CHAPTER - IV

Synthesis, Characterization and Optical Properties of Terbium doped Phosphors
INTRODUCTION

In fluorescent lamps and emission display, the visible light is generated by the kind of phosphors, which consists of pure host material intentionally doped with a small amount of impurities. Excitation in fluorescent lamps or plasma panels takes place by the UV photons generated as a result of discharge in these. The excitation in CRTs is due to the electrons with high kinetic energy whereas in devices based on electroluminescence the excitation is by electrons with low kinetic energy (<10eV). Research has enhanced the performance of luminescent materials to achieve physical limits [1-4]. The largest area of advancement in phosphor materials has been the use of rare-earth ions as activators. Green phosphors such as three-band fluorescent lamps (e.g., (Ce,Gd)MgB5O15:Tb³⁺) [5], projection television tubes (e.g., Y₃Al₅O₁₂:Tb³⁺) [6] and X-ray intensifying screens (e.g., Gd₂O₂S:Tb³⁺) [7] are widely used. Recently, research is being done to develop terbium doped new green phosphors as they find various applications. In case of Tb³⁺ ion, there are eight 4f-electrons (represented as 4f⁸ which is a half-filled 4f⁷ shell plus one). The 4f shell readily releases an electron and the intra-ionic transition 4f⁸→4f⁷5d 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. the crystal field) creating efficient absorption bands. The 4f-5d transitions are allowed for both absorption and emission processes; hence, we observe intense absorption bands in the UV region. As is well known, the efficient blue-green emissions of Tb³⁺ originate from the 5D₃→7F_j and 5D₄→7F_j transitions.

1. CaIn₂O₄:Tb (urea assisted) phosphor

The largest area of advancement in phosphor materials has been the use of rare-earth ions as activators. Recently, luminescent properties of rare-earth ions doped oxides of 13th group elements, such as borates [8], aluminates [9] and gallates [10] have been widely studied. From the fact that indium belongs to the same group as boron, aluminium and gallium in the periodic table, Kao and Chen [11-12] successfully prepared CaIn₂O₄:xTb phosphor by solid-state reactions. In the past also, the luminescence properties of Tb³⁺ in different host matrix have been extensively investigated [13-15]. 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 $^5D_4$ state at 545nm. For the phosphor applications it is desirable to have a fine particle size for high resolution flat panel displays and chemical purity for optimum chromaticity and brightness [16]. Several techniques have been used to prepare multi-component oxide phosphors such as solid-state reaction, sol-gel, hydrothermal synthesis, hydroxide precipitation and combustion method. Wet chemical methods are known to be better than solid-state reaction methods in intimate mixing of reactants, high product purity, fine particle size and low processing temperature [17]. Combustion method synthesis is a novel phosphor processing technique that has shown to produce fine particle size. This technique can produce a homogenous product in a short amount of time without the use of expensive high-temperature furnaces. The synthesized product is high in purity, usually single phase and chemically homogenous. To the best of author’s knowledge, this is the first report for the preparation of CaIn$_2$O$_4$:xTb phosphor by combustion method using urea as fuel.

A) SYNTHESIS

High purity calcium nitrate tetrahydrate [Ca(NO$_3$)$_2$·4H$_2$O], indium (III) nitrate pentahydrate [In(NO$_3$)$_3$·5H$_2$O], terbium (III) nitrate pentahydrate [Tb(NO$_3$)$_3$·5H$_2$O] and urea [H$_2$NCONH$_2$] from Aldrich chemicals were taken as starting materials. Tb$^{3+}$-doped calcium indate, with general formula (Ca$_{1-x}$Tb$_x$)In$_2$O$_4$ where $x = 0.12$, 0.5, 1, 1.5 and 2% was prepared by rapidly heating an aqueous concentrated solution containing calculated amounts of metal nitrates and urea in a pre-heated 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 [18]. 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 phosphor at low ignition temperature. The whole process was over in less than 3 min. The phosphor with composition CaIn$_2$O$_4$:xTb ($x=0.12\%$) exhibiting maximum brightness was further sintered at different temperatures ranging from 700°C to 1100°C. CaIn$_2$O$_4$:xTb ($x=0.12\%$) phosphor was also synthesized by solid-state reaction at 1400°C for 12 hrs.
for comparison studies. The theoretical equation for the formation of this phosphor may be written as:

$$\text{l-xCa(NO}_3\text{)}_2+\text{xTb(NO}_3\text{)}_3+2\text{ln(NO}_3\text{)}_3+7\text{CH}_4\text{N}_2\text{O} \rightarrow (\text{Ca}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4+\text{gaseous product}$$

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 phosphors. Fig. 4.1.1 shows the XRD patterns of as-synthesized CaIn$_2$O$_4$:xTb phosphor and of the samples sintered at various temperatures for 3 hrs. CaIn$_2$O$_4$ phase formation is initiated in the as-synthesized powder by combustion, which increases with increasing sintering temperature. An unidentified peak appearing near 30° in the as-synthesized phosphor and sintered phosphor at 700°C (Fig. 4.1.1a, b), also disappear on further sintering. As a result, a typical CaIn$_2$O$_4$ pattern [19] was observed in the XRD profiles. No peak corresponding to any of the source materials or allotropic forms was found after sintering at 900°C and 1100°C (Fig. 4.1.1c, d) suggesting that a pure compound with the same structure as CaIn$_2$O$_4$ exists. It indicates that single phase CaIn$_2$O$_4$ could be obtained by sintering it at 900°C for 3 hrs. The XRD pattern of the CaIn$_2$O$_4$:xTb showed the presence of broad peaks. The broad peaks either indicate particles of very small crystalline size or particles are semi-crystalline in nature. Presence of Ca, In, O and Tb in the as-prepared phosphors was confirmed by the EDAX technique as shown in Fig. 4.1.2.

![Fig. 4.1.1 Powder X-ray diffraction patterns of CaIn$_2$O$_4$:xTb$^{3+}$ with x = 0.12% (a) as-synthesized by combustion (b) sintered at 700°C (c) 900°C (d) 1100°C.](image-url)
ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). SEM images of samples sintered at different temperatures are shown in Fig. 4.1.3. The particles have more or less spherical shape. However, the particle size clearly depends on the sintering temperature. SEM observation of the as-synthesized sample by combustion process indicates that the particles tend to agglomerate, as shown in Fig. 4.1.3a. The size of the particles is in the range of 100nm. The average grain size increases with the increase in sintering temperature. After sintering at 1100°C, the average grain size is about 800nm as can be estimated from Fig. 4.1.3d. SEM image of the phosphor after sintering at 1100°C shows numerous bridges between individual sphere-like particles. Clearly, the particle size increases with the elevation of sintering temperature from 700°C to 1100°C.
C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphor were recorded with Minolta Spectroradiometer CS-1000. The photoluminescent emission spectra of CaIn$_2$O$_4$:xTb$^{3+}$ (x=0.12%) as-synthesized phosphor and sintered at various temperatures are shown in Fig. 4.1.4. The main emission peak in all the materials present at 545nm which is characteristic of Tb$^{3+}$ ($^5D_4\rightarrow^7F_5$). The electronic configuration of Tb$^{3+}$ (4f$^8$) is known to produce a number of sharp emission peaks from the parity forbidden, weak f-f transitions. The main four emission transitions in Tb$^{3+}$ produce emission at 490nm from $^5D_4\rightarrow^7F_6$, at 545nm from $^5D_4\rightarrow^7F_5$, at 585nm from $^5D_4\rightarrow^7F_4$ and at 620nm from $^5D_4\rightarrow^7F_3$. The CaIn$_2$O$_4$:xTb$^{3+}$ system shows observable changes in its PL emission spectra at different sintering temperatures. The as-synthesized samples at 500°C shows weak green light. PL intensities increased remarkably after sintering at 1100°C. Fig. 4.1.4 shows that the green emission transition at 545nm is enhanced distinctly by increasing sintering temperature. The weak and broad bands correspond to $^5D_4\rightarrow^7F_3$ and $^5D_4\rightarrow^7F_6$ transitions centered at 620nm and 490nm respectively are observed only after sintering at 1100°C as indicated by Fig. 4.1.4. All the above mentioned transitions are more intense in the phosphor sintered at 1100°C indicating proper doping of terbium ions into the host lattice. The green emission transition at
545nm ($^5D_4 \rightarrow ^7F_3$) is more intense in all the samples than other transitions, which can be explained by the large values of the reduced matrix elements at $J = 5$ and the Judd-Ofelt theory [20-21].

