium ion concentration.

The excitation pattern of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x = 0.25$-$10$ mol%) nanophosphor as a function of Eu$^{3+}$ ion concentration at 625 nm emission wavelength is depicted in Fig.4.1.6. The spectra display the efficient charge transfer from $2p$ orbital of O$^{2-}$ to Eu$^{3+}$ ion with most prominent peak at 394 nm. Fig.4.1.7 demonstrates the excitation behavior of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ nanophosphor at different emission wavelength input. The figure depicts that the excitation spectrum is predominantly occupied by CTB at lower emission wavelength while at higher emission wavelengths $f$-$f$ transitions of Eu$^{3+}$ ion are predominant.
Excitation spectra of $\text{Ba}_2\text{Y}_{0.95}\text{Eu}_{0.05}\text{AlO}_5$ nanophosphor as a function of emission wavelength.

It is well known that concentration of Eu$^{3+}$ ion is found to have prominent effect on the luminous efficacy of the nano-phosphor. The concentration directed luminescent analysis of $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ ($x = 0.25-10$ mol%) nanophosphor sintered at 1225°C is shown in Fig.4.1.8. The spectral transitions originating from various high energy states $^5\text{D}_{3,2,1,0}$ can be well indexed to different low energy $^7\text{F}_j$ levels of Eu$^{3+}$ ion.

Emission spectra of $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ sintered at 1225°C showing dependency of PL intensity on Eu$^{3+}$ ion concentrations, $\lambda_{ex} = 394$ nm.
It is observed that the high energy transitions $^5D_{3,2,1} \rightarrow ^7F_j$ are more prominent at low concentration of europium ion. These levels show faster transitions rates to $^7F_j$ level which get adequately populated and display blue/green chromatic tuning. However, as the europium ion concentration increases the depopulation from $^5D_0$ to $^7F_j$ levels increases. The higher transition rate of $^5D_0 \rightarrow ^7F_j$ level is responsible for the red chromaticity. Thus, concentration based luminescent tendency can be employed to achieve chromatic tunability from blue to red region. The luminous intensity parameter of $^5D_0 \rightarrow ^7F_j$ transition increases systematically with increasing Eu$^{3+}$ ion concentration up to 5 mol% and began to decrease afterwards as depicted in Fig. 4.1.9 due to concentration quenching effect.

Fig. 4.1.9 Variation of the emission intensity at 625 nm as a function of Eu$^{3+}$ concentration for Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x = 0.25-10$ mol%) nanophosphor sintered at 1225°C.

The over doping of Eu$^{3+}$ ion in Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ nanophosphor reduces the interionic distance between the adjacent europium ions facilitating non-radiative energy transfer, causing decrease in luminescence intensity. This decrease in luminescence intensity can be better expressed in terms of critical distance ($R_c$) between the neighboring luminescent ions, explaining the prevailing non-radiative cross relaxation process through equation (4.1.1) as:

$$R_c = 2 \left[ \frac{3V}{4\Pi x_c N} \right]^{1/3} \quad (4.1.1)$$
Where \( N \) represents the number of replaceable cations in the unit cell, \( x_c \) is critical concentration of dopant ion beyond which luminescence intensity decreases and \( V \) relates to the volume of unit cell [47]. By considering, \( x_c = 0.05 \), \( N = 2 \) and \( V = 287.68 \text{ Å}^3 \) from crystal structure analysis (JCPDS card no. 37-0292); the value of \( R_c \) is found to be 17.6441 Å. Such a higher value of critical distance discards the exchange interaction for cross relaxation as these prevail when the interionic distance between the luminescent centres is 4 Å for effective overlapping of wave functions of both ions. Radiative reabsorption cross relaxation channel is also not possible because the PL spectrum is devoid of any overlapping [48]. Thus, the cross relaxation must be channeled via multipolar interactions governed by the Dexter’s theory through equation (4.1.2) as:

\[
\frac{I}{x} = K\left[1 + \beta(x)Q/3\right]^{-1} \tag{4.1.2}
\]

Where \( x \) relates to dopant concentration greater than critical concentration, \( K \) and \( \beta \) are the constants for same excitation condition for given host while \( Q \) is the multipolar interaction constant and equal to 6, 8, 10 for dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively [49].

**Fig.4.1.10** Plot of \( \log (I/x) \) as a function of \( \log(x) \) in \( \text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5 \) nanophosphors.

The plot of \( I/x \) Vs \( x \) on a logarithmic scale is represented in Fig.4.1.10. The slope of the straight line curve is found to be -3.3144 yielding a \( Q \) value equal to 9.9432 \( \approx 10 \).
Hence, the results confirms that the quadrupole-quadrupole (q-q) interactions are solely accountable for concentration quenching arising from over doping of Eu$^{3+}$ ion beyond 5 mol% in Ba$_2$YAlO$_5$ host lattice.

The luminescence decay kinetics further gives a clear insight of distribution of Eu$^{3+}$ ion in the Ba$_2$YAlO$_5$ matrix. Fig.4.1.11 represents the photoluminescence decay profile for the emission at 625 nm ($^5D_0\rightarrow^7F_2$ transition) in Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ (x = 0.25-10 mol%) nanophosphors.

