INTRODUCTION

Rare earth activated naophosphors have been widely investigated for application in display devices, lights and detectors. However, for these applications nanophosphor particles must have good characteristics such as high brightness, spherical shape and narrow size distribution. The rare-earth ions have a partially filled 4f shell that is shielded by 5s² and 5p⁶ electrons. Due to this shielded partially filled 4f shell, the host has only a weak influence on the RE³⁺ energy levels, and the radiative emissions resemble those of the free ion in terms of their narrow spectral width [1–3], long excited-state lifetimes (milliseconds) and relatively low oscillator strengths. In recent years, rare earth ions-activated phosphors on the nanoscale have been attracting much interest of the scientists due to the excellent luminescence and potential applications in luminescent devices and display equipments. Trivalent Tb ions have been expected as one of the promising species which provide optical devices in blue and green color regions and many investigations have been conducted in various compounds. As is well known, the efficient blue-green emissions of Tb³⁺ originate from the ⁵D₃→⁷F₁ and ⁵D₄→⁷F₃ transition. In case of Tb³⁺ ion there are eight 4f-electrons (which is a half filled 4f⁷ and plus one electron) and the 4f shell readily releases an electron and the intra ionic transition ⁴f⁸→⁴f⁷⁵d¹ absorption takes place at a relatively low energy. The 5d orbit, being the outer orbit of the ion, is strongly influenced by the electric field of the surrounding ions creating intense absorption band. With Tb³⁺ activation, the emission is from ⁵D₃ and ⁵D₄ states to the ⁷F states. The relative intensities within the ⁵D₃ and ⁵D₄ states are only slightly affected by the host lattice. The main green color emission is from the ⁵D₄ state.

1. BaGd₂O₄:Tb

Rare earth ions doped nanophosphor of lanthanide oxides are new class of tags in biochemistry due to sharp emission spectra, long lifetime and lack of photobleaching [4]. Rare earth ions, especially Tb³⁺ ions are good activators for luminescence materials. The rare-earth sesquioxide gadolinium oxide (Gd₂O₃) and their mixed oxide like BaGd₂O₄ have been shown to be good hosts for the luminescence of rare-earth ions. These materials are promising phosphors for display applications [5-8], immunoassays [9] and biolabeling applications [10]. All these applications demand single phase and compositionally uniform high-purity powders with small and uniform particle size, for high resolution and high luminous efficiency.
However, it is expected that oxides of barium and rare earth metals when doped with Tb will show a variation of luminescence properties, depending upon the occupation of a particular lattice site by activator ions. In the present work, $\text{BaGd}_{2(1-x)}\text{O}_4:2x\text{Tb}^{3+}$ where $x=2$-$6 \text{ mol \%}$, nanophosphors have been synthesized by combustion method using urea as an organic fuel.

**A. SYNTHESIS**

High purity $[\text{Ba(NO}_3\text{)}_2]$, $[\text{Gd(NO}_3\text{)}_3 6\text{H}_2\text{O}]$, $[\text{Tb(NO}_3\text{)}_3 6\text{H}_2\text{O}]$ and $[\text{H}_2\text{NCONH}_2]$ chemicals were taken as starting materials. $\text{Tb}^{3+}$ doped nanocrystals with general formula $\text{BaGd}_{2(1-x)}\text{O}_4:2x\text{Tb}^{3+}$, where $x=2$-$6 \text{ mol \%}$, were prepared by heating rapidly an aqueous concentrated paste containing a calculated amount of metal nitrates and urea in a preheated furnace maintained at $500^\circ\text{C}$. Urea was used as a fuel and its amount was calculated using total oxidizing and reducing valencies [11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame, yielding voluminous solid. The combustion process utilizes the enthalpy of combustion for the formation and the solid obtained was again fired at $700^\circ\text{C}$–$900^\circ\text{C}$ for $3 \text{ hrs}$ to increase the brightness and crystallinity. The theoretical equation for the formation of this nanophosphor by combustion from metal nitrates and urea at about $500^\circ\text{C}$ may be shown as:

$$\text{Ba(NO}_3\text{)}_2 + 2(1-x)\text{Gd(NO}_3\text{)}_3 + 2x\text{Tb(NO}_3\text{)}_3 + ~7\text{CH}_4\text{N}_2\text{O} \rightarrow \text{BaGd}_{2(1-x)}\text{Tb}_{2x}\text{O}_4 + \text{gaseous products (where x= 2-6 mol \%)}.$$

**B. CHARACTERIZATION**

i) **X-ray diffraction (XRD)**

X-ray diffraction (XRD) spectra were recorded with high resolution Rigaku Ultima IV diffractometer in the y-2y configuration and using Cu $\text{K}_\alpha$ radiation ($1.541841 \text{ Å}$). XRD spectra of the $\text{BaGd}_2\text{O}_4:2\text{Tb}^{3+}$ nanophosphor prepared at $500^\circ\text{C}$, sintered at $700^\circ\text{C}$ and $900^\circ\text{C}$ are shown in Fig. 4.1.1. $\text{BaGd}_2\text{O}_4:2\text{Tb}^{3+}$ powder calcined at $700^\circ\text{C}$ and $900^\circ\text{C}$ has a polycrystalline structure composed of $\text{BaGd}_2\text{O}_4$ phase (JCPDS card no. 042-1496) and cubic $\text{Gd}_2\text{O}_3$ phase (JCPDS card no. 012-0797). But the XRD patterns of samples prepared at $500^\circ\text{C}$ show many additional peaks corresponding to those of pure $\text{Ba(NO}_3\text{)}_2$ in cubic phase (JCPDS card no. 004-0773). It seems that $500^\circ\text{C}$ is not a sufficient temperature to decompose $\text{Ba(NO}_3\text{)}_2$ to prepare
BaGd$_2$O$_4$ phase in their respective mixture. In general, the intensities of XRD peaks increase with increase of calcinations temperatures, which indicate better crystallinity. The effect of Tb$^{3+}$ ions concentration on BaGd$_2$O$_4$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature.

In table 4.1.1 the number of phases and the size of crystallites of all powders prepared at 500ºC, calcined at 700ºC and 900ºC are given. Sizes are calculated using Scherrer equation by taking three main peaks in each XRD pattern. It may be observed that the nanocrystals of size 25 nm to 80 nm can successfully be prepared by the combustion synthesis method. As expected the size of crystallites increases with increase of sintering temperature.

![XRD patterns of BaGd$_2$O$_4$:Tb$^{3+}$ powders as-prepared at 500ºC, calcined at 700ºC and 900ºC](image)

**Fig. 4.1.1** XRD patterns of BaGd$_2$O$_4$:Tb$^{3+}$ powders as-prepared at 500ºC, calcined at 700ºC and 900ºC

**Table 4.1.1 Crystallite size of different obtained phases calculated using the Scherrer formula.**

<table>
<thead>
<tr>
<th>Temperature Starting compounds</th>
<th>500 ºC</th>
<th>700 ºC</th>
<th>900 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaGd$_2$O$_4$:Tb$^{3+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6 mol %)</td>
<td>Phase</td>
<td>Grain size (nm)</td>
<td>Phase</td>
</tr>
<tr>
<td>BaGd$_2$O$_4$:Tb$^{3+}$</td>
<td></td>
<td>81.7</td>
<td></td>
</tr>
<tr>
<td>(4 mol %)</td>
<td>Ba(NO$_3$)$_2$</td>
<td>74.2</td>
<td>BaGd$_2$O$_4$</td>
</tr>
<tr>
<td>BaGd$_2$O$_4$:Tb$^{3+}$</td>
<td>BaGd$_2$O$_4$</td>
<td></td>
<td>Gd$_2$O$_3$</td>
</tr>
<tr>
<td>(2 mol%)</td>
<td>73</td>
<td>32</td>
<td>71</td>
</tr>
</tbody>
</table>
ii) Scanning electron micrographs (SEM)

The surface morphological features of the powder nanophosphor were studied by JEOL JSM-6300 scanning electron microscope (SEM) operating at 10 kV. The SEM micrographs of BaGd$_2$O$_4$:Tb$^{3+}$ calcined at 700°C and 900°C are shown in Figs. 4.1.2 and 4.1.3 respectively. These images exhibited homogeneous aggregates of varying shapes and sizes, which are composed of a large number of small elliptical shaped crystallites. In addition, it is noticeable that many pores and voids can also be seen in these SEM images. It is because in combustion synthesis the reaction takes place in a very short period with the evolution of lot of gases that generally yields nanosized materials with pore and voids.

Fig. 4.1.2 SEM micrograph of BaGd$_2$O$_4$:Tb$^{3+}$ powder calcined at 700°C

Fig. 4.1.3 SEM micrograph of BaGd$_2$O$_4$:Tb$^{3+}$ powder calcined at 900°C
C. LUMINESCENCE STUDIES

Photoluminescence (PL) experiments were performed in backscattering geometry used for exciting a He–Cd laser (325 nm) Q1 with an optical power of 30 mW. The emitted light was analyzed by HR-4000 Ocean Optics USB spectrometer optimized for the UV–vis range. For the photoluminescence measurement, 0.05 g powder samples were pressed into pellets (10 mm diameter and 1 mm thickness) and then exposed to a UV lamp at 325 nm. All measurements were carried out at room temperature. Fig. 4.1.4 shows the emission spectra of the BaGd$_2$O$_4$ doped with 4 mol % of Tb$^{3+}$ ions as-synthesized at 500ºC, calcined at 700ºC and 900ºC temperatures excited by 325 nm. There are four main emission peaks located at about 489, 542, 586 and 621 nm, which correspond to the four most significant transitions arising from the (4f) electron configuration of a Tb$^{3+}$ ion, namely the $^5D_4–^7F_n$ transitions with n=3–6 [12]. The predominant green colour from magnetic dipole transition $^5D_4 → ^7F_5$ of Tb$^{3+}$ was located at 545 nm. A similar result was previously reported by Park et al [7] for BaGd$_2$O$_4$:Tb$^{3+}$ powders prepared by solid state reaction method at high temperature. Photoluminescence increases with increase of temperature and was maximum for the samples heated to 900ºC.