The effect of various sintering temperatures on PL intensities was also examined. The PL intensities are displayed as a function of temperature in Fig. 4.1.5. From these results, it was observed that the PL intensity of the as-synthesized phosphor increased rapidly on sintering up to 1100°C and beyond this there was no observable change in the PL intensity. This may be due the improvement in doping, crystallinity, the decrease of the carbon impurities and the increase of particle size, as small particles do not have high luminous efficiency due to grain boundary effects [22]. By comparison of the as-prepared phosphor and the phosphors after sintering at high temperature, it was found that the larger the particles, the higher luminescence intensity they emit. The large particles have better structural perfection and smoother surface in general, which corresponds to fewer surface defects and lower reflection when excitation light radiates on phosphors. So the large particles have relatively higher luminescent efficiency than that of small ones under the same excitation intensity. Moreover, the Tb$^{3+}$ ion (92.3 pm) has similar radius with that of the Ca$^{2+}$ ion (99 pm), the Tb$^{3+}$ ions can substitute for the Ca$^{2+}$ ions easily in the lattice of CaIn$_2$O$_4$. In order to keep the electroneutrality of the compound, two Tb$^{3+}$ ions would substitute for three Ca$^{2+}$ ions. Therefore, two positive defects of $[\text{Tb}_{Ca}]$ and one negative Ca$^{2+}$ vacancy of $[\text{V}_{Ca}]^-$ would be formed. Then, the defect produced in the material can bring on non-radiative processes. In order to create more efficient luminescent materials, it is necessary to suppress non-radiative processes in which the energy of the excited state is used to excite the vibrations of the host lattice, i.e. to heat the host lattice [23]. Also, this is an indication that certain properties of the as-synthesized powders, such as crystallite size or disorder of the local environment surrounding the activator ions influence the PL spectra and thermal effects are important to extract the maximum luminous efficiency. However, the phosphor synthesized by combustion after sintering at 1100°C for 3 hrs was found to have more PL intensity than the sample prepared by solid-state at 1400°C for 12 hrs as indicated in Fig. 4.1.5. This may be due to the chemical energy released from the exothermic
reaction between the metal nitrates and urea which can rapidly heat the system to high temperatures (>1600°C) without an external source. The combustion method being a solution-based synthesis process offers molecular level mixing of the starting materials, favors a more homogeneous substitution, resulting in high PL intensity values. The emission color was analyzed and confirmed with the help of Commission Internationale de l'Éclairage (CIE) chromaticity coordinates diagram. The color coordinates of CaIn$_2$O$_4$:xTb (x=0.12%) are shown in Fig. 4.1.6. The color coordinates of the as-synthesized sample fall in the yellowish green region of the CIE chromaticity diagram (x=0.2862, y=0.4348) and shift towards deeper green region (x=0.2568, y=0.4527) after heat-treatment at 1100°C. The photoluminescence intensity of the phosphor sintered at 1100°C was found to be 47.34 cd/m$^2$. Kao observed that CaIn$_2$O$_4$:xTb (x=0.125%) was brighter than (Y$_{2.95}$Tb$_{0.05}$)Al$_2$O$_3$ under 254nm UV excitation. The fluorescence decay lifetime of the phosphor was in the range of microseconds and it meets the application requirement for CRT color televisions [12].

![Emission spectrum of CaIn$_2$O$_4$:xTb (x = 0.12%) phosphor: (a) as-synthesized by combustion (b) sintered at 700°C (c) 900°C (d) 1100°C.](image-url)

**Fig. 4.1.4** Emission spectrum of CaIn$_2$O$_4$:xTb (x = 0.12%) phosphor: (a) as-synthesized by combustion (b) sintered at 700°C (c) 900°C (d) 1100°C.
Fig. 4.1.5 Relative PL intensities as a function of temperature

- PL intensity of CaIn$_2$O$_4$:xTb with x=0.12% phosphor prepared by solid-state reaction at 1400°C
- PL intensity of CaIn$_2$O$_4$:xTb with x=0.12% phosphor prepared by combustion method and sintered at different temperatures.

Fig. 4.1.6. Commission Internationale de l'Eclairage color co-ordinates of CaIn$_2$O$_4$:xTb phosphor with x = 0.12%
(a) as-synthesized at 500°C (b) after heat-treatment at 1100°C.
2. CaIn$_2$O$_4$:Tb (glycine assisted) phosphor

Nanophase materials are being vigorously explored as most of the physical properties are size dependent and are markedly affected as the particle sizes tend to nanometer level. Phosphors are one of the materials that show promising behaviour when synthesized in nanophase. Many phosphors have been made in nanophase by employing different techniques. Trivalent terbium ions have been widely used as activators to obtain green phosphors and showed excellent luminescent properties. Kao and Chen [11-12] successfully prepared CaIn$_2$O$_4$:xTb phosphors by solid-state reactions. In the past also, the luminescence properties of Tb$^{3+}$ in different host matrix have been extensively studied [13-15]. With Tb$^{3+}$ activation, the emission is from $^5$D$_3$ and $^5$D$_4$ states to the $^7$F states. The relative intensities within the $^5$D$_3$ and $^5$D$_4$ states are only slightly affected by the host lattice. The main green color emission is from the $^5$D$_4$ state at 545nm. For high resolution phosphor applications, it is desirable to have fine particle size. Chemical purity should also be high for optimum chromaticity and brightness [16]. With the development of scientific technologies on materials, several chemical synthesis techniques, such as sol-gel [24-25], co-precipitation [26-27] and combustion methods, have received great attention recently. Combustion method synthesis is a novel phosphor processing technique that has been shown to produce fine particle size. This technique can produce a homogenous product in a short amount of time without the use of expensive high temperature furnaces. The synthesized product is high in purity, usually single phase and chemically homogenous. One of the cheapest amino acids, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), is known to act as a complexing agent for a number of metal ions as it contains a carboxylic acid group at one end and an amino group at the other end [28]. Amino acids become zwitter ions on dissolving in water with both positive and negative charges. Such types of zwitter ionic character of the glycine molecule can effectively complex metal ions of varying ionic sizes, which helps in preventing their selective precipitation to maintain compositional homogeneity among the constituents. On the other hand, glycine can also serve as a fuel during the combustion reaction, being oxidized by nitrate ions [29]. Recent research on combustion synthesis has been conducted in order to understand the role of the fuel in controlling particle size and microstructure.
of the product’s combustion. Only a few scientists [29] have tried to investigate this
effect for different fuel-to-oxidant ratios. To the best of author’s knowledge, this is
the first report for the preparation of CaIn$_2$O$_4$:xTb nanocrystals by combustion
method using glycine as a fuel.