![Figure 4.1.11](image)

**Fig.4.1.11** The luminescence decay curve for the 625 nm ($^5D_0\rightarrow^7F_2$ of Eu$^{3+}$) emission of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ nanophosphors sintered at 1225°C.

According to the figure all the decay curves are very well fitted into mono exponential function. The mono exponential fits can be derived from equation (4.1.3) as:

$$I = I_0\exp\left(-t/\tau\right)$$  \hspace{1cm} (4.1.3)

Where $\tau$ denotes the decay time for radiative emission, $I$ and $I_0$ are the luminescence intensities at time $t$ and 0, respectively. The single exponential nature of decay profile may arise due to the homogenous diffusion of dopant ion in the host lattice [50]. The decay life time values (ms) of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ (x = 0.25-10 mol%) nanophosphors are tabulated in Table 4.1.1. The decay values decreases from 1.312 to 0.586 ms as the europium ion concentration vary from 0.25 to 10 mol% due to increase in non-radiative energy transformations. The values show sharp decrease beyond 5 mol% due to multipolar interaction between the adjacent Eu$^{3+}$ ions.
Table 4.1.1 Lifetime and CIE coordinates of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ as a function of Eu$^{3+}$ ion concentration sintered at 1225°C

<table>
<thead>
<tr>
<th>Ba$<em>2$Y$</em>{(1-x)}$Eu$_x$AlO$_5$</th>
<th>Lifetime (ms)</th>
<th>CIE Coordinates ($x, y$)</th>
<th>Emission color</th>
<th>CCT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>2$Y$</em>{0.9975}$Eu$_{0.0025}$AlO$_5$</td>
<td>1.312</td>
<td>0.238, 0.258</td>
<td>Blue</td>
<td>21514</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.995}$Eu$_{0.005}$AlO$_5$</td>
<td>1.261</td>
<td>0.342, 0.317</td>
<td>White</td>
<td>5012</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.99}$Eu$_{0.01}$AlO$_5$</td>
<td>1.186</td>
<td>0.451, 0.326</td>
<td>Whitish orange</td>
<td>2018</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.97}$Eu$_{0.03}$AlO$_5$</td>
<td>1.131</td>
<td>0.526, 0.360</td>
<td>Orange</td>
<td>1733</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.95}$Eu$_{0.05}$AlO$_5$</td>
<td>1.041</td>
<td>0.603, 0.359</td>
<td>Red</td>
<td>1920</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.93}$Eu$_{0.07}$AlO$_5$</td>
<td>0.720</td>
<td>0.611, 0.356</td>
<td>Red</td>
<td>2018</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.9}$Eu$_{0.1}$AlO$_5$</td>
<td>0.586</td>
<td>0.621, 0.348</td>
<td>Red</td>
<td>2249</td>
</tr>
</tbody>
</table>

The photoluminescent properties of Eu$^{3+}$ doped Ba$_2$YAlO$_5$ nanophosphors are further explored by employing Judd-Ofelt theory, independently developed by Judd and Ofelt [51-52]. The Judd-Ofelt intensity parameters $\Omega_{\lambda}$ ($\lambda = 2, 4$) for the $^5D_0 \rightarrow ^7F_{2,4}$ transitions of Eu$^{3+}$ ion in Ba$_2$YAlO$_5$ host matrix have been calculated by utilizing intrinsic life time and integrated emission intensities dependent approach. The concentration controlled luminescent tendency of Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ ($x$=0.25-10 mol%) nanophosphors reveal the maximum intensification for Ba$_2$Y$_{0.95}$Eu$_{0.5}$AlO$_5$ hence, Ba$_2$Y$_{0.95}$Eu$_{0.5}$AlO$_5$ is used as optimal composition for Judd-Ofelt calculations. The intrinsic life time used in determining J-O parameters is taken to be 1.0416 ms. The total relative integrated emission intensity ($I$) for all $^5D_0 \rightarrow ^7F_{j}$ transitions collectively is dependent on the comprehensive radiative transition rate as follows:

$$I = \sum_{j=0,1,2,3,4,5,6} I_{7F_j} = a \sum_{j=0,1,2,3,4,5,6} A_{7F_j}$$

Where $a$ is the constant for transition from $^5D_0$ to $^7F_j$ spectral levels while $A_{7F_j}$ is the radiative rate for discrete transitions. The radiative rate and intrinsic life time are just reciprocal to each other, so the value of $a$ is determined to be 1.3534. By knowing the value of $a$, the individual radiative rates for $^5D_0 \rightarrow ^7F_j$ ($j = 1,2,3,4$) transitions are determined accordingly and tabulated in Table 4.1.2.