![Emission spectra of BaGd$_2$O$_4$:Tb$^{3+}$ nanophosphor as-prepared at 500ºC, calcined at 700ºC and 900ºC](image)

Fig. 4.1.4 Emission spectra of BaGd$_2$O$_4$:Tb$^{3+}$ nanophosphor as-prepared at 500ºC, calcined at 700ºC and 900ºC
2. ZrO$_2$:Tb

ZrO$_2$ have high refractive index, wide energy gap, low optical loss, chemical and photo chemical stability and excellent mechanical, electrical, thermal and optical properties [13,14]. These are attractive for applications in the electro-ceramic industry and as special refractory materials [15-18]. Zirconium oxide has been used widely as an interferometry filter and high power laser mirror [19]. Actually rare earth ions have been considered the most important optical activators for luminescent devices. The aim is to develop luminescent materials of three basic colours with higher radiative efficiency. Tb$^{3+}$-doped ZrO$_2$ has been synthesized by sol–gel process [20] and solvothermal method [21]. In the present work, Zr$_{1-x}$O$_2$:xTb$^{3+}$ where x=1-5 mol %, nanophosphors have been synthesized by combustion method using urea as an organic fuel.

A. SYNTHESIS

High purity [Zr(NO$_3$)$_4$.5H$_2$O], [Tb(NO$_3$)$_3$.6H$_2$O] and [H$_2$NCONH$_2$ ] chemicals were taken as starting materials. Tb$^{3+}$doped nanocrystals with general formula Zr$_{1-x}$O$_2$:xTb$^{3+}$ where x = 1-5 mol % were prepared by heating rapidly an aqueous concentrated paste containing calculated amount of metal nitrates and urea in a preheated furnace maintained at 500$^\circ$C. Urea was used as a fuel and its amount was calculated using total oxidizing and reducing valencies [11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The combustion process utilizes the enthalpy of combustion for the formation and the solid obtained was again fired at 700$^\circ$C to 1000$^\circ$C for 3 hrs to increase the brightness and crystallinity. The theoretical equation for the formation of these nanocrystals by combustion from metal nitrates and urea at about 500$^\circ$C may be shown as:

$$(1-x)\text{Zr(NO}_3\text{)}_4 + x\text{Tb(NO}_3\text{)}_3 + 5\text{CH}_4\text{N}_2\text{O} \rightarrow (\text{Zr}_{1-x}\text{Tb}_x)\text{O}_2 + \text{gaseous product}$$  

(x= 1-5 mol %)
B. CHARACTERIZATION

i) X-ray diffraction (XRD)

The structural characterization was done by high resolution XRD using Rigaku Ultima IV diffractometer in the 0-2θ configuration and using Cu Kα radiation (1.541841 Å). The XRD patterns of ZrO$_2$ doped with 5 mol % of Tb$^{3+}$ ions powder as-prepared at 500ºC, calcined at 700ºC and 1000ºC are shown in Fig. 4.2.1. ZrO$_2$:Tb$^{3+}$ powder at 1000ºC has a polycrystalline structure composed of monoclinic, cubic-tetragonal phases. XRD spectra of samples heated to 500ºC and 700ºC show the presence of only cubic-tetragonal phases. The reflection peaks near 30.2º, 35.2º, 50º, 60º and 62º may be assigned to the (111), (200), (202), (131) and (222) planes respectively of the cubic-tetragonal phases. ZrO$_2$ exists in three different phases namely at room temperature stable monoclinic phase and at high temperature stable tetragonal and cubic phases (metastable phases at room temperature). Cabanas et al and Yashima et al have reported on the basis of Raman studies that zirconia can exist in different phases at different temperatures [22, 23]. It is well known that the tetragonal-phase can be dramatically stabilized by the addition of solutes such as MgO, Y$_2$O$_3$, CaO, etc [24]. Tb$_2$O$_3$ may also be considered as another phase stabilizer for the zirconia. The metastable phases of zirconia, which may be prepared by various wet-chemical processes [25-28], have attracted much attention due to their scientific and technological importance. Some studies on nanocrystalline ZrO$_2$ have shown that pure metastable tetragonal and cubic phases can be stabilized at room temperature when the crystallite size is below a critical size primarily due to very high surface energy associated with it. When the crystallite size exceeds this size, the transformation of metastable phases to the monoclinic one occurs due to decrease in surface energy. The partial conversion of metastable phases to monoclinic at 1000ºC is due to increase in the crystallite size which is reflected in the high intensity and narrower peaks of spectra at 1000ºC than that of at 500ºC and 700ºC.

The size of particles was also calculated using the Scherrer formula. The average particle size for different phases of ZrO$_2$:Tb$^{3+}$ at 500ºC, 700ºC and 1000ºC are given in table 4.2.1. The average particle size has been determined from the peaks corresponding to the (1,1,1) plane of cubic or monoclinic lattices. It is evident from the table that the size of crystallites increases with the increase of temperature to 1000ºC.
The average particle sizes are 22.1 nm and 29.8 nm for the cubic and monoclinic crystallites of ZrO$_2$:Tb$^{3+}$ respectively. In ZrO$_2$:Tb$^{3+}$ powders, nanoparticles of cubic ZrO$_2$ are only formed at temperatures lower than 700°C.

![Fig. 4.2.1 XRD patterns of ZrO$_2$:Tb$^{3+}$ powders as-prepared at 500°C, calcined at 700°C and 1000°C](image)

Table 4.2.1. Crystallite size of ZrO$_2$:Tb$^{3+}$ calculated from the Scherrer formula.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Size at 500°C (nm)</th>
<th>Size at 700°C (nm)</th>
<th>Size at 1000°C (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic ZrO$_2$ JCPDS 00-007-0337 (1,1,1)</td>
<td>5</td>
<td>8</td>
<td>22.1</td>
</tr>
<tr>
<td>Monoclinic ZrO$_2$ JCPDS 00-0036-0420 (1,1,1)</td>
<td>-</td>
<td>-</td>
<td>29.8</td>
</tr>
</tbody>
</table>

**ii) Scanning electron micrographs (SEM)**

The surface morphological features of the nanocrystals were studied by JEOL-JSM6300 scanning electron microscope (SEM) operating at 10 kV respectively. In Fig. 4.2.2 (a,b,c) the typical scanning electron microscope images of ZrO$_2$:Tb$^{3+}$
nanopowder as-prepared at 500ºC, calcined at 700ºC and 1000ºC are displayed. It is remarkable that all the samples have similar morphology. These images exhibited homogeneous aggregates of varying shapes and sizes, which are composed of a large number of small cuboids and broken cuboids. The particle size of the nanocrystals at higher temperature has been observed in the range of 20-30 nm for the cubic and monoclinic crystallites of ZrO$_2$:Tb$^{3+}$, which is in full agreement with the data from XRD patterns. In addition, it is noticeable that many pores and voids can also be seen in these SEM images. It is because in combustion synthesis the reaction takes place in very short period with the evolution of lot of gases that generally yields nanosized materials with pore and voids.

Fig. 4.2.2. SEM micrographs of ZrO$_2$:Tb$^{3+}$ powders (a) as-prepared at 500ºC (b) calcined at 700ºC (c) calcined at 1000ºC
C. LUMINESCENCE STUDIES

Photoluminescence (PL) experiments were performed in back-scattering geometry using for excitation a He–Cd laser (325 nm) with an optical power of 30 mW. The emitted light was analyzed by HR14000 Ocean Optics USB spectrometer optimized for the UV–VIS range. For the photoluminescence measurement, 0.05 g powder samples were pressed into pellets (10 mm diameter and 1 mm thickness), then exposed to a UV lamp at 325 nm. All measurements were carried out at room temperature. Fig. 4.2.3 shows emission spectra of ZrO$_2$:Tb$^{3+}$ powders as-synthesized at 500°C, calcined at 700°C and 1000°C after exciting them by ultraviolet radiation. There are four main emission peaks located at about 488 nm, 542 nm, 588 nm and 620 nm which correspond to the four most significant transitions arising from the (4f) electron configuration of a Tb$^{3+}$ ion, namely the $^5D_4 \rightarrow ^7F_n$ transitions with n=3-6. The predominant green colour from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 542 nm. A similar result was previously reported by García-Hipólito et al for ZrO$_2$:Tb$^{3+}$ films synthesized by pneumatic spray pyrolysis [29]. The photoluminescence was maximum for the samples prepared with 5 mol % of Tb$^{3+}$ ions heated at 1000°C.

![Emission spectra of ZrO$_2$:Tb$^{3+}$ nanophosphor as-prepared at 500°C, calcined at 700°C and 1000°C](image)

Fig. 4.2.3 Emission spectra of ZrO$_2$:Tb$^{3+}$ nanophosphor as-prepared at 500°C, calcined at 700°C and 1000°C
It is observed that with the increase of Tb ions, photoluminescence increases, however the emission intensity tends to decrease after 5 mol % of Tb ions because of non-radiative interaction between ions as the resonant energy transfer becomes stronger. As the concentration is increased, the terbium ions are packed closer and closer together, which favours the transfer of energy from one terbium ion to the next by a resonance process, the energy eventually reaches a sink from which it is dissipated by non-radiative processes rather than by the emission of visible light [30,31].