A) SYNTHESIS

High purity calcium nitrate tetrahydrate [Ca(NO$_3$)$_2$·4H$_2$O], indium (III) nitrate
pentahydrate [In(NO$_3$)$_3$·5H$_2$O], terbium (III) nitrate pentahydrate [Tb(NO$_3$)$_3$·5H$_2$O]
and glycine [NH$_2$CH$_2$COOH] from Aldrich chemicals were taken as starting
materials. Tb$^{3+}$-doped indate, with general formula (Ca$_{1-x}$Tb$_x$)In$_2$O$_4$ where x = 0.12,
0.5, 1 and 2% were prepared by rapidly heating an aqueous concentrated solution
containing calculated amounts of metal nitrates and glycine in a pre-heated furnace
maintained at 500°C. The amount of glycine used during combustion was calculated
using the total oxidizing and reducing valencies. 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 theoretical
equation for the formation of these nanocrystals by combustion from metal nitrates
and glycine at about 500°C may be shown as:

\[
1-x\text{Ca(NO}_3\text{)}_2+x\text{Tb(NO}_3\text{)}_3+2\text{In(NO}_3\text{)}_3+\text{NH}_2\text{CH}_2\text{COOH} \rightarrow (\text{Ca}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4+\text{gaseous}
\]

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 phosphors. Fig. 4.2.1 shows the x-ray
diffraction pattern of CaIn$_2$O$_4$:xTb nanocrystals. The adiabatic flame temperature of
the combustion process has an important effect on the crystallite size of the
synthesized powders. Flame temperature can be controlled by adjusting the glycine to
nitrate ratio (G/N), and thereby control the crystallite size of the powders. The results
of combustion made CaIn$_2$O$_4$:xTb nanocrystals indicate that the lower G/N value
leads to the smaller crystallite size. Although there is broadening of the diffraction peaks as the G/N decreases, all samples are of the same structure with the JCPDS card No. 33-1336. The average size of the crystallites can be estimated from the full-width at half-maximum of the peaks using the Scherrer equation. The calculated particle size of samples a, b, c is about 40, 35 and 15nm, respectively.

![X-ray diffraction patterns of CaIn$_2$O$_4$:Tb$^{3+}$ nanocrystals](image)

**Fig. 4.2.1** The X-ray diffraction patterns of CaIn$_2$O$_4$:Tb$^{3+}$ nanocrystals

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

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). Fig. 4.2.2 shows typical SEM photographs of the as-synthesized nanocrystals with a G/N value of 0.57. The pores in the microstructure of the aggregated grains are formed due to the liberation of large amount of gases during combustion reaction. The sizes of the spherical particles range from 35nm to 55nm, similar to the sizes estimated using the XRD method.
C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphors were recorded with Minolta Spectroradiometer CS-1000. The photoluminescent emission spectrum of CaIn$_2$O$_4$:xTb with x = 0.12, 0.5 and 1% shown in Fig. 4.2.3. All Tb$^{3+}$-doped nanocrystals when exposed to 254nm UV light showed a uniform green color, indicating homogeneous doping. It is well known that the saturation of Tb-activated phosphors depends strongly on the activator concentration. At low activator concentration, the luminescence stems from the $^5$D$_3$ and $^5$D$_4$ level of Tb$^{3+}$ and at higher concentration, the $^5$D$_3$ level empties non-radiantly into the $^5$D$_4$ level through cross relaxation [30]. A blue emission at a wavelength below 485nm originating because of the transition between the $^5$D$_3$ excited state and $^7$F$_j$ ground state has been observed [11]. The strongest peak in all these nanocrystals is at about 546nm stemming from the $^5$D$_4$ $\rightarrow$ $^7$F$_5$ transition. The nanocrystals with different terbium concentrations ranging from 0.12 to 2% were prepared to examine the PL emission intensity dependence on the activator concentration. The room temperature emission spectra of all the nanocrystals were recorded under the same conditions (Fig. 4.2.3). Maximum brightness was observed in the sample with 0.12% of terbium concentration and the brightness decreased on increasing Tb$^{3+}$ concentration from 0.12% to 2%. This decrease in brightness with increasing activator concentration also observed by Kao [11] in CaIn$_2$O$_4$:xTb prepared by solid-state process. It may be due
to the well-established theory of concentration quenching [31]. However, Kao and Chen [12] have observed that CaIn₂O₄:xTb (x=0.125%) is much brighter than (Y₂₉₅Tb₀.₅)Al₅O₁₂ under 254nm UV excitation.

![Emission spectra of CaIn₂O₄:xTb nanocrystals with Tb cone.](image)

**Fig. 4.2.3 Emission spectra of CaIn₂O₄:xTb nanocrystals with Tb conc.**

(a) 1% (b) 0.5% (c) 0.12%

3. SrIn₂O₄:Tb phosphor

In recent years great efforts have been made to develop efficient phosphor systems. Among these, a number of works have been carried out on investigations of the luminescent properties for borates [8], aluminates [9] and gallates [10]. Since indium belongs to the same group as boron, aluminium and gallium in the periodic table, with the outer electron configuration being the same and presumably exhibiting similar chemical properties, it was suggested that metal indates might also act as a host lattice for luminescence. With this consideration, the research was extended to ternary Sr-In-O system. SrIn₂O₄ is a host matrix for phosphor, since the band gap of 3.6eV [32] is wide enough to incorporate visible luminescence centers such as rare-earth ions. This matrix is a CaFe₂O₄ structure with octahedral cation co-ordination [33]. The rare-earth ions prefer these octahedral sites due to their highly ionic nature [34]. A higher conductivity than that of the conventional phosphors is needed for the development of improved FED (field emission display) [35], this system has that potential. Kao and Chen [11-12] successfully prepared SrIn₂O₄:xTb phosphor by
solid-state reactions. In the past also, the luminescence properties of Tb$^{3+}$ in different host matrix have been extensively studied [13-15]. With Tb$^{3+}$ activation, the emission is from $^5D_3$ and $^5D_4$ states to the $^7F$ states. The relative intensities within the $^5D_3$ and $^5D_4$ states are only slightly affected by the host lattice. The main green color emission is from the $^5D_4$ state at 545nm. For the phosphor application it is desirable to have a fine particle size for high resolution flat panel displays and chemical purity for optimum chromaticity and brightness [16]. Several techniques have been used to prepare multi-component oxide phosphors such as solid-state reaction, sol-gel, hydrothermal synthesis, hydroxide precipitation and combustion method. Wet chemical methods are known to be better than solid-state reaction methods in intimate mixing of reactants, high product purity, fine particle size and low processing temperature [17]. Combustion method synthesis is a novel phosphor processing technique that has been shown to produce fine particle size. This technique can produce a homogenous product in a short amount of time without the use of expensive high-temperature furnaces. The synthesized product is high in purity, usually single phase and chemically homogenous. To the best of author’s knowledge, this is the first report for the preparation of SrIn$_2$O$_4$:xTb phosphor by combustion method using urea as a fuel.