The radiative transition rate of crystal field free, magnetic dipole driven $^5D_0 \rightarrow ^7F_1$ transition can be formulated within Judd-Ofelt framework as [53-54]:
\[ A_{j-j'}^{md} = \frac{64 \pi^4 \nu^3}{3h(2j + 1)^n} S_{md} \]  \hspace{1cm} (4.1.5)

Where \( h \) denotes the Planck’s constant \( (h = 6.626 \times 10^{-27} \text{erg s}) \), \( 2j+1 \) relates to the initial state’s degeneracy, \( \nu \) is the wavenumber for \( j \rightarrow j' \) transition, \( n \) is refractive index of the host and \( S_{md} \) is magnetic dipole line strength \( (S_{md} = 7.83 \times 10^{-42}) \). By computing the above equation for refractive index of host lattice, the value of \( n \) is found to be 2.2851. Subsequently, the J-O parameters can be determined by using the expression for the electric dipole driven transition from \( j \) state to \( j' \) state as:

\[ A_{j-j'}^{ed} = \frac{64 \pi^4 e^2 \nu^3}{3h(2j + 1)^n} \frac{n(n^2 + 2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda \langle \psi_j | U^\lambda | \psi_{j'} \rangle \]  \hspace{1cm} (4.1.6)

Where \( e \) denotes the electronic charge \( (4.80 \times 10^{-10} \text{esu}) \) and \( \langle \psi_j | U^\lambda | \psi_{j'} \rangle \) is the reduced matrix element for \( j \rightarrow j' \) electric dipole transition. From equation (4.1.6) the value of \( \Omega_2 \) and \( \Omega_4 \) are determined to be 5.5180 and 0.4511 respectively, where \( \Omega_2 \) is in the unit of \( 10^{-20} \text{cm}^2 \). The fluorescence branching ratios \( (\beta_j) \) tabulated in Table 4.1.2 are determined by using the expression as:

\[ \beta_j = \frac{A_{j-j'}}{\sum_{j=0,1,2,3,4,5,6} A_{j-j'}} \]  \hspace{1cm} (4.1.7)

**Table 4.1.2 The nature of transition, energy and transition rate for the \( ^5D_0 \rightarrow ^7F_j \) (\( j=1, 2, 3, 4 \)) transitions of Eu\(^{3+} \) in Ba\(_2\)Y\(_{0.95}\)Eu\(_{0.05}\)AlO\(_5\) nanophosphors.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Type</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Transition Rate (s(^{-1}))</th>
<th>( \beta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^5D_0 \rightarrow ^7F_0 )</td>
<td>Forbidden</td>
<td>17301.03</td>
<td>83.62</td>
<td>0.086</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_1 )</td>
<td>Magnetic dipole</td>
<td>17006.80</td>
<td>143.82</td>
<td>0.149</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_2 )</td>
<td>Electric dipole</td>
<td>16000.00</td>
<td>690.61</td>
<td>0.717</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_3 )</td>
<td>Forbidden</td>
<td>15174.50</td>
<td>16.27</td>
<td>0.016</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_4 )</td>
<td>Electric Dipole</td>
<td>14265.33</td>
<td>28.76</td>
<td>0.029</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_5 )</td>
<td>Forbidden</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>( ^5D_0 \rightarrow ^7F_6 )</td>
<td>Electric Dipole</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

As the spectrum is devoid of \( ^5D_0 \rightarrow ^7F_6 \) transition, so \( \Omega_6 \) is not calculated. The electric dipole transitions \( ^5D_0 \rightarrow ^7F_{0,3} \) are forbidden, thus, J-O intensity parameters \( (\Omega_{0,3}) \) are also not determined because for these forbidden transitions the value of
reduced matrix element is zero [55-56]. On comparing the $\Omega_{2,4}$ values of $\text{Ba}_2\text{Y}_{0.95}\text{Eu}_{0.05}\text{AlO}_5$ nanophosphor with other Eu$^{3+}$ ion doped host matrices, it is concluded that the Eu$^{3+}$ ion occupy the lower symmetrical sites and high covalency between the Eu$^{3+}$ ion and the ligand [57]. The value of $\Omega_2$ is dependent on the ligand field around the Eu$^{3+}$ ion and hence is found to be different for different hosts. Moreover, the value of $\Omega_2$ for $\text{Ba}_2\text{Y}_{0.95}\text{Eu}_{0.05}\text{AlO}_5$ nanophosphor is found to be much higher than $\Omega_4$ indicating the higher radiative rate for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. This observation infers better luminescent properties with color purity for application in field of white LEDs.

![Fig.4.1.12 CIE chromaticity diagram for $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ ($x = 0.25\text{-}10\text{ mol\%}$) sintered at 1225°C nanophosphors at $\lambda_{\text{ex}} = 394\text{ nm}$.