3. **BaZrO$_3$:Tb**

Barium-zirconate finds its applications as deposition substrate and crucibles for the superconductor YBa$_2$CuO$_7$ synthesis [32,33]. The aim is to develop luminescent materials of three basic colours with higher radiative efficiency. A little work has been done in the area of luminescent properties of BaZrO$_3$ doped with rare earth oxides in the form of powders and single crystals. In the present work, Ba$_{1-x}$ZrO$_3$:$x$Tb$^{3+}$ where $x$ = 1-5 mol %, nanophosphors have been synthesized by combustion method using urea as an organic fuel. The route used is technically simple, affordable, and versatile compared to the other existing chemical routes.

**A. SYNTHESIS**

High purity [Ba(NO$_3$)$_2$], [Zr(NO$_3$)$_4$:5H$_2$O], [Tb(NO$_3$)$_3$:6H$_2$O] and [H$_2$NCONH$_2$] chemicals were taken as starting materials. Tb$^{3+}$doped nanocrystals with general formula Ba$_{1-x}$ZrO$_3$:xTb$^{3+}$ where $x$ = 1-5 mol % were prepared by heating rapidly an aqueous concentrated paste containing calculated amount of metal nitrates and urea in a preheated furnace maintained at 500°C. Urea was used as a fuel and its amount was calculated using total oxidizing and reducing valencies as reported by Ekambaram and Patil [11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The combustion process utilizes the enthalpy of combustion for the formation and the solid obtained was again fired at 700°C to 1000°C for 3 hrs to increase the brightness and crystallinity. The theoretical equation for the formation of these nanocrystals by combustion from metal nitrates and urea at about 500°C may be shown as:

$$(1-x)\text{Ba(NO}_3\text{)}_2 + x\text{Tb(NO}_3\text{)}_3 + \text{Zr(NO}_3\text{)}_4 + 5\text{CH}_4\text{N}_2\text{O} \rightarrow (\text{Ba}_{1-x}\text{Tb}_x)\text{ZrO}_3 + \text{gaseous product} \ (x= 1-5 \text{ mol} \%)$$
B. CHARACTERIZATION

i) X-ray diffraction (XRD)

The structural characterization was done by high resolution XRD using Rigaku Ultima IV diffractometer in the 0-20 configuration and using Cu Kα radiation (1.541841 Å). The XRD patterns of BaZrO₃ doped with 5 mol % of Tb³⁺ ion powders as-prepared at 500°C, calcined at 700°C and 1000°C are shown in Fig.4.3.1. Intensities and positions of diffraction peaks of BaZrO₃: Tb³⁺ nanopowders heated to 700°C and 1000°C corresponds to that of BaZrO₃ cubic perovskite with space group Pm3m (JCPDS card no.006-0399) indicating that almost all of the additive Tb³⁺ ions were successfully incorporated into the ABO₃ perovskite structure. But the XRD patterns of samples prepared at 500°C show many additional peaks correspond to those of pure Ba(NO₃)₂ in cubic phase (JCPDS card no. 004-0773) and ZrO₂ in tetragonal phase (JCPDS card no. 034-1084). It seems that 500°C is not sufficient temperature to prepare pure cubic perovskite structure. In general, the intensities of XRD peaks increase with increase of calcinations temperature which indicates better crystallinity. The effect of Tb³⁺ ions concentration on BaZrO₃ lattices seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. With the increase in the temperature, the crystal size becomes large.

The size of particles was also calculated using the Scherrer formula. The average particle size for different phases of BaZrO₃: Tb³⁺ at 500°C, 700°C and 1000°C are given in table 4.3.1. The average particle size has been determined from the peaks corresponding to the (1,1,1) plane of cubic or monoclinic lattices. It is evident from the table that the size of crystallites increases with the increase of temperature to 1000°C. The average particle size is 23.5 nm for BaZrO₃: Tb³⁺ cubic crystallites. In BaZrO₃: Tb³⁺ powders, nanocrystals of cubic ZrO₂ coexist with bigger sized cubic Ba(NO₃)₂ crystals when prepared at 500°C. It seems that nanoparticles of BaZrO₃ cannot be prepared by the combustion synthesis method at 500°C and further heat treatment is required.
Table 4.3.1. Crystallite size of BaZrO$_3$:Tb$^{3+}$ calculated from the Scherrer formula

<table>
<thead>
<tr>
<th>Phase</th>
<th>Size at 500°C (nm)</th>
<th>Size at 700°C (nm)</th>
<th>Size at 1000°C (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic Ba(NO$_3$)$_2$</td>
<td>76.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>JCPDS 00-004-0773 (1,1,1)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cubic ZrO$_2$</td>
<td>4.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>JCPDS 00-007-0337 (1,1,1)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic BaZrO$_3$</td>
<td>-</td>
<td>19.3</td>
<td>23.5</td>
</tr>
<tr>
<td>JCPDS 00-006-0399 (1,1,1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ii) Scanning electron micrographs (SEM)

The surface morphological features of the nanocrystals were studied by using JEOL-JSM6300 scanning electron microscope operating at 10 kV respectively. In Fig. 4.3.2 (a,b,c) the typical scanning electron microscope images of BaZrO$_3$:Tb$^{3+}$ of the nanophosphor as-prepared at 500°C, calcined at 700°C and 1000°C are displayed. It is remarkable that all the samples have similar morphology. These images exhibited
homogeneous aggregates of varying shapes and sizes, which are composed of a large number of small cuboids and broken cuboids. The average particle size of the nanocrystals at higher temperature has been observed in the range of 20-25 nm, which is in full agreement with the data from XRD patterns. In addition, it is noticeable that many pores and voids can also be seen in these SEM images. It is because in combustion synthesis the reaction takes place in very short period with the evolution of lot of gases that generally yields nano sized materials with pore and voids.

Fig. 4.3.2. SEM micrographs of BaZrO$_3$:Tb$^{3+}$ powders (a) as-prepared at 500ºC (b) calcined at 700ºC (c) calcined at 1000ºC

C. LUMINESCENCE STUDIES

Photoluminescence (PL) experiments were performed in back-scattering geometry using for excitation a He–Cd laser (325 nm) with an optical power of 30 mW. The emitted light was analyzed by HR14000 Ocean Optics USB spectrometer optimized for the UV–VIS range. For the photoluminescence measurement, 0.05 g powder samples were pressed into pellets (10 mm diameter and 1 mm thickness), then
exposed to a UV lamp at 325 nm. All measurements were carried out at room temperature. Fig. 4.3.3 shows emission spectra of BaZrO$_3$:Tb$^{3+}$ powders heated to 500°C, 700°C and 1000°C after exciting them by ultraviolet radiation (325 nm). There are four main emission peaks located at about 488 nm, 542 nm, 588 nm and 620 nm which correspond to the four most significant transitions arising from the (4f) electron configuration of a Tb$^{3+}$ ion, namely the $^5D_4 \rightarrow ^7F_n$ transitions with n=3-6. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 542 nm. The photoluminescence was maximum for the samples prepared with 5 mol % of Tb$^{3+}$ ions heated at 1000°C. It is expected that with the increase of Tb ions, photoluminescence should increase. However, the emission intensity tends to decrease after 5 mol % of Tb ions because of non-radiative emissions.

![Emission spectra of BaZrO$_3$:Tb$^{3+}$ nanoparticles as-prepared at 500°C, calcined at 700°C and 1000°C.](image)

**Fig. 4.3.3** Emission spectra of BaZrO$_3$:Tb$^{3+}$ nanoparticles as-prepared at 500°C, calcined at 700°C and 1000°C.

4. **SrZnO$_2$:Tb**

Nanocrystalline materials are becoming important for research due to the variation of material’s properties with size. These materials exhibit variable and controllable properties, especially, the change of energy structure, surface properties and enhanced luminescence quantum efficiency [34]. The surface and interface of nanocrystal play an important role in the optical and electronic properties [35]. Tb$^{3+}$ ions are promising species that provide optical devices in blue and green color regions.
and various compounds have been investigated for display applications [36-39]. Tb$^{3+}$ doped SrZnO$_2$ lattice has been synthesized by conventional solid state [40] and combustion method [41]. In the present work, Sr$_1$-$x$ZnO$_2$:xTb$^{3+}$ nanocrystals where $x = 0.10$-1.0 mol % were synthesized by sol-gel method using citric acid as chelating agent and reported for the 1st time to the best knowledge of the authors.

A. SYNTHESIS

High purity [Zn(NO$_3$)$_2$.xH$_2$O], [Sr(NO$_3$)$_2$], [Tb(NO$_3$)$_3$.5H$_2$O] and [C$_6$H$_8$O$_7$.H$_2$O] chemicals were used as starting materials. Tb$^{3+}$ doped nanocrystals with general formula Sr$_1$-$x$ZnO$_2$:xTb$^{3+}$ where $x = 0.1$-1.0 mol % were prepared by sol-gel method using citric acid as a chelating agent. The flow diagram of the synthesis of SrZnO$_2$:Tb$^{3+}$ nanophosphor by sol-gel process is shown in Fig.4.4.1. The starting materials were weighed according to stoichiometry and dissolved in DI water. The smaller amount of diluted HNO$_3$ is added to get a transparent solution. Molar ratio of metal ions to citric acid taken was 1:2 [42]. The mixture was stirred for 24 hrs at room temperature. The mixture was then heated under constant stirring at 80°C for 2 hrs, which made the mixture denser forming the ‘sol’. Then, the sol was heated at 120°C until a gel was formed and dried subsequently to get a whitish fluffy powder. The dried gel was collected and subjected to further heat treatment at various temperatures ranging from 700°C to 1100°C for 3 hrs.