A) SYNTHESIS

High purity strontium nitrate [Sr(NO$_3$)$_2$], indium (III) nitrate pentahydrate [In(NO$_3$)$_3$·5H$_2$O], terbium (III) nitrate pentahydrate [Tb(NO$_3$)$_3$·5H$_2$O] and urea [H$_2$NCONH$_2$] from Aldrich chemicals were taken as starting materials. Tb$^{3+}$-doped strontium indate, with general formula (Sr$_{1-x}$Tb$_x$)In$_2$O$_4$ where x = 0.12, 0.5, 1, 1.5 and 2% were prepared by rapidly heating an aqueous concentrated solution containing calculated amounts of metal nitrates and urea in a pre-heated 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 [18]. 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 phosphor at low ignition.
temperature. The theoretical equation for the formation of this phosphor may be written as:

\[ 1-x\text{Sr(NO}_3\text{)}_2+x\text{Tb(NO}_3\text{)}_3+2\text{In(NO}_3\text{)}_3+7\text{CH}_4\text{N}_2\text{O} \rightarrow (\text{Sr}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4+\text{gaseous product} \]

\[ \text{Tb}^{3+}\text{-doping in the host matrices (indates) involves atomic level substitution of ions present in these lattices by activator ions. This type of substitution generally require high-temperature and long processing times, where as facile combustion synthesis of these phosphors require low ignition temperature and short time duration. The energy released from the reaction can produce temperatures in excess of 1500°C. The reaction is self-propagating and is able to sustain this high-temperature long enough, about 45s for the reaction to come to completion, to form the desired phosphors.} \]

**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 phosphors. X-ray diffraction pattern of this phosphor show all the prominent lines correspond to SrInxxOy [19]. XRD spectrum of SrInxxOy:xTb phases, where x=0.12% is shown in Fig. 4.3.1. No peak corresponding to any of the source material was observed, indicating that pure crystalline compound with the same structure as SrInxxOy has been synthesized by the combustion method.
ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). The SEM micrographs of the as-prepared phosphors, shown in Fig. 4.3.2 reflect the agglomerate particle nature of the phosphors. The average agglomerate particle size of the phosphors prepared by combustion lies below 2μm.

![SEM micrograph of SrIn$_2$O$_4$:Tb$^{3+}$ phosphor at 500°C](image)

Fig. 4.3.2 SEM micrograph of SrIn$_2$O$_4$:Tb$^{3+}$ phosphor at 500°C

C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphor were recorded with Minolta Spectroradiometer CS-1000. The photoluminescent emission spectrum of SrIn$_2$O$_4$:xTb with x = 0.12, 0.5 and 1% shown in Fig. 4.3.3. All Tb$^{3+}$-doped oxides when exposed to 254nm UV light showed a uniform green color, indicating homogeneous doping. It is well known that the saturation of Tb-activated phosphor depends strongly on the activator concentration. At low activator concentration the luminescence stems from both the 5D$_3$ and 5D$_4$ levels of Tb$^{3+}$ and at higher concentration the 5D$_3$ level empties non-radiantly into the 5D$_4$ level through cross relaxation [30].
Fig. 4.3.3. Emission spectrum of SrIn$_2$O$_4$:xTb phosphor with $x = 0.12$, 0.5 and 1\% respectively.

A blue emission at a wavelength below 485\,nm originating from the transition between the $^5D_3$ excited state and $^7F_j$ ground state was observed [11]. The strongest peak in all these phosphors is at about 545\,nm stemming from the $^5D_4 \rightarrow ^7F_5$ transition. The phosphors with different terbium concentrations ranging from 0.12 to 2\% were prepared to examine the PL emission intensity dependence on the activator concentration. The room temperature emission spectra of all the phosphors were recorded under the same conditions (Fig. 4.3.3). The emission color of the as-prepared phosphor was analyzed and confirmed with the help of Commission Internationale de l'Eclairage (CIE) chromaticity co-ordinates diagram. The color co-ordinates were found to fall in the yellowish green region ($x=0.2789$ and $y=0.4127$) of the CIE chromaticity diagram as shown in Fig. 4.3.4.
4. **CaAl$_2$O$_4$:Tb Phosphor**

An important class of fluorescent lamp and plasma display phosphors is based on compounds in the alkaline-earth rare-earth aluminate systems [36]. These phosphors fall in three broad classes: i) Binary alkaline-earth aluminates such as CaAl$_2$O$_4$ [37]. ii) Alkaline-earth hexaaluminates related to magnetoplumbite and beta-alumina and their superstructures [38-46]. iii) Rare-earth hexaaluminates with the magnetoplumbite structure [47-50]. A variety of activators were used of which the most important are Eu$^{2+}$, Ce$^{3+}$, Tb$^{3+}$ and to a lesser extent, Mn$^{2+}$ [51-55]. The compounds MAI$_2$O$_4$, M=Ca, Sr and Ba, are formed of a three dimensional framework of corner-sharing AlO$_4$ tetrahedra. Each oxygen is shared with two aluminum ions so that each tetrahedron has one net negative charge. Charge balance is accomplished by the large divalent cations which occupy interstitial sites within the tetrahedral framework. The tetrahedral framework is isostructural with the SiO$_2$ polymorph, tridymite, so that these compounds are stuffed tridymite structures [56]. CaAl$_2$O$_4$ has
a stuffed tridymite structure but transforms to at least three other polymorphs at higher pressure [57]. In the stuffed tridymite structure there are two sites for the large cation, each with 9-fold coordination.

Calcium aluminates are important cement materials, which have been studied by many researchers. But the use of CaAl₂O₄ as the luminescent host, until now, is rarely reported. The Tb³⁺ activated alkaline earth aluminates are an important class of phosphorescent materials for their quantum efficiency in the visible region. Conventionally, monocalcium aluminate has been prepared by long lasting sintering of the solid oxide mixture at temperatures exceeding 1400°C. It has been synthesized involving the path of high energetic attrition milling of the reactants at temperatures lower than 1300°C [58] and has also been prepared at even lower temperature by pechni process [59]. Tb-doped calcium monoaluminate has been synthesized by solid-state method using B₂O₃ as flux at 1350°C [60]. The combustion process is an efficient method for the preparation of phosphors due to proper mixing of starting materials and relatively low reaction temperature resulting in more homogeneous products than those produced via solid-state reaction. In view of this, in the present work CaAl₂O₄:Tb³⁺ phosphor has been synthesized by low temperature initiated combustion process using urea as a fuel.

A) SYNTHESIS

High purity aluminium nitrate nonahydrate [Al(NO₃)₃.9H₂O], calcium nitrate tetrahydrate [Ca(NO₃)₂.4H₂O], terbium (III) nitrate pentahydrate [Tb(NO₃)₅.5H₂O] and urea [H₂NCONH₂] from Aldrich chemicals were taken as starting materials. Tb⁺⁺⁺-doped aluminates, with general formula (Ca₁₋ₓTbx)Al₂O₄ where x = 0.12, 0.25, 0.5, 1, 1.5 and 2% were prepared by rapidly heating an aqueous concentrated solution containing calculated amounts of metal nitrates and urea in a preheated furnace maintained at 500°C. Urea was used as a fuel for combustion and its amount was calculated using total oxidizing and reducing valencies as reported by Ekambaram and Patil [18]. 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 phosphor at low
ignition temperature. The solid obtained was milled to fine powder and again fired at
900°C to 1100°C for 2-3 hrs in inert atmosphere, which prevented Tb³⁺ from being
oxidized to Tb⁴⁺. The theoretical equation for the formation of this phosphor may be
written as:

\[ l-x\text{Ca(NO}_3\text{)}_3+x\text{Tb(NO}_3\text{)}_3+2\text{Al(NO}_3\text{)}_3+ \rightarrow \text{gaseous products} \]

\[ \text{~7CH}_4\text{N}_2\text{O} \rightarrow \text{Ca}_1-x\text{Tb}_x\text{Al}_2\text{O}_4(\text{s}) \]

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 phosphors. XRD spectra of the
CaAl₂O₄:Tb³⁺ phosphor prepared at 500°C, sintered at 900°C and 1100°C are shown
in Fig. 4.4.1. XRD spectrum of the as-synthesized CaAl₂O₄:Tb³⁺ phosphors at 500°C were
amorphous in nature. It was observed that spectra of the further heated powder at
1100°C for 3 hrs showed an increase in the intensity of the peaks indicating better
crystallinity. The XRD pattern matched perfectly with that reported for CaAl₂O₄
JCPDS (70-0134). The results proved that the phosphor prepared in this work are
almost single CaAl₂O₄ phase and the little amount of Tb³⁺ ions have almost no effect
on the CaAl₂O₄ phase composition.