The emission color corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ ($x = 0.25\text{-}10\text{ mol\%}$) nanophosphors sintered at 1225°C have been summarized in Table 4.1.1. The emission color is checked by employing Commission International De l’Eclairage (CIE 1931) chromaticity diagram and is represented in Fig.4.1.12. The figure shows the systematic shifting of color coordinates from blue (0.2383, 0.2584) to red region (0.6210, 0.3480). On comparison with standard CIE color coordinates for white light (0.3333, 0.3333) our sample $\text{Ba}_2\text{Y}_{0.995}\text{Eu}_{0.005}\text{AlO}_5$ exhibits well matched color coordinates (0.3423, 0.3170) while $\text{Ba}_2\text{Y}_{0.90}\text{Eu}_{0.10}\text{AlO}_5$ sample exhibits color coordinates (0.6210, 0.3480) in the red region. To better understand the quality
of achieved light the correlated color temperature CCT (K) are also determined by employing the McCamy’s empirical relation as:

\[
\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (4.1.8)
\]

Where \( n \) equal to \((x-x_e)/(y-y_e)\) is the inverse slope line, \((x, y)\) are the color coordinates of synthesized nanophosphor and \((x_e, y_e)\) is the epicentre \((0.3320, 0.1858)\) [58]. The CCT values are tabulated in Table 4.1.1 along with decay life time values and color coordinates. The CCT values vary from 19156 to 2249 K, which fall in well acceptable range for the white light and red emission [59-60]. Thus, the chromatic tuning from blue to red region marks the applicability of this Eu\(^{3+}\) doped Ba\(_2\)YAlO\(_5\) nanophosphor in the field of white light emitting materials.
SECTION-4.2

4.2.1 Introduction

In recent years, much growing interest is observed in the area of rare earth doped phosphor materials. The rare earth doped phosphors are the pivotal centre of research owing to its unique and interesting electronic, optical and chemical properties originating from the deeply buried $4f$ shell electrons. These shielded shell electrons remain free from any interaction with outer ligand environment in the crystal lattice and results in energy absorption and relaxation leading to the efficient luminescent properties [61-63]. On grounds of these sharp $f$-$f$ transitions with high lumen, color purity, high efficiency these rare earth doped phosphors are extensively utilized in optical display systems like field emission display (FED), plasma display panel (PDP) and lighting systems (SSL) [64-72]. Specifically, in the solid state lighting system, the rare earth doped phosphor materials are exhaustively explored to obtain the white light.

Currently, at commercial level, the white light is generated by coating a blue emitting chip with yellow phosphor YAG:Ce$^{3+}$ but yields white light with poor color rendering index due to lack of red emitting component. This deficiency can be overcome by employing another suitable route for generation of white light by blending the red, green and blue (RGB) phosphors with the near ultraviolet exited chip. Therefore, the white light generated through this route has high color rendering index and is supposed to display excellent potential for high efficiency solid state lighting materials [73]. Thus on being one of the essential components of LEDs, the new green emitting phosphors are highly needed which possess the good luminescent efficiency, so can be utilized for white light generation with improved optical performance. Among the rare earth dopant ions, trivalent Tb ion is widely explored as a dopant ion in the various host matrices to achieve the green emission in the visible region of spectrum. The green emission originates from the $^{5}D_{4}\rightarrow ^{7}F_{5}$ transition positioned around 545 nm when excited by near ultraviolet source.

Additionally, the ternary aluminate host matrices require much attention due to their good crystallographic stability, chemical durability and inherent luminescent properties. These aluminate host matrices have much more stability than the fluoride and sulfide hosts and are ecologically well acceptable with safer or non-toxic features
Thus, these features make these hosts as good enough to accommodate the trivalent rare earth ion. Among the aluminate host matrices, Ba$_2$YAlO$_5$ host matrix is proposed as suitable host matrix with high degree of crystallinity to be probed as an efficient luminescent material. Ba$_2$YAlO$_5$ crystallize in perovskite phase prototype with general formula ABX$_3$ having pseudo BCC bravais lattice. As accounted by Kovba et al., Ba$_2$YAlO$_5$ acquires monoclinic lattice with space group $P2_1/1$ having unit cell parameters as; $a = 7.231(7)$ Å, $b = 7.430(2)$ Å, $c = 6.022$ Å, $\gamma = 117.23(6)^\circ$ and $Z = 2$ [22].

Furthermore for the development of nano crystalline phosphor material with good luminescent efficiency, a number of synthetic routes are available in the literature [24]. But in the present study, the solution combustion method is employed to develop the homogenous product with maximum purity and crystallinity within nano range with heat treatment process [23]. Herein, the systematic structural and optical behavior of solution combustion synthesized Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanophosphor ($x = 0.25-7$ mol%) are presented in detail. The effect of concentration of Tb$^{3+}$ on luminescent properties of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nano-crystalline phosphor including radiative, non-radiative energy transfer process is also studied. To the best of author’s knowledge, no analysis is found in literature about the luminescent investigation of Tb$^{3+}$ doped Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ host lattice. The chromatic index in the green region proclaims the utilization of this terbium doped nano-crystalline Ba$_2$YAlO$_5$ host matrix as one of green component of phosphor converted white light emitting materials.