![Flow diagram of the synthesis of SrZnO$_2$:Tb$^{3+}$ nanophosphor by sol-gel process](image)

Fig.4.4.1. Flow diagram of the synthesis of SrZnO$_2$:Tb$^{3+}$ nanophosphor by sol-gel process
B. CHARACTERIZATION

i) X-ray diffraction (XRD)

X-ray diffraction (XRD) spectra were recorded using D/Max 2000–Ultima plus to check the crystal structures of the nanophosphors. XRD spectra of the SrZnO$_2$:Tb$^{3+}$ nanophosphor as synthesized, calcined at 700°C and 1100°C for 3 hrs are shown in Fig. 4.4.2. It can be seen that all the diffraction peaks are coincident with the JCPDS card no. 41-0551, no additional peaks were observed which implied that the Tb$^{3+}$ dopant was well incorporated into the structure of SrZnO$_2$. In general, the intensities of XRD peaks increases but line width decreases with increase of calcinations temperatures, which indicate better crystallinity. The effect of Tb$^{3+}$ ions concentration on SrZnO$_2$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. The size of the crystallites can be estimated with the help of the Scherrer equation, $D = \frac{0.94\lambda}{\beta \cos \theta}$, where $D$ is the average grain size, $\lambda$ is the X-ray wavelength (0.15405 nm), and $\theta$ and $\beta$ are the diffraction angle and full-width at half-maximum (FWHM, in radian) of an observed peak. The calculated average particle size ($D$) of nanocrystals were found to be 20 nm for as-synthesized and 52 nm after heat-treatment at 1100°C. With the increase in the temperature, the crystal size becomes large.

![XRD patterns of SrZnO$_2$:Tb$^{3+}$ nanophosphor as-synthesized, calcined at 700°C and 1100°C](image)

Fig.4.4.2 XRD patterns of SrZnO$_2$:Tb$^{3+}$ nanophosphor as-synthesized, calcined at 700°C and 1100°C
ii) **Scanning electron micrographs (SEM)**

The surface morphological features of the powder nanophosphor were studied by Philips XL30 scanning electron microscope (SEM). The SEM micrograph of SrZnO$_2$:Tb$^{3+}$ nanophosphor as-synthesized and calcined at 1100°C are shown in Figs. 4.4.3 and 4.4.4 respectively. The as-synthesized particles have very small crystalline size. The average particle size of nanocrystals was found to be 20-50 nm which is in full agreement with the data from XRD patterns. It was observed that with the increase in the temperature, the particle size increases.

![SEM image of as-synthesized SrZnO$_2$:Tb$^{3+}$ nanophosphor](image1)

**Fig. 4.4.3** SEM image of as-synthesized SrZnO$_2$:Tb$^{3+}$ nanophosphor

![SEM image of SrZnO$_2$:Tb$^{3+}$ nanophosphor calcined at 1100°C](image2)

**Fig. 4.4.4** SEM image of SrZnO$_2$:Tb$^{3+}$ nanophosphor calcined at 1100°C
D. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig. 4.4.5 (a,b) shows the emission spectra of SrZnO$_2$:Tb$^{3+}$ calcined at 700°C and 1100°C for 3 hrs respectively. In case of Tb$^{3+}$ there are eight 4f-electrons (represented as 4f$^8$ which is a half-filled 4f$^7$ shell plus one). The 4f shell readily releases an electron and the intra-ionic transition 4f$^8$–4f$^7$5d absorption takes place at relatively low energy. The 5d orbit, being the outer orbit of the ion, is strongly influenced by the electric field of the surrounding ions (i.e. crystal-field) creating efficient absorption bands. The 4f–5d transitions are allowed for both absorption and emission processes and hence we observe intense absorption bands in the UV region for all oxide hosts. For Tb$^{3+}$ in SrZnO$_2$, the excitation into 4f–5d absorption bands is followed by green $^5$D$_4$–$^7$F$_5$ emission. The excited electrons of the 4f$^7$–5d state decay stepwise to $^5$D$_3$ or $^5$D$_4$ state, thereby giving lattice phonons. The green emission for wavelength above 490 nm corresponds to the transition $^5$D$_4$ → $^7$F$_j$ and the blue emission for wavelength below 490 nm corresponds to the transition $^5$D$_3$ → $^7$F$_j$. The intensity of the blue emission peaks is much weaker than that of the green emission peaks as a consequence of the cross relaxation from the $^5$D$_3$ to the $^5$D$_4$ energy levels. The enhancement of the cross relaxation is due to the high ions concentration leading to a strong emission of $^5$D$_4$ → $^7$F$_j$ transition. Infact, spectral energy distribution of Tb emission strongly depends on the Tb concentration, and $^5$D$_3$ emission of Tb$^{3+}$ decreases with increases Tb$^{3+}$ concentration [43,44]. The main four emission transitions in SrZnO$_2$:Tb$^{3+}$ nanocrystals produce emission at 405 nm from $^5$D$_3$ → $^7$F$_5$, at 435 nm from $^5$D$_3$ → $^7$F$_4$, at 545 nm from $^5$D$_4$ → $^7$F$_5$, at 585 nm from $^5$D$_4$ → $^7$F$_4$. The predominant green color from magnetic dipole transition $^5$D$_4$ → $^7$F$_5$ of Tb$^{3+}$ located at 545 nm. The emission wavelength does not vary with the terbium concentration but emission intensity changes with the terbium concentration. The photoluminescence was maximum for the samples prepared with 0.2 mol % of Tb$^{3+}$ ions heated at 1100°C.

The emission color was analyzed and confirmed with the help of *Commission Internationale de l'Eclairage* (CIE) chromaticity co-ordinates diagram. The color co-ordinates for SrZnO$_2$:Tb$^{3+}$ (x=0.2 mol %) nanocrystals are shown in Fig. 4.4.6. It is clear from the figure that color co-ordinates of the as-synthesized sample fall in bluish green region (x=0.273, y=0.412) which shifted towards green region calcined at.
$700^\circ C (x=0.254, y=0.441)$ and shifted towards deeper green region after heat treatment at $1100^\circ C (x=0.233, y=0.492)$.

Fig. 4.4.5. Emission spectra of SrZnO$_2$:Tb$^{3+}$ nanophosphor (a) calcined at 700$^\circ$C (b) calcined at 1100$^\circ$C

Fig. 4.4.6. CIE color coordinates of SrZnO$_2$:Tb$^{3+}$ nanoparticles as synthesized, calcined at 700$^\circ$C and 1100$^\circ$C
5. YAlO$_3$: Tb

Yttrium orthoaluminate (YAlO$_3$) phosphors activated with rare-earth ions have been particularly attractive due to their potential applications in optoelectronic devices for many years [45-47]. The YAlO$_3$ phosphor has a perovskite structure with distorted YO$_{12}$ and YA$_{18}$ polyhedra with the space group of D$_{2h}^{16}$ (Pbnm) [48]. The melting point of YAlO$_3$ is high at 1875°C, so it is a stable host material with strong chemical bond strengths [49]. YAlO$_3$ is an excellent host lattice for the trivalent lanthanides, which can very easily substitute the trivalent yttrium (Y). YAlO$_3$ phosphor doped with Tb$^{3+}$ was synthesized by combustion process [50]. In the present work, Y$_{1-x}$AlO$_3$:xTb$^{3+}$ where x = 0.10 - 3.0 mol % nanocrystals were synthesized by sol-gel method using tartaric acid as chelating agent.

A. SYNTHESIS

High purity [Y(NO$_3$)$_3$.4H$_2$O], [Al(NO$_3$)$_3$.9H$_2$O], [Tb(NO$_3$)$_3$.5H$_2$O] and [C$_4$H$_6$O$_6$] chemicals were used as starting materials. Tb$^{3+}$ doped nanocrystals with general formula Y$_{1-x}$AlO$_3$:xTb$^{3+}$ where x = 0.10 - 3 mol % were prepared by sol-gel method using tartaric acid as a chelating agent. The flow diagram of the synthesis of YAlO$_3$:Tb$^{3+}$ nanophosphor by sol-gel process is shown in Fig.4.5.1.

![Flow diagram for the synthesis of YAlO$_3$:Tb$^{3+}$ nanophosphor by sol-gel method](image)

Fig.4.5.1 Flow diagram for the synthesis of YAlO$_3$:Tb$^{3+}$ nanophosphor by sol-gel method
The starting materials were weighed according to stoichiometry and dissolved in DI water. The smaller amount of diluted HNO$_3$ is added to get a transparent solution. Molar ratio of metal ions to tartaric acid taken was 1:2. The mixture was stirred for 24 hrs at room temperature. The mixture was then heated under constant stirring at 80°C for 2 hrs, which made the mixture denser forming the ‘sol’. Then, the sol was heated at 120°C until a gel was formed and dried subsequently to get a gray fluffy powder. The dried gel was collected and subjected to further heat treatment at various temperatures ranging from 700°C to 1100°C for 3 hrs.

**B. CHARACTERIZATION**

i) **X-ray diffraction (XRD)**

X-ray diffraction (XRD) spectra were recorded using D/Max 2000–Ultima plus to check the crystal structures of the nanophosphors. XRD spectra of the YAlO$_3$:Tb$^{3+}$ nanophosphor before calcination, calcined at 700°C and 1100°C for 3 hrs are shown in Fig. 4.5.2. The XRD of the gel before calcinations shows broad peaks indicating amorphous nature. The powder calcined at 700°C also show peak broadening which indicates that it is still amorphous. However, the peak intensity increases and the linewidth decrease with an increase of calcination temperature, indicating grain growth of YAlO$_3$:Tb$^{3+}$ nanocrystals with increase in temperature. The pattern of the peaks was similar to that reported in the literature for the parent lattice.