![Fig. 4.4.1 XRD pattern of CaAl₂O₄:Tb phosphor as-prepared at 500°C, sintered
at 900°C and 1100°C](image-url)
ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). The SEM micrograph of the as-prepared phosphor, sintered at 900°C and 1100°C are shown in Figs. 4.4.2 (a,b,c) respectively. The particle size of the powder synthesized at 500°C was very small and the particles tend to agglomerate. Agglomeration is known to decrease with the increase of heating temperature [61]. 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 1100°C was almost eliminated, producing well-formed particles having size less than 1μm.

Fig. 4.4.2 SEM micrographs of Tb$^{3+}$-doped CaAl$_2$O$_4$
(a) As-synthesized at 500°C (b) after sintering at 900°C (c) at 1100°C
C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphor were recorded with Minolta Spectroradiometer CS-1000. The observed luminescent emission of the as-prepared nanoparticles at 500°C was quite weak which was greatly enhanced by simple firing of this powder. The nanoparticles prepared by present method were again fired at varying temperatures between 700°C to 1100°C and their emission spectra were compared at each step. It was noticed that the nanoparticles made by combustion method when heated at 1100°C for 3 hrs, had better luminescence intensity. The emission spectrum of CaAl$_2$O$_4$:Tb$^{3+}$ on excitation at 254nm is shown in Fig. 4.4.3.

The electronic configuration of Tb$^{3+}$ (4f$^6$) is known to produce a number of sharp emission peaks from the parity forbidden, weak f-f transitions. The main four emission transitions in Tb$^{3+}$ produce emission at 490nm from $^5D_4 \rightarrow ^7F_6$, at 545nm from $^5D_4 \rightarrow ^7F_5$, at 585nm from $^5D_4 \rightarrow ^7F_4$ and at 620nm from $^5D_4 \rightarrow ^7F_3$. The CaAl$_2$O$_4$:xTb$^{3+}$ system shows observable changes in its PL emission spectra for various sintering temperatures.

All the above mentioned transitions are clearer in the phosphor sintered at 1100°C indicating proper doping of terbium ions into the host lattice. The green emission transition at 545nm ($^5D_4 \rightarrow ^7F_3$) is more intense in all the samples than other transitions because of the fact that it is a magnetic-dipole allowed transition with $\Delta J = \pm 1$.

The emission intensity at 545nm of Tb$^{3+}$ ions was investigated as a function of Tb$^{3+}$ ions concentration in CaAl$_2$O$_4$ phosphor shown in Fig. 4.4.4. It was found that the PL emission intensity is increased with the increase of the concentration, reaching a maximum value at 1% for Tb$^{3+}$ ions and then decreased with increasing the concentration. This is because of a well-known phenomenon of concentration quenching [31] in rare-earth doped system due to mutual Tb$^{3+}$-Tb$^{3+}$ ions interactions.
Fig. 4.4.3 Emission spectrum of CaAl₂O₄: Tb³⁺ phosphor sintered at 1100°C

Fig. 4.4.4 Relative PL intensities of CaAl₂O₄: Tb³⁺ phosphor as a function of concentration of Tb³⁺ ions
5. YPO₄: Tb Phosphor

Rare-earth activated multi-component oxide phosphors have been widely investigated for applications in display devices, lights and detectors. However, for these applications phosphor particles must have good characteristics such as high brightness, spherical shape and narrow size distribution. For preparing small sized LnPO₄: Ce, Tb (Ln= La, Y, Gd) phosphor particles modified solid-state reactions and aqueous solution techniques have been thoroughly investigated. Verstegen et al. [62] introduced the high quality tricolor luminescent lamp based on rare-earth ions. Erdei et al. [63-64] prepared Ce³⁺, Tb³⁺; LaPO₄ green phosphors by a newly developed hydrolyzed colloidal reaction (HCR) technique at room temperature (<100°C) and in atmospheric pressure by utilizing a subsequent calcining and reductive treatments, respectively.

The phosphors have been used for the green component of three band emission type of luminescent lamps and CRTs because of their high quantum efficiency and stability at high temperature. The green emitting components of these types of lamps are based on Tb³⁺ ions, because it has a sharp emission around 545nm with high intensity, which is close to the theoretical optimum wavelength for the green component of a tricolor lamp [65-66]. Over the past few years Rambabu et al have been actively involved in the preparation and characterization of a wide variety of rare-earth doped powder phosphors for their use in color TV monitors, fluorescent lamps and X-ray intensifying screens [67-69]. Keeping in view the commercial applications of green and blue emitting phosphors, researchers have prepared and characterized the Tb³⁺, Ce³⁺ doped LnPO₄ (Ln = Y, Gd and La) powder phosphors [70-74]. LnPO₄:Tb³⁺ (Ln = La, Y and Gd) phosphors has also been synthesized by precipitation technique utilizing subsequent calcining in inert atmosphere [75]. To the best of author’s knowledge, this is the first report for the preparation of terbium doped yttrium orthophosphate phosphor by combustion using metal nitrates as precursors and urea as a fuel, with an optimum green emission. This technique received great attention recently [76-77].
A) SYNTHESIS

High purity yttrium nitrate hexahydrate \([\text{Y(NO}_3\text{)}_3.6\text{H}_2\text{O}]\), terbium (III) nitrate pentahydrate \([\text{Tb(NO}_3\text{)}_3.5\text{H}_2\text{O}]\), ammonium hydrogen phosphate \([\text{(NH}_4\text{)}_2\text{HPO}_4]\) and urea \([\text{H}_2\text{NCONH}_2]\) from Aldrich chemicals were used as starting materials. \(\text{Tb}^{3+}\)-doped orthophosphates with general formula \((\text{Y}_{1-x}\text{Tb}_x)\text{P}_4\) where \(x=1-5\text{mol}\%\) were prepared by rapidly heating an aqueous concentrated solution containing calculated amounts of metal nitrates, ammonium hydrogen phosphate 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 [18]. 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 phosphors at low ignition temperature. The theoretical equation for the formation of this phosphor may be written as:

\[
1-x\text{Y(NO}_3\text{)}_3+x\text{Tb(NO}_3\text{)}_3+\text{NH}_4\text{HPO}_4+2\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Y}_{1-x}\text{Tb}_x\text{P}_4 (s)+\text{gaseous products}
\]

\(\text{Tb}^{3+}\) doping in the host matrices (phosphates) involves atomic level substitution of ions present in these lattices by activator ions. This type of substitution generally require high temperature and long processing times, whereas facile combustion synthesis of these phosphors require low ignition temperature and short time duration. The energy released from the reaction can produced temperature in excess of 1500°C. The reaction is self-propagating and is able to sustain this high temperature long enough, about 45s for the reaction to come to form the desired phosphors.