4.2 Experimental

4.2.1 Materials and synthesis

A time saving and cost effective urea assisted solution combustion approach was applied to obtain a series of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25-7$ mol%) nanophosphors. The high purity metal nitrates such as Ba(NO$_3$)$_2$, Y(NO$_3$)$_3$.6H$_2$O, Tb(NO$_3$)$_3$.6H$_2$O and Al(NO$_3$)$_3$.6H$_2$O were used. The raw materials and organic fuel urea were weighed according to stoichiometric composition and dissolved in minimum amount of deionized water taken in a 250 mL capacity beaker. The solution was continuously stirred to obtain clear solution. The beaker was then introduced into the furnace for few minutes whose temperature was set at 500°C. The stoichiometric quantity of urea was estimated according to the total valencies in the balanced redox reaction [25]. The
nitrate ions present in the solution leads to oxidation of urea and the resultant heat trigger the self spreading exothermic reaction to form stoichiometrically controlled oxide [26]. The temperature of reaction materials may rise up to 1600°C within few minutes which followed by dehydration, foaming and decomposition. The gases escaped during the process burn with flame which finally produces the desired product [23-24]. The solid was then taken out of furnace, cooled at room temperature, grounded to fine powdered form and sintered at different temperatures to obtain the maximum crystallinity.

4.2.2 Material characterization

High resolution Rigaku Ultima-IV X-ray powder diffractometer powered with Cu Kα radiation at 40 kV voltage and 40 mA tube current setting was assessed for analyzing the qualitative structural properties of Ba₂Y₁₋ₓTbxAlO₅ (x = 0.25-7 mol%) nanophosphors. The X-ray diffraction profile was collected within 2θ range 10-80° with scan rate 2° min⁻¹. The morphological features were examined by using Tecnai-G² transmission electron microscope (TEM). TEM analysis was used to confirm crystallite size as calculated by X-ray diffraction studies. The optical features of the synthesized nanophosphors were examined by assessing Hitachi F-7000 fluorescence spectrophotometer assembled with Xe-lamp. The optical data was recorded at scan rate of 1200 nm min⁻¹, 400 V PMT voltage set up and keeping excitation and emission slit width 2.5 nm. Chromaticity color coordinates was also examined. All the studies were examined at room temperature and atmospheric conditions.

4.2.3 Results and discussion

4.2.3.1 Structural properties

The solution combustion synthesized as prepared sample at 500°C is heat treated at different temperatures to obtain the single pure phased Ba₂Y₁₋ₓTbxAlO₅ crystalline phosphor in the nano domain. Fig.4.2.1 depicts the X-ray diffraction profile of Ba₂Y₀.97Tb₀.03AlO₅ sample sintered at 1225°C for 4 hours in two slots accompanying the standard JCPDS card no. 37-0292. The inset of the figure highlights the diffraction profile of heat treated samples at different temperatures for 4 h in two slots accompanying the respective reference JCPDS. It shows that the sample sintered at 900°C and 1100°C crystallize in Al₂Y₄O₉ phase, which is in accordance with JCPDS
card no. 83-0935. At 900°C as well as 1100°C, the requisite Ba$_2$YAlO$_5$ phase is missing. The sample is further sintered at 1225°C for 4 h yields pure single phased Ba$_2$YAlO$_5$ lattice which is in accordance with the diffraction profile of the JCPDS card no. 37-0292, confirming that Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ crystallize in monoclinic lattice with $P2_1/ (11)$ space group.

Fig.4.2.1 XRD profile of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ nanophosphor along with standard data of Ba$_2$YAlO$_5$ (JCPDS Card No. 37-0292). Inset showing effect of sintering temperature accompanying JCPDS Card No. 83-0935.

Ba$_2$YAlO$_5$ host matrix is found to have similar general formula as ABX$_3$ or ABO$_3$ perovskite prototype. In ABX$_3$ structure, A positions are acquired by Ba ions, B positions are shared orderly by Y and Al ions while X positions are acquired by oxygen atoms or oxygen vacancy [21]. The BO$_6$ octahedra in ABO$_3$ prototype are arranged in such a manner to form the network via corner sharing in which oxygen atoms are linked in two different environments. In first environment, the oxygen atoms are coordinated in bridging position between neighboring B sites and in second arrangement coordinated by A cations resided in dodecahedral interstices of oxygen sublattice as explained by Kumar et al. in perovskite ceramic oxide of the type Ba$_2$YZrO$_{6-d}$ [27]. In this perovskite phase prototype, the A or B sites of the unit cell are likely to get substituted by the incoming rare earth dopant ion. But it is proclaimed that the B sites acquired by trivalent Y ion are expected to replaced by the Tb$^{3+}$ ion,
The similar ionic valence of both the ions is also appropriate for substitution without creating any charge compensation issue. A or B sites occupied by Ba$^{2+}$ and Al$^{3+}$ ion if get substituted by Tb$^{3+}$ ion, may cause larger structural default in monoclinic host lattice due to large difference in ionic radii with respect to Tb$^{3+}$ ion (Ba$^{2+} = 1.38$ Å, Al$^{3+} = 0.53$ Å) [30-31]. Hence, Tb$^{3+}$ ions expectedly substitute Y$^{3+}$ ions randomly from its coordinative sites as inferred from the similar diffraction profile of the Tb$^{3+}$ doped powder with respect to the undoped host lattice.