![XRD Spectra](image)

**Fig. 4.5.2.** Powder X-ray diffraction patterns of YAlO$_3$:Tb$^{3+}$ nanophosphor as-synthesized, calcined at 700°C and 1100°C
ii) **Scanning electron micrographs (SEM)**

The surface morphological features of the nanocrystals were studied by Philips XL30, scanning electron microscope (SEM). The typical scanning electron microscope (SEM) images of $\text{YAlO}_3:\text{Tb}^{3+}$ nanophosphor calcined at 700°C and 1100°C are displayed in Figs. 4.5.3 and 4.5.4 respectively. It is observed that the particles size of the as-synthesized nanophosphor was very small and particles tend to agglomerate. With an increase of temperature, particle size increased and agglomeration decreased. In fact agglomeration of the as-synthesized powder after heat treatment at 1100°C was almost eliminated, producing well formed particles.

![SEM image of $\text{YAlO}_3:\text{Tb}^{3+}$ nanophosphor calcined at 700°C](image1)

**Fig 4.5.3 The SEM image of $\text{YAlO}_3:\text{Tb}^{3+}$ nanophosphor calcined at 700°C**

![SEM image of $\text{YAlO}_3:\text{Tb}^{3+}$ nanophosphor calcined at 1100°C](image2)

**Fig 4.5.4 The SEM image of $\text{YAlO}_3:\text{Tb}^{3+}$ nanophosphor calcined at 1100°C**
The particle size of the nanocrystals has been observed in the range of 20-80 nm, which is in full agreement with the data from XRD patterns. It may be mentioned that crystalline powder and nanometer dimension of the powder with high strength would be very useful for the application, as this nanocrystalline phosphor can result in enhanced luminescent intensity.

C. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig.4.5.5 (a,b) shows the emission spectra of YAlO$_3$:Tb$^{3+}$ calcined at 700°C and 1100°C for 3 hrs respectively. The different emission peaks in Tb$^{3+}$ doped YAlO$_3$ nanophosphor were observed at 403, 435, 543, 585 and 620 nm, which have been assigned to the following transitions respectively:

$^5D_3 \rightarrow ^7F_5, \quad ^5D_3 \rightarrow ^7F_4, \quad ^5D_4 \rightarrow ^7F_5, \quad ^5D_4 \rightarrow ^7F_4, \quad ^5D_4 \rightarrow ^7F_3$

The predominant green colour from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 543 nm. The spectral energy distribution of Tb$^{3+}$ ions emission is strongly dependent on the quantity of tartaric acid. As tartaric acid is added stoichiometric quantities that molar ratio of 1:2 to the metal ions. The spectral energy distribution is also strongly dependent on the terbium concentration. The emission wavelength does not vary with the terbium concentration but emission intensity changes with the terbium concentration. The photoluminescence was maximum for the samples prepared with 2 mol % of Tb$^{3+}$ ions heated at 1100°C. However, the emission intensity tends to decrease after 2 mol % of Tb ions because of non-radiative emissions.

The emission color was analyzed and confirmed with the help of Commission Internationale de l'Eclairage (CIE) chromaticity co-ordinates diagram. The color co-ordinates for YAlO$_3$:Tb$^{3+}$ (x=2 mol %) nanocrystals are shown in Fig. 4.5.6. It is clear from the figure that color co-ordinates of the as-synthesized sample fall in the bluish green region (x=0.2755, y=0.3812) which shifted towards green region calcined at 700°C(x=0.2389, y=0.4358) and shifted towards deeper green region after heat treatment at 1100°C(x=0.2107, y=0.5124).
Fig. 4.5.5 Emission spectra of YAlO$_3$:Tb$^{3+}$ nanophosphor (a) calcined at 700°C (b) calcined at 1100°C

Fig. 4.5.6 CIE color coordinates of YAlO$_3$: Tb$^{3+}$ nanophosphor as-synthesized, calcined at 700°C and 1100°C
6. CaAl$_{1.8}$Y$_{0.2}$O$_4$: Tb

Many phosphors have been made in nanophase by employing different techniques. Much more attention has been directed to the sol-gel approach in luminescent materials because the direct advantages of this technology include obtaining novel chemical compositions with excellent purity and more convenient preparation method [51-53]. The sol-gel process is a wet chemical technique widely used in the fields of materials science and ceramic engineering. The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants, such as rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. Through a sol-gel process it is possible to synthesize phosphors with small size. It is easy to control composition and homogeneity [54-58]. In the present work, CaAl$_{1.8}$Y$_{0.2-x}$O$_4$:xTb$^{3+}$ where x = 1-5 mol % nanocrystals were synthesized by sol-gel method using citric acid as a chelating agent.

A. SYNTHESIS

High purity [Ca(NO$_3$)$_2$.4H$_2$O], [Y(NO$_3$)$_3$.6H$_2$O], [Al(NO$_3$)$_3$.9H$_2$O], [Tb(NO$_3$)$_3$.5H$_2$O] and [C$_6$H$_8$O$_7$.H$_2$O] chemicals were used as starting materials. Tb$^{3+}$ doped nanocrystals with general formula CaAl$_{1.8}$Y$_{0.2-x}$O$_4$:xTb$^{3+}$ where x = 1-5 mol % were prepared by sol-gel method using citric acid as a chelating agent. The flow diagram of the synthesis of CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb nanophosphor by sol-gel process are shown in Fig. 4.6.1.

![Flow diagram of the synthesis of CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb nanophosphor by sol-gel process.](image)

Fig. 4.6.1. Flow diagram of the synthesis of CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb$^{3+}$ nanophosphor by sol-gel process.
The starting materials were weighed according to stoichiometry and dissolved in DI water. The minimum amount of diluted HNO₃ is added to get a transparent solution. Molar ratio of metal ions to citric acid taken was 1:2. The mixture was stirred for 24 hrs at room temperature. The mixture was then heated under constant stirring at 80°C for 2 hrs, which made the mixture denser forming the ‘sol’. Then, the sol was heated at 120°C until a gel was formed and dried subsequently to get a whitish fluffy powder. The dried gel was collected and subjected to further heat treatment at various temperatures ranging from 700°C to 1000°C for 3 hrs.

**B. CHARACTERIZATION**

i) X-ray diffraction (XRD)

X-ray diffraction (XRD) spectra were recorded with high resolution Rigaku Mini Flex’ ii diffractometer. XRD spectra of the CaAl₁.₈Y₀.₂O₄: Tb³⁺ nanophosphor before calcination, calcined at 700°C and 1000°C are shown in Fig. 4.6.2.

![X-ray diffraction patterns of CaAl₁.₈Y₀.₂O₄: Tb³⁺ nanophosphor](image)

**Fig.4.6.2.** Powder X-ray diffraction patterns of CaAl₁.₈Y₀.₂O₄: Tb³⁺ nanophosphor as-synthesized, sintered at 700°C and 1000°C

The as-synthesized nanophosphor by sol-gel method consists of CaO and some other phases in addition to CaAl₁.₈Y₀.₂₋₄O₄. It can also be seen from Fig. 4.6.2 that the
peak intensity increases with an increase in sintering temperature, which indicate better crystallinity. The effect of Tb$^{3+}$ ions concentration on CaAl$_{1.8}$Y$_{0.2}$O$_4$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. The size of the crystallites can be estimated with the help of the Scherrer equation, $D = \frac{0.941\lambda}{\beta \cos \theta}$, where $D$ is the average grain size, $\lambda$ is the X-ray wavelength (0.15405nm), and $\theta$ and $\beta$ are the diffraction angle and full-width at half-maximum (FWHM, in radian) of an observed peak. The calculated average particle size (D) of nanocrystals were found to be 19 nm for as-synthesized and 32 nm after heat treatment at 1000°C. With the increase in the temperature, the crystal size becomes large.

ii) Scanning electron micrographs (SEM)

The surface morphological features of the nanocrystals were studied by Philips XL30, scanning electron microscope (SEM). The SEM image of CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb$^{3+}$ nanophosphor calcined at 700°C and 1000°C for 3 hrs are shown in the Figs.4.6.3 and 4.6.4. The particle size of the as-synthesized nanophosphor was very small and particles tend to agglomerate. With an increase of temperature, particle size increased and agglomeration decreased (Fig.4.6.4). In fact agglomeration of the as-synthesized powder after heat treatment at 1000°C was almost eliminated, producing well formed particles. The particle size of the nanocrystals has been observed in the range of 20-35 nm, which is in full agreement with the data from XRD patterns.

![Fig.4.6.3 SEM image of CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb$^{3+}$ nanoparticles calcined at 700°C](image)

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Fig. 4.6.4. SEM image of CaAl_{1.8}Y_{0.2}O_{4}: Tb^{3+} nanoparticles calcined at 1000°C

C. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig. 4.6.5 (a,b) shows the emission spectra of CaAl_{1.8}Y_{0.2}O_{4}:Tb^{3+} nanophosphor calcined at 700°C and 1000°C for 3 hrs respectively. The emission spectra show peaks at 403, 435, 543, 585 and 620 nm, which have been assigned to the $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions respectively. The predominant green colour from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 543 nm. It was observed that the PL intensity of the nanoparticles increased rapidly on calcination up to 1000°C and beyond this there was no observable change in the PL intensity. This is mainly due to the improvement in doping, good activation and high crystallinity. Furthermore, it is also clear that the luminescence intensity strongly depends on the calcination temperatures. The spectral energy distribution is also strongly dependent on the terbium concentration. The emission wavelength does not vary with the terbium concentration but emission intensity changes a lot with the terbium concentration. The photoluminescence was maximum for the samples prepared with 3 mol % of Tb$^{3+}$ ions heated at 1000°C. However, the emission intensity tends to decrease after 3 mol % of Tb$^{3+}$ ions because of non-radiative emissions.