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 phosphors. XRD spectra (Fig. 4.5.1) of the phosphor \(\text{YPO}_4:\text{Tb}^{3+}\) shows that the as-prepared powder at 500°C was amorphous in nature. It was observed that spectra of the further heated powder at 1000°C for 3 hrs...
showed an increase in the intensity of the peaks and fully crystallized particles. The phosphor particles synthesized by combustion had high crystallinity at low post treatment temperature even without any flux because of well mixing of each component inside the particles obtained by combustion method.

![X-ray diffraction of YPO₄:Tb³⁺ phosphor](image)

**Fig. 4.5.1 X-ray diffraction of YPO₄:Tb³⁺ phosphor**

ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). The SEM micrograph of the as-synthesized phosphors at 500°C by combustion is shown in Fig. 4.5.2. This micrograph reflects the agglomerate particle nature of the phosphors with unusual morphology i.e. forming a porous and foamy structure due to liberation of by-product gases during combustion. Further heating of the as-prepared phosphor at 1000°C for 3 hrs revealed that phosphor after thermal treatment possesses almost regular shape particles (Fig.4.5.3) with uniform size distribution. The crystallite size cannot be measured exactly from the SEM micrograph shown in Fig. 4.5.3. It is evident, however, that the crystallites have size in the range of 25nm to 45 nm. The crystallite
size has been observed to increase with increasing sintering temperature ranging from 700°C to 1000°C.

Fig. 4.5.2 SEM micrograph of as-prepared YPO₄: Tb³⁺ phosphor at 500°C

Fig. 4.5.3 SEM micrograph of YPCUrTb³⁺ after heat-treatment at 1000°C

C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphor were recorded with Minolta Spectroradiometer CS-1000. The observed luminescent emission of the as-prepared phosphor at 500°C was quite weak which was greatly enhanced by simple heating of
these powders at 1000°C for 3 hrs. The phosphors prepared by present method were again heated at varying temperatures between 700°C to 1000°C and their emission spectra were compared at each step. It was noticed that phosphors sample made by combustion method when heated at 1000°C, had better luminescence intensity. The emission spectra of YPO₄: Tb³⁺ phosphor is, shown in Fig. 4.5.4. All the recorded emission spectra of this phosphor shows, the following emission transitions [63,78].

$^{5}D_{4} \rightarrow ^{7}F_{6}, ^{7}F_{5}, ^{7}F_{4}, ^{7}F_{3}$

The main emission peak in this phosphor was observed at 543-545nm on excitation at 370nm which is due to the $^{5}D_{4} \rightarrow ^{7}F_{5}$ transition. This peak is responsible for the green color and confirms the incorporation of Tb³⁺ in the phosphate host. From the spectral features, it has been noticed that the intensity of the emission peaks increases with the increase in terbium concentration up to 5mol% and then decreases with increasing the Tb³⁺ concentration. This decrease in brightness with increasing activator concentration may be due to the well-established theory of concentration quenching.

Fig. 4.5.4 Emission spectrum of YPO₄: Tb³⁺ phosphor
6. SrZnO$_2$:Tb Phosphor

Scientists now project revolutionary advances in material sciences, optoelectronics, biology and medicine arising from the practice of nanotechnology. In fact, in the past few years, the interest of the scientific community was devoted to the progress achieved in the synthesis, structural characterization and physical properties of nanostructures. Due to their peculiar characteristics and size effects, nanocrystals often show some novel physical properties that are different from those of the bulk and that are of great interest both for fundamental studies and for potential technological applications [79-83]. Researchers have undertaken investigations of the influence of particle size on the optical and electronic properties of nanocrystal materials of rare-earth oxides [84-85]. Tb$^{3+}$ ions have been expected to be a promising species for providing optical devices in blue and green color regions and many investigations have been conducted in various compounds [86-87]. In the past, the luminescence properties of Tb$^{3+}$ in different host matrix were also extensively studied [13-14]. With Tb$^{3+}$ activation, the emission is from $^5$D$_3$ and $^5$D$_4$ states to $^7$F states. The relative intensities within the $^5$D$_3$ and $^5$D$_4$ states are only slightly affected by the host lattice. The main green emission is from the $^5$D$_4$ state at 545nm. Several techniques have been used to prepare multi-component nanosized oxide particles such as sol-gel [88], hydrothermal synthesis [89], high-energy milling [90] and combustion method [91]. Combustion synthesis is a novel phosphor processing technique that has been shown to produce fine particle size. This technique can produce a homogenous product in a short amount of time without the use of expensive high temperature furnaces. The as-synthesized product is high in purity, usually single phase and chemically homogenous. Recently, a new phosphor SrZnO$_2$:Tb$^{3+}$ has been synthesized by conventional solid-state reaction [92] and a low level of Tb$^{3+}$ was found to be an efficient dopant for the desirable luminescent properties of the material. To the best of author’s knowledge, this is the first report for the preparation of SrZnO$_2$:Tb$^{3+}$ nanocrystals by using combustion with metal nitrates as precursors and urea as a fuel.

A) SYNTHESIS

High purity zinc nitrate hydrate [Zn(NO$_3$)$_2$.xH$_2$O], strontium nitrate [Sr(NO$_3$)$_2$], terbium (III) nitrate pentahydrate [Tb(NO$_3$)$_3$.5H$_2$O] and urea
[H$_2$NCONH$_2$] from Aldrich chemicals were taken as starting materials. Tb$^{3+}$-doped nanocrystals with general formula (Sr$_{1-x}$Tb$_x$)ZnO$_2$ where x = 0.12, 0.25, 0.30, 0.50, 1.0 and 2.0 mol% were prepared by rapidly heating an aqueous concentrated solution containing calculated amounts of metal nitrates and urea in a pre-heated furnace maintained at 500°C. Urea was used as a fuel for combustion and its amount was calculated using total oxidizing and reducing valencies as reported by Ekambaram and Patil [18]. The aqueous solution undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. In case of combustion synthesis, instantaneous and in-situ very high temperatures, combined with release of large volumes of volatiles from the liquid mixture are likely to result in production of nanoparticles in a fluffy form. The as-synthesized nanocrystals were sintered at different temperatures from 700°C to 1100°C in order to know the effect of sintering on the particles’ sizes/shapes and luminescence properties. The theoretical equation for the formation of SrZnO$_2$:Tb$^{3+}$ nanocrystals may be written as:

$$(1-x)\text{Sr}(\text{NO}_3)_2 + x\text{Tb}(\text{NO}_3)_3 + \text{Zn}(\text{NO}_3)_2 + 3.5\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Sr}_{1-x}\text{Tb}_x\text{ZnO}_2(s) + \text{gaseous products}$$

Tb$^{3+}$-doping in the host matrices generally require high temperatures and long processing times, where as facile combustion synthesis of these nanoparticles require low ignition temperature and short time duration. The energy released from the reaction can produce temperatures in excess of 1500°C. The reaction is self-propagating and is able to sustain this high temperature long enough, about 45s for the reaction to come to completion to form the desired products.