![Fig.4.2.2 XRD profile of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ (x = 0.25-7 mol%) nanophosphors along with standard data of Ba$_2$YAlO$_5$ (JCPDS Card No. 37-0292).](image)

The diffraction profile of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ (x = 0.25-7 mol%) is also recorded to elucidate the effect of concentration of Tb$^{3+}$ ion on the monoclinic lattice demonstrated in Fig.4.2.2 accompanying the reference JCPDS. It is observed from the figure that the varying concentration of Tb$^{3+}$ ion from 0.25 to 7 mol% is not found to have any remarkable effect on the diffraction peaks of the monoclinic lattice and the diffraction profile of all mol% samples very well accord to the standard JCPDS card no. 37-0292. The average crystallite size is measured by using Scherrer’s equation $D = \frac{0.941 \lambda}{\beta \cos \theta}$, where D depicts the average crystallite size, $\lambda$ is X-ray wavelength used (0.1548 nm), $\theta$ is diffraction angle and $\beta$ is full width at half maximum (FWHM) of an observed peak [76]. The average crystallite size of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ samples with terbium concentration varying from 0.25 to 7 mol% is calculated to be 91.64,
75.15, 63.39, 72.51, 89.38, 81.18, 61.31 nm and the corresponding FWHM 0.096, 0.136, 0.143, 0.139, 0.101, 0.107 and 0.147°, respectively.

4.2.3.2 Morphological characteristics

Fig.4.2.3 demonstrates the TEM image of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ sample. The figure illustrates the more or less spherical shaped particles with well defined boundaries. The particles show some degree of agglomeration. The particle size analyzed from TEM analysis within the range of 65-95 nm is in well accordance with crystallite size estimated from Scherrer’s equation. The nanosized particles have much greater surface area than the volume, reduced internal scattering and decreased non-radiative energy relaxation phenomenon than the bulk materials [32-33]. These characteristics result in improved electrical and optical performance of the nano-crystalline phosphor.

![TEM micrograph of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ powder sintered at 1225°C.](image)

4.2.3.3 Optical properties

Trivalent terbium doped Ba$_2$YAlO$_5$ nanophosphor is noted to have good luminescent features on irradiation with near ultraviolet light. Fig.4.2.4 demonstrates the photoluminescent spectral scanning of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ nanophosphor on applying $\lambda_{em} = 546$ nm and $\lambda_{ex} = 368$ nm, respectively. The excitation spectrum comprise of two types of excitation bands originating due to the characteristic excitation peaks of Tb$^{3+}$ ion in the region 200-300 nm and the other from 300-400 nm
range. The first type of excitation band accord to spin allowed $4f^8 \rightarrow 4f^7 5d$ transition of Tb$^{3+}$ ion ($\Delta s = 0$) with maxima at 281 nm [77-79]. The second type of excitation band in the region above 300 nm corresponds to $f-f$ transitions of Tb$^{3+}$ ion. The peak positioned at 317, 339, 351, 377 nm along with the sufficiently intense peak at 368 nm are attributed to $7F_6 \rightarrow 5H_7$, $7F_6 \rightarrow 5L_6$, $7F_6 \rightarrow 5L_9$, $7F_6 \rightarrow 5D_3$ and $7F_6 \rightarrow 5L_{10}$ transitions of Tb$^{3+}$ ion, respectively [80-81]. The maximum intensity peak at 368 nm proclaims that Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ nanophosphor can be efficiently pumped by the near ultraviolet light.

![Fig.4.2.4 Excitation and emission spectrum of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ nanophosphor sintered at 1225°C ($\lambda_{em} = 546$ nm and $\lambda_{ex} = 368$ nm, respectively).](image)

The photoluminescence emission spectrum of Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ nanophosphor is observed on applying $\lambda_{ex} = 368$ nm. The spectrum displays the characteristic emission peaks of trivalent terbium ion arising from $^5D_4$ to $^7F_j$ levels [77, 80]. The peaks positioned at 485 nm (blue region), 546 nm (green region), 591 nm (yellow region), 624 nm (red region) corresponds to $^5D_4 \rightarrow 7F_{6,5,4,3}$ transitions. The emission transitions $^5D_4 \rightarrow 7F_{3,4}$ are electrical as well as magnetic dipole forbidden transitions while $^5D_4 \rightarrow 7F_5$ and $^5D_4 \rightarrow 7F_6$ transitions are electric dipole and magnetic dipole driven transitions, respectively [82]. The relatively intense electric dipole driven $^5D_4 \rightarrow 7F_5$ transitions reveal the asymmetric environment around the luminescent centre and is found to be responsible for the green emission of the Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ crystalline sample. All emission peaks present in the spectrum are further split in number of
lines due to presence of electric field around the luminescent centre. The symmetry around the dopant ion has a control over the splitting of (2J+1) degenerate levels into number of lines. The splitting of $^5\text{D}_4 \rightarrow ^7\text{F}_j$ levels can be explained on the basis of Stark splitting [45-46].

Fig.4.2.5 Energy transfer mechanism for Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25-7$ mol%) nanophosphors sintered at 1225°C.