The emission color was analyzed and confirmed with the help of Commission Internationale de l’Eclairage (CIE) chromaticity co-ordinates diagram. The color co-ordinates for CaAl_{1.8}Y_{0.2}O_{4}:Tb^{3+} (x=3 mol %) nanocrystals are shown in Fig. 4.6.6. It is
clear from the figure that color co-ordinates of the as-synthesized sample fall in the yellowish green region \((x=0.2821, y=0.4123)\) which shifted towards green region calcined at \(700^\circ C(x=0.2733, y=0.4461)\) and shifted towards deeper green region after heat treatment at \(1000^\circ C(x=0.221, y=0.4812)\).

**Fig.4.6.5.** Emission spectra of \(\text{CaAl}_{1.8}\text{Y}_{0.2-x}\text{O}_4: x\text{Tb}^{3+}\) nanophosphor (a) calcined at \(700^\circ C\) (b) calcined at \(1000^\circ C\)

**Fig.4.6.6.** CIE color coordinates of \(\text{CaAl}_{1.8}\text{Y}_{0.2-x}\text{O}_4: x\text{Tb}^{3+}\) (x= 3 mol %) nanophosphor as-synthesized, calcined at \(700^\circ C\) and \(1000^\circ C\)
7. SrY$_2$O$_4$ :Tb

Rare earth ions doped inorganic compounds form an important class of phosphors as they possess many interesting properties such as excellent chemical stability, high luminescence efficiency and flexible emission colors with different activators [59,60]. Now a days, researchers have been focused on the synthesis and investigation of the properties of rare earth ions doped host lattices, which has been synthesized by many wet chemistry routes. SrY$_2$O$_4$ is widely used as a luminescent host lattice material for many of the phosphors. In the present work, SrY$_{2(1-x)}$O$_4$:2xTb$^{3+}$ where x=1-5 mol % nanocrystals were synthesized by sol-gel method using tartaric acid as an complexing agent.

A. SYNTHESIS

High purity chemicals [Sr(NO$_3$)$_2$], [Y(NO$_3$)$_3$.6H$_2$O], [Tb(NO$_3$)$_3$.6H$_2$O] and [C$_4$H$_6$O$_6$] were taken as starting materials. Tb$^{3+}$ doped nanocrystals with general formula, SrY$_{2(1-x)}$O$_4$:2xTb$^{3+}$ where x=1-5 mol % were prepared by sol-gel method using tartaric acid as a chelating agent. The starting materials were weighed according to stoichiometry and dissolved in DI water. The minimum amount of diluted HNO$_3$ is added to get a transparent solution. Molar ratio of metal ions to tartaric acid taken was 1:2. The mixture was stirred for 24 hrs at room temperature. The mixture was then heated under constant stirring at 80°C for 2 hrs, which made the mixture denser forming the ‘sol’. Then, the sol was heated at 120°C until a gel was formed and dried subsequently to get a gray fluffy powder. The dried gel was collected and subjected to further heat treatment at various temperatures ranging from 700°C to 1100°C for 3 hrs.

B. CHARACTERIZATION

i) X-ray diffraction (XRD)

X-ray diffraction (XRD) spectra were recorded with high resolution Rigaku Mini Flex’ ii diffractometer. XRD spectra of the SrY$_2$O$_4$:Tb$^{3+}$ nanophosphor as-prepared, calcined at 700°C and 1100°C are shown in Fig. 4.7.1. The line width slightly decreases and peak intensity increases with an increase of calcination temperature, indicating grain growth of SrY$_2$O$_4$:Tb$^{3+}$ nanocrystals with increase in temperature. The effect of Tb$^{3+}$ ions concentration on SrY$_2$O$_4$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. The size of the crystallites can be estimated with the help of the Scherrer
equation, \( D = 0.941\lambda/\beta \cos \theta \), where \( D \) is the average grain size, \( \lambda \) is the X-ray wavelength (0.15405 nm), and \( \theta \) and \( \beta \) are the diffraction angle and full-width at half-maximum (FWHM, in radian) of an observed peak. The calculated average particle size (D) of nanocrystals was found to be 29 nm for as-synthesized and 52 nm after heat-treatment at 1100°C. With the increase in the temperature, the crystal size becomes large.

![Figure 4.7.1](image)

**Fig. 4.7.1** Powder X-ray diffraction patterns of \( \text{SrY}_2\text{O}_4: \text{Tb}^{3+} \) nanophosphor as-synthesized, calcined at 700°C and 1100°C

**ii) Scanning electron micrographs (SEM)**

The surface morphological features of the powder nanophosphor were studied by Philips XL30, scanning electron microscope (SEM). The typical scanning electron microscope (SEM) images of as-synthesized \( \text{SrY}_2\text{O}_4: \text{Tb}^{3+} \) nanophosphor and calcined at 1100°C are displayed in Figs. 4.7.2 and 4.7.3 respectively. For the as-synthesized nanophosphor the particles size was very small and particles tend to agglomerate. With an increase of temperature, particle size increased and agglomeration decreased. The
particle size of the nanocrystals has been observed in the range of 30-55 nm, which is in full agreement with the data from XRD patterns.

Fig.4.7.2 SEM image of as-prepared SrY$_2$O$_4$:Tb$^{3+}$ nanophosphor

Fig.4.7.3 SEM image of SrY$_2$O$_4$:Tb$^{3+}$ nanophosphor calcined at 1100°C

C. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig.4.7.4 (a,b) shows the emission spectra of SrY$_2$O$_4$:Tb$^{3+}$ nanophosphor calcined at 700°C and 1100°C for 3 hrs respectively. The emission spectra show peaks at 403, 435, 543 and 585 nm, which have been assigned to the $^5$D$_3$ → $^7$F$_5$, $^5$D$_3$ → $^7$F$_4$, $^5$D$_4$ → $^7$F$_5$ and $^5$D$_4$ → $^7$F$_4$ transitions respectively. The predominant green colour from magnetic dipole transition $^5$D$_4$ → $^7$F$_5$ of Tb$^{3+}$ was located at 543 nm.
It was observed that the PL intensity of the nanoparticles increased rapidly on calcination up to 1100°C and beyond this there was no observable change in the PL intensity. This is mainly due to the improvement in doping, good activation and high crystallinity. Furthermore, it is also clear that the luminescence intensity strongly depends on the calcination temperatures. The spectral energy distribution is also strongly dependent on the terbium concentration. The emission wavelength does not vary with the terbium concentration but emission intensity changes a lot with the terbium concentration. The photoluminescence was maximum for the samples prepared with 3 mol % of Tb$^{3+}$ ions heated at 1100°C. However, the emission intensity tends to decrease after 3 mol % of Tb ions because of non-radiative emissions.

The emission color was analyzed and confirmed with the help of *Commission Internationale de l’Eclairage* (CIE) chromaticity co-ordinates diagram. The color co-ordinates for SrY$_2$O$_4$:Tb$^{3+}$ (x=3 mol %) nanocrystals are shown in Fig. 4.7.5. It is clear from the figure that color co-ordinates of the as-synthesized sample fall in the bluish green region (x=0.2603, y=0.3901) which shifted towards green region calcined at 700°C(x=0.2789, y=0.4376) and shifted towards deeper green region after heat treatment at 1100°C(x=0.2134, y=0.4763).

Fig.4.7.4. Emission spectra of SrY$_2$O$_4$:Tb$^{3+}$ nanophosphor (a) calcined at 700°C (b) calcined at 1100°C
8. Sr₃Y(PO₄)₃:Tb

Phosphate-based compositions are excellent host matrices applied in fluorescent lamps and color TV monitors [61,62]. A new class of phosphate host materials isostructural with eulytite compounds are gaining great attention due to their high performance. Sr₃Y(PO₄)₃ belong to the larger family of the eulytite type compounds, which acts as good host luminescence material for many of the phosphors. Sr₃Y(PO₄)₃ doped with Tb³⁺, Eu³⁺,Ce³⁺ and Pr³⁺ has been synthesized by modified wet chemical method [63]. In the present work, Sr₃Y₁ₓ(PO₄)₃:xTb³⁺ where x=1-5 mol % nanocrystals were synthesized by combustion method using urea as an organic fuel.

A. SYNTHESIS

High purity [Sr(NO₃)₂], [(NH₄)₃HPO₄], [Y(NO₃)₃·4H₂O], [Tb(NO₃)₃·6H₂O] and [H₂NCONH₂] chemicals were taken as starting materials. Tb³⁺ doped nanocrystals with general formula Sr₃Y₁ₓ(PO₄)₃:xTb³⁺ where x=1-5 mol % were prepared by heating rapidly an aqueous concentrated paste containing calculated amount of ammonium phosphate, metal nitrates and urea in a preheated furnace maintained at 500°C. Urea was used as a fuel and its amount was calculated using total oxidizing and reducing valencies as reported Ekambaram and Patil [11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases.
These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The combustion process utilizes the enthalpy of combustion for the formation and crystallization of the nanocrystals at low ignition temperature. The solid obtained was again fired at 700°C to 900°C for 3 hrs to increase the brightness. The theoretical equation for the formation of this nanophosphor by combustion from metal nitrates and urea at about 500°C may be shown as:

\[ 3\text{Sr(NO}_3\text{)}_2 + (1-x)\text{Y(NO}_3\text{)}_3 + x\text{Tb(NO}_3\text{)}_3 + 3(\text{NH}_4\text{)}_2\text{HPO}_4 + \sim 7.5\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Sr}_3\text{Y}_{1-x}\text{Tb}_x(\text{PO}_4)_3 + \text{gaseous products} \quad \text{(where} \ x = 1-5 \ \text{mol} \ %) \]

**B. CHARACTERIZATION**

i) **X-ray diffraction (XRD)**

X-ray diffraction (XRD) spectra were recorded using D/Max 2000–Ultima plus to check the crystal structures of the nanophosphors. XRD spectra of the \( \text{Sr}_3\text{Y(PO}_4\text{)}_3:\text{Tb}^{3+} \) nanophosphor prepared at 500°C, sintered at 700°C and 900°C are shown in Fig.4.8.1. The XRD data indicated that \( \text{Sr}_3\text{Y(PO}_4\text{)}_3 \) was single cubic phases and belong to the family of the eulytite type compounds, which was in good agreement with those in JCPDS card no. 44 – 0320.