B) CHARACTERIZATION

i) X-ray diffraction (XRD)

X-ray diffraction (XRD) spectra were recorded using D/Max 2000–Ultimaplus to check the crystal structures of the phosphors. Fig. 4.6.1 shows the XRD patterns of as-synthesized SrZnO$_2$:Tb$^{3+}$ nanocrystals and of the samples heat-treated at various temperatures for 2 hrs. The XRD pattern of the SrZnO$_2$:Tb$^{3+}$ showed broad peaks indicating either particles of very small crystalline size or particles of a semi-crystalline nature [93]. The nanoparticles synthesized by combustion at 500°C and the sample heat-treated at 700°C consist of some ZnO and other phases in addition to
SrZnO$_2$. As can be seen in Fig. 4.6.1, almost pure phase diffraction peaks of SrZnO$_2$ are predominant in the XRD patterns of the sample heat-treated at 900°C. All the peaks of the sample heat-treated at 1100°C for 2 hrs can be indexed well to the perfect single-phase SrZnO$_2$ material which is in good agreement with the reference pattern JCPDS database (No.41-0551). There is no diffraction peak corresponding to any starting material or allotropic form. It can also be seen from Fig. 4.6.1 that the peak position does not change with the change in sintering temperature. The sizes of the crystallites of the samples heat-treated at 700°C, 900°C, and 1100°C having the SrZnO$_2$ phase, can be estimated with the help of the Scherrer equation: 

$$D = \frac{0.941\lambda}{\beta\cos\theta}$$

where $D$ is the average crystallite size, $\lambda$ is the X-ray wavelength (0.15405nm) and $\theta$ and $\beta$ are the diffraction angle and the full-width at half-maximum (FWHM, in radian) of an observed peak (113), respectively [94]. The calculated average crystallite size ($D$) of SrZnO$_2$:Tb$^{3+}$ nanophosphors as-synthesized at 500°C and sintered at 700°C, 900°C and 1100°C are found to be 18, 27, 36 and 43nm respectively.

**Fig. 4.6.1** X-ray diffraction patterns of SrZnO$_2$:Tb$^{3+}$ as-synthesized by combustion at 500°C and after heat-treatment at 700°C, 900°C and 1100°C.
ii) Scanning electron micrographs (SEM)

The surface morphological feature of the powder phosphor was studied by Philips XL30 scanning electron microscope (SEM). A SEM image of the as-synthesized particles at 500°C by combustion is shown in Fig. 4.6.2. The as-synthesized nanophosphors have a very small crystallite size and a cuboid-like morphology. The narrow size distribution of these nanocrystals is very uniform. However, with an increase of sintering temperature, specific sintering between grains leading to heavy agglomeration can be observed. The crystallite size cannot be measured exactly from the SEM micrographs shown in Fig. 4.6.2. It is evident, however, that the crystallites have sizes range from ~20nm to ~45nm size. The crystallite size has been observed to increase with increasing sintering temperature from 700°C to 1100°C.

iii) Transmission electron micrographs (TEM)

The TEM image of the nanophosphor was studied using Jeol JEM-2100F model. A TEM image of the as-synthesized SrZnO$_2$:Tb$^{3+}$ nanophosphor shown in Fig. 4.6.3, reveals that the SrZnO$_2$:Tb$^{3+}$ nanocrystals exhibit narrow size distribution with...
a slight agglomeration and cuboid-like shape with crystallite sizes in the range of 16nm to 27nm, which is in good agreement with the data from XRD patterns.

Fig. 4.6.3 TEM of nanometer-sized Tb<sup>3+</sup> doped SrZnO<sub>2</sub>

C) LUMINESCENCE STUDIES

Photoluminescence spectra of the phosphor were recorded with Minolta Spectroradiometer CS-1000. The emission spectra of SrZnO<sub>2</sub>:Tb<sup>3+</sup> nanophosphor on excitation at λ<sub>exc</sub> = 254nm show several emission lines distributed in two groups as shown in Fig. 4.6.4. In case of Tb<sup>3+</sup> ion, there are eight 4f-electrons (represented as 4f<sup>8</sup> which is a half-filled 4f<sup>7</sup> shell plus one). The 4f shell readily releases an electron and the intra-ionic transition 4f<sup>8</sup>-4f<sup>2</sup>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. the crystal field) creating efficient absorption bands [31]. The 4f-5d transitions are allowed for both absorption and emission processes; hence, we observe intense absorption bands in the UV region for all oxide hosts. For Tb<sup>3+</sup> in SrZnO<sub>2</sub>, the excitation into 4f-5d absorption bands is followed by green ⁵D₄ → ⁷F₅ emission. The excited electrons of the 4f<sup>7</sup>-5d state decay stepwise to ⁵D₃ or ⁵D₄ state, thereby giving lattice phonons. The green emission for wavelength above 490nm...
corresponds to the transition $^5D_4 \rightarrow ^7F_3$ and the blue emission for wavelength below 490nm corresponds to the transition $^5D_3 \rightarrow ^7F_4$. The intensity of the blue emission peaks (405 and 435nm) is much weaker than that of the green emission peaks (490, 545 and 585nm) as a consequence of the cross relaxation from the $^5D_3$ to the $^5D_4$ energy levels. The enhancement of the cross relaxation is due to the high ion concentration, leading to a strong emission from $^5D_4 \rightarrow ^7F_7$ transitions. In fact, the spectral energy distribution of terbium emission strongly depends on the terbium concentration and $^5D_3$ emission of Tb$^{3+}$ decreases with increasing Tb$^{3+}$ concentration [95]. The four main emission transitions in SrZnO$_2$:Tb$^{3+}$ nanocrystals produce emission at 405nm from $^5D_3 \rightarrow ^7F_5$, at 435nm from $^5D_3 \rightarrow ^7F_4$, at 545nm from $^5D_4 \rightarrow ^7F_5$ and at 585nm from $^5D_4 \rightarrow ^7F_4$. The predominant green color from magnetic-dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ located at 545nm. To study the influence of the activator concentration on the emission intensity of nanocrystals, different samples with terbium amount varying from 0.12 to 2 mol% were synthesized. Fig. 4.6.4 also shows a comparison of relative brightness as a function of Tb$^{3+}$ ion concentration. Maximum brightness was observed in the sample with a terbium concentration of 0.25mol% and the brightness decreased with further increasing in Tb$^{3+}$ concentration as shown for 0.5% and 1mol%. This decrease in brightness with increasing activator concentration may be due to the well-established theory of concentration quenching [31]. The SrZnO$_2$:Tb$^{3+}$ phosphor shows observable changes in its PL emission spectra for various sintering temperatures. The green emission transition peak at 545nm ($^5D_4 \rightarrow ^7F_5$) is more intense in all the samples than the other transitions. The effect of sintering temperature on the PL intensities of the main green peak was also examined. The PL intensities are displayed as a function of temperature in Fig. 4.6.5. From these results, it was observed that the PL intensity of the as-synthesized phosphor increased rapidly on sintering temperature upto 1100°C, beyond which there was no observable change in the PL intensity. This is mainly due to the improvement in doping of Tb$^{3+}$ ions in the host matrix. The intensities of $^5D_4$ emissions increase with increasing of sintering temperature while those of the $^5D_3$ emissions decrease. At high temperatures, the probability for cross-relaxation increases which results in more $^5D_4$ emission. The rate of cross-relaxation depends on two conditions. The first condition is the ratio of donors to acceptors. An excess of acceptors results in direct energy transfer from a
donor to an acceptor. With an excess of donors, energy is transferred primarily by migration or hopping between donors until an acceptor is found. The second condition affecting the rate of cross-relaxation is the temperature of the crystalline environment. Cross-relaxation is a phonon-assisted process. Phonons can provide the additional energy to minimize the energy mismatch between coupled transitions. A reduction in the temperature will reduce the number of available phonons and, for transfer between transitions with large energy mismatches, reduce the observed rate of energy transfer [96]. A number of current models have been used to describe the effect of temperature and concentration on the rate of cross-relaxation [97]. Richardson et al. also observed that the cross-relaxation rate increased as the temperature was increased [98].