The simplified energy level diagram illustrating the down conversion energy transfer (ET) mechanism via radiative and non-radiative transitions is displayed in Fig.4.2.5. The $^5\text{D}_4$ excitation level get sufficiently populated through non-radiative energy relaxation process from the high energy excited levels of terbium ion. After sufficient population build up in $^5\text{D}_4$ excited level, it gets depopulated radiatively to the various $^7\text{F}_j$ levels of Tb$^{3+}$ ion. The excitation spectra of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25-7$ mol%) nanophosphor as a function of Tb$^{3+}$ ion concentration is also recorded by rooting $\lambda_{em} = 546$ nm and is displayed in Fig.4.2.6. The excitation spectra exhibits the similar characteristic excitation peak irrespective of Tb$^{3+}$ ion content although differ in intensity of the observed peaks.
The Tb$^{3+}$ ion content does not have any measurable effect on the monoclinic lattice crystallization of Ba$_2$YAlO$_5$ host matrix as revealed by XRD data. But it is well acceptable that the luminescent properties of the rare earth doped nanophosphor are very much influenced by the concentration of dopant ion.

Fig.4.2.6 Excitation spectra of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25$-7 mol\%) nanophosphor as a function of terbium ion concentration.

The effect of Tb$^{3+}$ ion content on luminescent properties of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25$-7 mol\%) nanophosphor is analyzed as depicted in Fig.4.2.7. All the spectral transitions are very well indexed to $^5$D$_4 \rightarrow ^7$F$_j$ transitions.

Fig.4.2.7 Emission spectra of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ sintered at 1225°C showing dependency of PL intensity on Tb$^{3+}$ ion concentration, $\lambda_{ex} = 368$ nm.
The figure reveals that the luminescence emission intensity increases as a function of Tb$^{3+}$ ion concentration up to 3 mol% and then decreases afterwards. The high intensity of $^5D_0 \rightarrow ^7F_j$ transition in the spectra infers higher transition rate from $^5D_0$ to $^7F_j$ level and found responsible for green chromatic index. The plot of emission intensity corresponding to $^5D_0 \rightarrow ^7F_3$ transition against the varying terbium ion concentration from 0.25 to 7 mol % is depicted in Fig.4.2.8. It is clearly observed from the figure that the emission intensity first increases up to 3 mol% and then decreases sharply due to the emergence of concentration quenching phenomenon.

![Fig.4.2.8 Variation of the emission intensity at 546 nm as a function of Tb$^{3+}$ concentration for Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25$-$7$ mol%) nanophosphor sintered at 1225°C.](image)

The increasing concentration of Tb$^{3+}$ ion beyond 3 mol% in Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ ($x = 0.25$-$7$ mol%) nanophosphor reduces the interionic distance between the adjacent terbium ions. This facilitates the non-radiative energy transfers among the nearby luminescent centres and leads to the decrease in luminescent intensity. To further explain the concentration quenching phenomenon in detail, the critical distance ($R_c$) between the adjacent luminescent ions is calculated in order to demonstrate the non-radiative energy transformations by applying equation (4.1.1) as explained earlier in section-4.1 of this chapter. By taking $x_c = 0.03$, $N = 2$ and $V = 287.68$ Å$^3$ from crystal structure analysis (JCPDS card no. 37-0292); the value of $R_c$ is determined to be 20.9218 Å. The higher value of critical distance makes the exchange interaction path
ineffective because these occur when luminescent centres are 4 Å far apart as effective overlapping of wave function of both ions takes place so that luminescent centres relaxes via non-radiative cross relaxation. As the photoluminescence spectrum shows no broad overlapping of excitation and emission spectrum; so the radiative reabsorption channel is also not possible for cross relaxation. Therefore, the non-radiative cross relaxation occur by multipolar interactions directed by Dexter’s theory through equation (6.1.2).

Fig.4.2.9 Plot of log (I/x) against log(x) in Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanophosphors.

$I/x$ is plotted against $x$ on logarithmic scale to obtain the straight line curves as presented in Fig.4.2.9. The slope of the straight line is found to be -2.1631; yielding a $Q$ value 6.4893 $\approx$ 6. Therefore, the results elicit that the dipole-dipole interactions among the luminescent centres are found responsible for non-radiative cross relaxation leading to concentration quenching beyond 3 mol% in Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanophosphors.

The photoluminescence decay kinetics further illustrates the distribution of Tb$^{3+}$ ion in Ba$_2$YAlO$_5$ host lattice and the prevailing non-radiative energy relaxation mechanism. Fig.4.2.10 represents the normalized fitted decay profile for the emission at 546 nm ($^5$D$_4$$\rightarrow$$^7$F$_5$ transition) in Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanophosphors. All the decay curves are very well fitted into single exponential functions. The single exponential fits are governed by equation (4.1.3). The single exponential decay dynamics infers
the uniform diffusion Tb$^{3+}$ ion in the host matrix [50]. The decay lifetime values (ms) of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ (0.25-7 mol%) nanophosphors are listed in Table 4.2.1.

![Graph showing luminescence decay curve](image)

Fig.4.2.10 The luminescence decay curve for the 546 nm ($^5$D$_4$$\rightarrow$$^7$F$_5$ of Tb$^{3+}$) emission of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanocrystals sintered at 1225°C.