![XRD spectra](image)

**Fig. 4.8.1** Powder X-ray diffraction patterns of \( \text{Sr}_3\text{Y(PO}_4\text{)}_3:\text{Tb}^{3+} \) nanophosphor as-prepared at 500°C, calcined at 700°C and 900°C.
In general, the intensities of XRD peaks increase with increase of calcinations temperatures, which indicate better crystallinity. The crystallite size of the Sr$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor has been calculated by Debye Scherrer equation $D = \frac{0.941 \lambda}{\beta \cos \theta}$ where $\beta(2\theta)$ is the width of the pure diffraction profile in radians, $\lambda$ is the wavelength of the X-rays (0.15405 nm), $\theta$ is the diffraction angle, and $D$ is the average diameter of the crystallite. The calculated average particle size (D) of nanocrystals were found to be 23 nm for as-synthesized at 500°C and 47 nm after heat-treatment at 900°C. With the increase in the temperature, the crystal size becomes large.

ii) Scanning electron micrographs (SEM)

The surface morphological features of the powder phosphor were studied by Philips XL30, scanning electron microscope (SEM). The typical scanning electron microscope (SEM) images of as-synthesized Sr$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor at 500°C and calcined at 900°C are displayed in Figs. 4.8.2 and 4.8.3 respectively. For the powder synthesized at 500°C by combustion, the particle size was very small and the particles tend to agglomerate. Agglomeration is known to decrease with the increase of heating temperature. With an increase of temperature, particle size increased and agglomeration decreased. In fact agglomeration of the as-synthesized powder after heat-treatment for 3 hrs at 900°C was almost eliminated, producing well-formed. The particle size of the nanocrystals has been observed in the range of 20-50 nm, which is in full agreement with the data from XRD patterns.

Fig. 4.8.2 SEM image of Sr$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor as-prepared at 500°C
C. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig. 4.8.4 (a,b) shows the emission spectra of Sr₃Y(PO₄)₃:Tb³⁺ nanophosphor as prepared at 500°C and sintered at 900°C respectively. The emission spectra show peaks at 403, 435, 543 and 585 nm, which have been assigned to the ⁵D₃ → ⁷F₅, ⁵D₃ → ⁷F₄, ⁵D₄ → ⁷F₅ and ⁵D₄ → ⁷F₄ transitions respectively. The predominant green colour from magnetic dipole transition ⁵D₄ → ⁷F₅ of Tb³⁺ was located at 547 nm. It was observed that the PL intensity of the nanoparticles increased rapidly on calcination up to 900°C and beyond this there was no observable change in the PL intensity. This is mainly due to the improvement in doping, good activation and high crystallinity. Furthermore, it is also clear that the luminescence intensity strongly depends on the calcination temperatures. The spectral energy distribution is also strongly dependent on the terbium concentration. The emission wavelength does not vary with the terbium concentration but emission intensity changes a lot with the terbium concentration. The photoluminescence was maximum for the samples prepared with 5 mol % of Tb³⁺ ions heated at 900°C. However, the emission intensity tends to decrease after 5 mol % of Tb ions because of non-radiative emissions.

The emission color was analyzed and confirmed with the help of Commission Internationale de l’Eclairage (CIE) chromaticity co-ordinates diagram. The color co-ordinates for Sr₃Y(PO₄)₃:Tb³⁺ (x=5 mol %) nanocrystals are shown in Fig. 4.8.5. It
is clear from the figure that color co-ordinates of the as-synthesized sample fall in the bluish green region (x=0.2387, y=0.2871, L\textsubscript{v}=29.16 cd/m\(^2\)) which shifted towards green region after heat treatment at 700\(^o\)C (x=0.2196, y=0.3956, L\textsubscript{v}=49.26 cd/m\(^2\)) and shifted towards deeper green region after heat treatment at 900\(^o\)C (x=0.2138, y=0.3808, L\textsubscript{v}=64.98 cd/m\(^2\)).

Fig.4.8.4. Emission spectra of Sr\(_3\)Y(PO\(_4\))\(_3\):Tb\(^{3+}\) nanophosphor (a) as-prepared at 500\(^o\)C (b) calcined at 900\(^o\)C

Fig.4.8.5. CIE color coordinates of Sr\(_3\)Y(PO\(_4\))\(_3\):Tb\(^{3+}\) (x= 5 mol %) nanophosphor as-synthesized at 500\(^o\)C, calcined at 700\(^o\)C and 900\(^o\)C
9. Ca$_3$Y(PO$_4$)$_3$:Tb

Recently, phosphate compounds have emerged as an important class of luminescent materials because of high thermal stability and the tetrahedral rigid three dimensional matrix of phosphate is ideal for charge stabilization [64,65]. Ca$_3$Y(PO$_4$)$_3$ belong to the larger family of the eulytite type compounds. A larger number of compounds isostructural with eulytite have been reported over the past 20 years [66-71]. Eulytite structural phosphates have been shown to be better hosts for rare earth ions [72-76]. In the present work, Tb$^{3+}$ doped Ca$_3$Y(PO$_4$)$_3$ nanocrystals were synthesized by combustion method using urea as an organic fuel. To the best of our knowledge, this is the first report to synthesize Ca$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanocrystals were synthesized by combustion method using urea as an organic fuel.

A. SYNTHESIS

High purity [Ca(NO$_3$)$_2$.4H$_2$O], [(NH$_4$)$_2$HPO$_4$], [Y(NO$_3$)$_3$.4H$_2$O], [Tb(NO$_3$)$_3$.6H$_2$O] and [H$_2$NCONH$_2$] chemicals were taken as starting materials. Tb$^{3+}$ doped nanocrystals with general formula Ca$_3$Y$_{1-x}$(PO$_4$)$_3$:xTb where x=1-5 mol % were prepared by heating rapidly an aqueous concentrated paste containing calculated amount of metal nitrates and urea in a preheated furnace maintained at 500ºC. Urea was used as a fuel and its amount was calculated using total oxidizing and reducing valences as reported by Ekambaram and Patil [11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The combustion process utilizes the enthalpy of combustion for the formation and crystallization of the nanocrystals at low ignition temperature. The solid obtained was again fired at 700ºC to 900ºC for 3 hrs to increase the brightness. The theoretical equation for the formation of this nanophasphor by combustion from metal nitrates and urea at about 500ºC may be shown as:

\[
3\text{Ca(NO}_3\text{)}_2 + (1-x)\text{Y(NO}_3\text{)}_3 + x\text{Tb(NO}_3\text{)}_3 + 3(\text{NH}_4)_2\text{HPO}_4 + \sim 7.5\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Ca}_3\text{Y}_{1-x}\text{Tb}_x\text{(PO}_4\text{)}_3 + \text{gaseous products (where x= 1-5 mol %)}
\]
B. CHARACTERIZATION

i) X-ray diffraction (XRD)

X-ray diffraction (XRD) spectra were recorded using D/Max 2000−Ultima plus to check the crystal structures of the nanophosphors. XRD spectra of the Ca$_3$Y(PO$_4$)$_3$:Tb nanophosphor prepared at 500°C, sintered at 700°C and 900°C are shown in Fig.4.9.1. The XRD data indicated that Ca$_3$Y(PO$_4$)$_3$ was single cubic phases and belong to the family of the eulytite type compound. In general, the intensities of XRD peaks increase with increase of calcinations temperatures, which indicate better crystallinity. The effect of Tb$^{3+}$ ion concentration on Ca$_3$Y(PO$_4$)$_3$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations.

![XRD spectra](image)

**Fig. 4.9.1** Powder X-ray diffraction patterns of Ca$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor as-prepared at 500°C, calcined at 700°C and 900°C

ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder nanophosphor was studied by Philips XL30 scanning electron microscope (SEM). The SEM micrograph of Ca$_3$Y(PO$_4$)$_3$:Tb as-synthesized at 500°C and sintered at 900°C are shown in Figs. 4.9.2 and 4.9.3. The narrow size distribution of the nanoparticles is very uniform with spherical shape. For the powder synthesized at 500°C by combustion method, the
particle size was very small and the particles tend to agglomerate. Agglomeration is known to decrease with the increase of heating temperature. With an increase of temperature, particle size increased and agglomeration decreased. The particle size of Ca₃Y(PO₄)₃:Tb³⁺ nanophosphor has been observed in the range of 30-55 nm, which is in full agreement with the data from XRD patterns.

![Fig. 4.9.2. SEM image of Ca₃Y(PO₄)₃:Tb³⁺ nanophosphor as-prepared at 500°C](image)

Fig. 4.9.3. SEM image of Ca₃Y(PO₄)₃:Tb³⁺ nanophosphor calcined at 900°C

C. LUMINESCENCE STUDIES

The emission spectra of the nanophosphor were recorded with Minolta Spectroradiometer CS-1000. Fig.4.9.4 (a,b) shows the emission spectra of Ca₃Y(PO₄)₃:Tb³⁺ nanophosphor as-prepared at 500°C and sintered at 900°C for 3 hrs respectively. The emission spectra show peaks at 403, 435, 543 and 585 nm, which have been assigned to the $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_4$ transitions.
respectively. The predominant green colour from magnetic dipole transition $^5\mathrm{D}_4 \rightarrow ^7\mathrm{F}_5$ of Tb$^{3+}$ was located at 547 nm. It was observed that the PL intensity of the nanoparticles increased rapidly on calcination up to 900°C and beyond this there was no observable change in the PL intensity. This is mainly due to the improvement in doping, good activation and high crystallinity. Furthermore, it is also clear that the luminescence intensity strongly depends on the calcination temperatures. The spectral energy distribution is also strongly dependent on the terbium concentration. It is expected that with the increase of Tb ions, photoluminescence should increase. However, the emission intensity tends to decrease after 5 mol % of Tb ions because of non-radiative interaction between ions as the resonant energy transfer becomes stronger. As the concentration is increased, the terbium ions are packed closer and closer together, which favours the transfer of energy from one terbium ion to the next by a resonance process; the energy eventually reaches a sink from which it is dissipated by non-radiative processes rather than by the emission of visible light.