The emission colors of the as-synthesized nanocrystals by combustion method and of those after sintering at 1100°C were analyzed with the help of CIE chromaticity coordinates. The color co-ordinates of as-synthesized nanocrystals were found to fall into the bluish-green region of the CIE chromaticity diagram. After heat-treatment at 1100°C, emission color shifted toward yellowish green and the hue of the nanocrystals became a deeper green.

Fig. 4.6.4 PL spectra of SrZnO₂:xTb nanocrystals with x=0.12%,0.25%,0.5% and 1mol% respectively.
CONCLUSION

The terbium doped phosphors described in this chapter were synthesized using urea/glycine as an organic fuel by combustion method. Combustion synthesis is a novel phosphor processing technique that has shown to produce fine particle size. This technique can produce a homogenous product in a short amount of time without the use of expensive high temperature furnaces. The as-synthesized product is high in purity, usually single phase and chemically homogenous. The phosphors thus obtained were characterized by X-ray diffraction (XRD) techniques, EDAX technique, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and their photoluminescence properties were studied by spectroradiometer.

1. CaIn$_2$O$_4$:Tb$^{3+}$ phosphors having general formula (Ca$_{1-x}$Tb$_x$)In$_2$O$_4$ where x=0.12, 0.5, 1, 1.5 and 2% have been synthesized by combustion route using urea as a fuel in a pre-heated furnace at 500°C. The observed luminescent emission of the as-prepared samples at 500°C was quite weak, thus the solid obtained was again fired at varying
temperatures between 700°C to 1100°C for 3 hrs to increase the brightness. The 
emission spectra of this phosphor showed strongest peak at about 545nm stemming 
from $^{5}D_4 \rightarrow 7F_5$ transition. Maximum brightness was observed in the sample with 
0.12% of terbium concentration and the brightness decreased on increasing terbium 
concentration from 0.12 to 2% due to concentration quenching. The synthesized 
phosphor products were of high purity, usually single phase and chemically 
homogenous. The size of the as-synthesized phosphor particles was ~100nm. The 
average grain size increases with increase in sintering temperature. The average 
particle size of the phosphor powders sintered at 1100°C was found to be ~800nm.

$\text{CaIn}_2\text{O}_4$ is a potentially effective host lattice for green phosphors containing the Tb$^{3+}$ 
ions as an activator. This phosphor meets the requirements for CRT applications.

2. $\text{CaIn}_2\text{O}_4$:Tb$^{3+}$ phosphors having general formula $(\text{Ca}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4$ where $x=0.12,$ 
0.5, 1 and 2% have been synthesized by combustion route using glycine as a fuel in a 
pre-heated furnace at 500°C. The prepared phosphors when exposed to 254nm UV 
light showed a uniform green color indicating homogenous doping. The emission 
spectra of these phosphors showed strongest peak at about 546nm stemming from $^{5}D_4 
\rightarrow 7F_5$ transition. The maximal brightness was obtained for the sample with terbium 
concentration 0.12%. The brightness decreased on increasing Tb$^{3+}$ concentration from 
0.12 to 2%, this presumably was due to the well established theory of concentration 
quenching. The flame temperature of combustion process has an important effect on 
the crystallite size of the synthesized phosphors. By adjusting the glycine to nitrate 
ratio (G/N), the flame temperature was controlled which controlled the crystallite size, 
producing nanosized phosphors having particle size 35-55nm, similar to the sizes 
estimated using XRD method. This phosphor finds use in cathode ray tubes.

3. $\text{SrIn}_2\text{O}_4$:Tb$^{3+}$ phosphors having general formula $(\text{Sr}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4$ where $x=0.12,$ 0.5, 
1, 1.5 and 2% have been synthesized by combustion route using urea as a fuel in a 
pre-heated furnace at 500°C. The prepared phosphors when exposed to 254nm UV 
light showed a uniform green color indicating homogenous doping. The emission 
spectra of these phosphors showed strongest peak at about 545nm stemming from $^{5}D_4 
\rightarrow 7F_5$ transition. Maximum brightness was observed in the sample with 0.12% of 
terbium concentration and the brightness decreased on increasing terbium
concentration from 0.12 to 2% due to concentration quenching. The XRD patterns revealed pure crystalline phase of SrIn$_2$O$_4$:xTb and the phosphor powders had average particle size below 2μm. This phosphor is needed for the development of improved field emission display (FED) applications as it has high conductivity and it is also used as a potential phosphor for CRT.

4. CaAl$_2$O$_4$:Tb$^{3+}$ nanocrystals having general formula (Ca$_{1-x}$Tb$_x$)Al$_2$O$_4$ where x=0.12, 0.5, 1, 1.5 and 2% have been synthesized by combustion route using urea as a fuel in a pre-heated furnace at 500°C. The observed luminescent emission of the as-prepared nanoparticles at 500°C was quite weak, thus the solid obtained was again fired at varying temperatures between 700°C to 1100°C for 3 hrs to increase the brightness. The emission spectra of this phosphor showed strongest peak at about 545nm stemming from $^5$D$_4$ $\rightarrow$ $^7$F$_5$ transition. The maximal brightness was obtained for the sample with terbium concentration 1%. The brightness decreased on increasing Tb$^{3+}$ concentration beyond 1%, this presumably was due to the well-established theory of concentration quenching. The particle size of the powder synthesized at 500°C was very small and the particles tend to agglomerate. In fact agglomeration of the as-synthesized powder after heat-treatment for 3 hrs at 1100°C was almost eliminated, producing well-formed particles having size less than 1μm. These phosphors can be exploited for fluorescent lamp to get better green color and higher lumen output.

5. YPO$_4$:Tb$^{3+}$ phosphors having general formula (Y$_{1-x}$Tb$_x$)PO$_4$ where x=1-5mol% have been synthesized by combustion route using urea as a fuel in a pre-heated furnace at 500°C. The as-prepared phosphors when exposed to 370nm UV light showed a uniform green color indicating homogenous doping. The emission spectra of these phosphors showed strongest peak at about 543-545nm stemming from $^5$D$_4$ $\rightarrow$ $^7$F$_5$ transition. From the spectral features, it has been noticed that the intensity of the emission peaks increased with the increase in terbium concentration up to 5mol% and then decreased with increasing the Tb$^{3+}$ concentration. This decrease in brightness with increasing activator concentration may be due to the well-established theory of concentration quenching. The crystallites have size in the range of 25nm to 45 nm. The crystallite size has been observed to increase with increasing sintering temperature ranging from 700°C to 1000°C.
6. SrZnO₂:Tb³⁺ phosphors having general formula (Sr₁₋ₓTbₓ)ZnO₂ where x=0.12-2 mol% have been synthesized by combustion route using urea as a fuel in a preheated furnace at 500°C. The samples were again fired at 700°C to 1100°C in order to determine the effect of sintering on the particle size and luminescence properties. The PL spectra confirm that the SrZnO₂:Tb³⁺ nanocrystals emit in both the green and blue spectral regions and the green emission was found to dominate the blue. The predominant green color from the magnetic-dipole transition ⁵D₄ → ⁷F₅ of Tb³⁺ was located at 545 nm. The intensities of green emission increased with increase of sintering temperature while those of the blue emission decreased. A low level of Tb³⁺ was found to be an efficient dopant for achieving the desired luminescent properties of the material. The crystal sizes of the nanophosphors ranging from 27 nm to 43 nm were calculated by applying Scherrer’s equation to the FWHM of the diffraction peaks, and the results were in agreement with the sizes indicated by scanning electron microscopy and transmission electron microscopy.
REFERENCES

19. JCPDS Card No. 33-1336.