The decay values decreases from 2.356 to 1.244 ms with increase in concentration of Tb$^{3+}$ from 0.25 to 7 mol % due to increase in non-radiative cross relaxation processes. The decrease is sharp beyond 3 mol% due to multipolar interaction between the neighboring Tb$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Ba$<em>2$Y$</em>{(1-x)}$Tb$_x$AlO$_5$</th>
<th>Lifetime (ms)</th>
<th>CIE Coordinates (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>2$Y$</em>{0.9975}$Tb$_{0.0025}$AlO$_5$</td>
<td>2.356</td>
<td>0.206, 0.420</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.995}$Tb$_{0.005}$AlO$_5$</td>
<td>2.292</td>
<td>0.257, 0.520</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.99}$Tb$_{0.01}$AlO$_5$</td>
<td>2.175</td>
<td>0.289, 0.565</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.97}$Tb$_{0.03}$AlO$_5$</td>
<td>2.019</td>
<td>0.289, 0.579</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.95}$Tb$_{0.05}$AlO$_5$</td>
<td>1.691</td>
<td>0.290, 0.590</td>
</tr>
<tr>
<td>Ba$<em>2$Y$</em>{0.93}$Tb$_{0.07}$AlO$_5$</td>
<td>1.244</td>
<td>0.291, 0.619</td>
</tr>
</tbody>
</table>

Table 4.2.1 Lifetime and CIE coordinates of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ as a function of Tb$^{3+}$ ion concentration sintered at 1225°C

The emission color related to $^5$D$_4$$\rightarrow$$^7$F$_3$ transition of Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ (0.25-7 mol%) nano-crystalline phosphor is analyzed by using Commission International De
I’Eclairage (CIE 1931) chromaticity diagram and presented in Fig. 4.2.11. The corresponding color coordinate values have been listed in Table 4.2.1 along with decay values. The chromatic index lie in the green region with coordinates ranging from 0.2061, 0.4206 to 0.2915, 0.6195.

![CIE chromaticity diagram](image)

**Fig. 4.2.11** CIE chromaticity diagram for $\text{Ba}_2\text{Y}_{(1-x)}\text{Tb}_x\text{AlO}_5$ ($x = 0.25$-$7$ mol\%) sintered at 1225°C nanophosphors at $\lambda_{\text{ex}} = 368$ nm.

The sample $\text{Ba}_2\text{Y}_{0.93}\text{Tb}_{0.07}\text{AlO}_5$ displays well matched color coordinates (0.2915, 0.6195) compared with the European broadcasting unit (EBU, illuminant green = 0.29, 0.60). The chromatic index in the green region unveils the utilization of this $\text{Ba}_2\text{Y}_{(1-x)}\text{Tb}_x\text{AlO}_5$ nanophosphor as one of the green component of the tricolor based phosphor converted white light emitting diodes.

**Conclusions**

Color tunable $\text{Ba}_2\text{Y}_{(1-x)}\text{Eu}_x\text{AlO}_5$ ($x = 0.25$-$10$ mol\%) and $\text{Ba}_2\text{Y}_{(1-x)}\text{Tb}_x\text{AlO}_5$ ($x = 0.25$-$7$ mol\%) nanophosphors have been synthesized for the first time using economic and time saving urea assisted solution combustion approach. Single phased nanophosphor is obtained by heat treatment at 1225°C. X-ray diffraction profile reveal that the doping with different amount of $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ ions does not have any considerable effect on the host lattice and confirms the crystallization of these nanophosphors in monoclinic lattice. TEM analysis infers more or less spherical shaped particles in nano scale. Photoluminescence analysis indicates that these
nanophosphors can be efficiently excited by NUV light unveiling its suitability for near UV excited white LEDs. The shifting of luminescent intensity from high energy $^5D_{3,2,1} \rightarrow ^7F_j$ to $^5D_0 \rightarrow ^7F_j$ transition levels as a function of europium concentration accounts for the blue to red chromatic tuning. The concentration controlled luminescent behavior depicts $\text{Ba}_2\text{Y}_{0.95}\text{Eu}_{0.05}\text{AlO}_5$ as optimal composition. The high value of critical distance claims quadrupole-quadrupole interactions responsible for non-radiative cross relaxation. The Judd-Ofelt intensity parameters and refractive index of the host are calculated by employing Judd-Ofelt theory to confirm the practical application of the synthesized nanophosphor. The CCT values and chromatic tuning from blue to red region proclaim this an efficient nanophosphor for NUV excited white light emitting materials. In case of $\text{Ba}_2\text{Y}_{(1-x)}\text{Tb}_x\text{AlO}_5$ ($x = 0.25-7$ mol%) nanophosphor characteristic green emission attributed to $^5D_4 \rightarrow ^7F_5$ transition at 546 is achieved on excitation by NUV light. Beyond the optimal composition as $\text{Ba}_2\text{Y}_{0.97}\text{Tb}_{0.03}\text{AlO}_5$, concentration quenching phenomenon prevails due to dipole-dipole interactions. The chromaticity index in the green region proposed the applicability of this $\text{Tb}^{3+}$ doped nanophosphor as one of the green component of tricolor based phosphor converted WLEDs.

References