![Emission spectra of Ca$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor (a) as-prepared at 500°C (b) calcined at 900°C](image)

**Fig. 4.9.4.** Emission spectra of Ca$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ nanophosphor (a) as-prepared at 500°C (b) calcined at 900°C

The emission color was analyzed and confirmed with the help of *Commission Internationale de l'Eclairage* (CIE) chromaticity co-ordinates diagram. The color co-ordinates for Ca$_3$Y(PO$_4$)$_3$:Tb$^{3+}$ (x=5 mol %) nanocrystals are shown in Fig. 4.9.5. It
is clear from the figure that color co-ordinates of the as-synthesized sample fall in the bluish green region (x=0.2423, y=0.2966) which shifted towards green region after heat treatment at 900°C (x=0.2196, y=0.3956). The nanocrystals having green emission and good PL intensity (68.1 cd/m²) might be promisingly applicable for display applications.

CONCLUSION

The terbium doped nanophosphors described in this chapter were synthesized by combustion and sol-gel method. Briefly, combustion synthesis consists of firing of an aqueous solution that contains metal nitrates and a proper organic fuel between temperatures range of 400–600°C. The reaction is highly exothermic, very fast and self-sustaining. This results in a dry, crystalline, fine oxide powder. A key feature of this technique is that the heat required to drive the synthesis is mainly provided by the exothermic reaction of the reagents. Thus it reduces the requirement of external heating source.

The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants, such as rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. This route is faster than solid state reaction and leads a mixture at molecular level of the constituent and a better chemistry homogenized.
The nanophosphors thus obtained were characterized by X-ray diffraction (XRD) techniques, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and their photoluminescence properties were studied by spectrophotometer or spectroradiometer.

1. **BaGd$_2$O$_4$:Tb$^{3+}$** was prepared by combustion method using urea as an organic fuel. The optimum concentration of Tb$^{3+}$ was found to be 4 mol % of Gd$^{3+}$ in the host lattices. The samples were prepared at 500°C and again fired at varying temperatures between 700°C to 900°C to improve luminescence intensity. It was noticed that the phosphor sample heated at 900°C, had better luminescence intensity. The XRD patterns of samples prepared at 500°C show many additional peaks corresponding to those of pure Ba(NO$_3$)$_2$ in cubic phase but the intensities of XRD peaks increase with increase of calcinations temperatures, which indicate better crystallinity. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 542 nm. The particle size of the nanophosphor was found to have an average range of about 25-80 nm.

2. **ZrO$_2$:Tb$^{3+}$** was prepared by combustion technique using urea as an organic fuel. The nanocrystals were synthesized by heating rapidly an aqueous concentrated paste containing a calculated amount of metal nitrates and urea in a preheated furnace maintained at 500°C. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. The solid obtained was again fired at 700°C to 1000°C for 3 hrs to increase the brightness and crystallinity. The XRD spectra of samples heated to 500°C and 700°C shows the presence of only cubic –tetragonal phases but at 1000°C had a polycrystalline structure composed of monoclinic, cubic-tetragonal phases. These images exhibited homogeneous aggregates of varying shapes and sizes, which are composed of a large number of small cuboids and broken cuboids. The particle size of the nanocrystals at higher temperatures has been observed in the range of 20-30 nm for the cubic and monoclinic crystallites of ZrO$_2$:Tb$^{3+}$. The photoluminescence was maximum for the samples prepared with 5 mol % of Tb$^{3+}$ ions heated at 1000°C. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 542 nm.

3. **BaZrO$_3$:Tb$^{3+}$** has been synthesized by combustion method using urea as an organic fuel. The nanophosphors were prepared at 500°C and again fired at varying temperatures between 700°C to 1000°C to improve luminescence intensity. XRD pattern showed that intensities and positions of diffraction peaks of BaZrO$_3$:Tb$^{3+}$ samples heated to 700°C and 1000°C corresponds to that of BaZrO$_3$ cubic perovskite
indicating that almost all of the additive Tb$^{3+}$ ions were successfully incorporated into the ABO$_3$ perovskite structure. The SEM images exhibited homogeneous aggregates of varying shapes and sizes, which are composed of a large number of small cuboids and broken cuboids. The average particle size of the nanocrystals at higher temperature has been observed in the range of 20-25 nm. The photoluminescence was maximum for the samples prepared with 5 mol % of Tb$^{3+}$ ions heated at 1000ºC. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 542 nm.

4. SrZnO$_2$:Tb$^{3+}$ was prepared by sol-gel method using citric acid as a chelating agent. The optimum concentration of Tb$^{3+}$ was found to be 0.2 mol % of Sr$^{2+}$ in the host lattices. The XRD patterns of the nanocrystals showed broad peaks indicating either particles of very small size or semi crystalline nature. The SEM micrographs showed that all the samples have similar morphology. As we increase the temperature gradually from 700ºC to 1100ºC, the particles size increases from 20 nm to 50 nm but the crystallinity of the nanoparticles was increased. The predominant green colour from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 545 nm.

5. YAlO$_3$:Tb$^{3+}$ was synthesized by sol-gel process using tartaric acid as a chelating agent. It is observed that the particles size of the as-synthesized nanophosphor was very small and particles tend to agglomerate. With an increase of temperature, particle size increased and agglomeration decreased. In fact agglomeration of the as-synthesized powder after heat treatment at 1100ºC was almost eliminated, producing well formed particles. The particle size of the nanocrystals has been observed in the range of 20-80 nm, which is in full agreement with the data from XRD patterns. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at 545 nm.

6. CaAl$_{1.8}$Y$_{0.2}$O$_4$:Tb$^{3+}$ was synthesized by sol-gel method using citric acid as a chelating agent. The as-synthesized nanophosphor by sol-gel method consists of CaO and some other phases in addition to CaAl$_{1.8}$Y$_{0.2}$O$_4$. It can also be seen that the the peak intensity increases with an increase in sintering temperature, which indicate better crystallinity. The effect of Tb$^{3+}$ ions concentration on CaAl$_{1.8}$Y$_{0.2}$O$_4$ lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. The diffraction lines are not well aligned with those in the XRD patterns of the nanocrystals. It may be due to the incorporation of yttrium in the CaAl$_2$O$_4$ phase. All the diffraction peaks of the sample after treated at 1000ºC for 3 hrs can be indexed well to the perfect single-phase CaAl$_{1.8}$Y$_{0.2}$O$_4$ material. The main emission peak from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ was located at
543 nm. The particle size of the nanophosphor was found to have an average range of about 20-35 nm.

7. SrY2O4: Tb3+ has been prepared by sol-gel process using tartaric acid as a chelating agent. The samples were calcined at different temperatures at 700°C, 900°C and 1100°C to increase the brightness. The line width slightly decreases and peak intensity increases with an increase of calcination temperature, indicating grain growth of SrY2O4:Tb3+ nanocrystals with increase in temperature. The effect of Tb3+ ions concentration on SrY2O4 lattice seems to be negligible as XRD patterns remain the same at different doping concentrations for each temperature. The optimum concentration of Tb3+ was found to be 2 mol % of Y3+ in the host lattices. The nanocrystals prepared under an UV source revealed green luminescence that was attributed to transition \( ^5D_4 \rightarrow ^7F_5 \) of Tb3+ ions located at 543 nm. The particle size of the nanophosphor was found to have an average range of about 20-55 nm.

8. Sr3Y(PO4)3: Tb3+ was synthesized by combustion technique employing urea as an organic fuel. The samples were prepared at 500°C and again fired at 900°C for 3 hrs to increase luminescence intensity. It was noticed that the phosphor heated at this temperature had better luminescence intensity. This is mainly due to improvement in doping and crystallinity. The optimum concentration of Tb3+ was found to be 5 mol % of Y3+ in the host lattices. The XRD patterns showed that no any peak corresponding to terbium has been observed, demonstrating that Tb3+ ions are dispersed in Sr3Y(PO4)3 matrix. The main emission peak from magnetic dipole transition \( ^5D_4 \rightarrow ^7F_5 \) of Tb3+ was located at 547 nm. The particle size of the nanophosphor was found to have an average range of about 20-50 nm.

9. Ca3Y(PO4)3: Tb3+ was synthesized by combustion method employing urea as an organic fuel. Photoluminescence spectra of the phosphors prepared at 500°C were quite weak, thus the solid obtained was again fired at 700°C to 900°C for 3 hrs to increase the brightness. The optimum concentration of Tb3+ was found to be 5 mol % of Y3+ in the host lattices. The XRD data indicated that Ca3Y(PO4)3 was single cubic phases and belong to the family of the eulytite type compound. In general, the intensities of XRD peaks increase with increase of calcinations temperatures, which indicate better crystallinity. The effect of Tb3+ ion concentration on Ca3Y(PO4)3 lattice seems to be negligible as XRD patterns remain the same at different doping concentrations. The main emission peak from magnetic dipole transition \( ^5D_4 \rightarrow ^7F_5 \) of Tb3+ was located at 547 nm. The particle size of the nanophosphor was found to have an average range of about 30-55 nm.
REFERENCES


75. A. Chagraoui, DES de 3e’ me Cycle de Spe’ cialité’, Faculty of Sciences, Rabat, Morocco, (1987).