Introduction

The objectives of this chapter is to give a brief introduction to history of \textit{E. Tirucalli} Plant, Green combustion method, nanomaterials, phosphors, chemical and physical aspect of doping, effect of dopant ions on luminescence, Importance of Silver and oxide nanoparticles.

1.1 History of \textit{E. Tirucalli} Plant

Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles \cite{1}. The source of the plant extract is known to influence the characteristics of the nanoparticles \cite{2}. This is because different plant extracts contain different concentrations and combinations of organic reducing agents \cite{3-5}. Typically, a plant extract-mediated bioreduction involves mixing the aqueous extract with an aqueous solution of the relevant metal salt. The reaction occurs at room temperature and is generally complete within a few minutes. In view of the number of different chemicals involved, the bioreduction process is relatively complex.

\textit{E. Tirucalli} (Fig. 1.1) belongs to genus Euphorbia one of the 8000 species within the family of Euphorbiaceous. It is a small tree endemic to tropical areas with pencil like branches. \textit{E. Tirucalli} is generally evergreen since its stems and branches remain green. It bears white latex and has different medical features. The different parts of the plant is used in medicine for the treatment of painful muscular spasm, dysentery, fever, rheumatism, asthma and as an expectorant purgative etc \cite{6,7}. \textit{E. Tirucalli} is a plant with good enough quantities of latex i.e. milky liquid, when any mechanical damages, their tissues are broken and secrete the milky latex, consisting of several biologically active compounds, including proteins, amino acids, carbohydrates, lipids, vitamins, alkaloids
resins and tannins. Predominantly, milky latex contains calotropin, catotoxin, calcilin, gigatin, 4-deoxy-phorbal ester, gallic acids, glucosides, ingenol phenols, phorbol esters, proteases, succinic acid etc [8, 9].

Fig. 1.1. (a) *E. Tirucalli* plant and (b) latex collected from the plant.

An esterase is a hydrolase enzyme that splits into an acid and an alcohol in a chemical reaction with water called hydrolysis.

\[ R^1COOR^1 + H_2O \leftrightarrow R^1COOH + R^1OH \]

The term esterase has been used to indicate (designate) member of a complex class of hydrolases.

- **Hydrolase** is an enzyme that catalyses the chemical bond

- These include phosphoric monoester hydrolases, phosphoric diester monohydrolases, thiolester hydrolases, sulphuric ester hydrolases and carboxylic acid ester hydrolases.

- **Esterases** in general are further divided into several subclasses:
  1. Carboxyl esterases
  2. Aryl esterases
  3. Acetyl esterases
  4. Cholin esterases
Most of the tissues of a plant including root are known to possess one or the other types of carboxylic ester hydrolases. There are number of species in the family of Euphorbiaceae (Table 1.1). Among them, *E. Tirucalli* has been identified for present study. Euphorbiaceae family plant latex is traditionally used to treat various skin diseases, digestive system, respiratory system, reproductive system etc.

Chemical synthesis methods may lead to the presence of some toxic chemical species absorbed on the surface of the nanoparticles that may have adverse effects in medical applications. Increasing awareness about the environment has led researchers to focus on ‘green chemistry’ and develop a simple and eco-friendly technology. Recently, biosynthetic methods employing biological micro-organism such as bacteria [10] and fungus [11, 12] have emerged as a viable alternative to more complex chemical synthetic procedures to obtain nanomaterials. Use of plant extract for the synthesis of nanoparticles could be advantageous over other environmentally benign biological processes by eliminating the elaborate process of maintaining cell cultures [13, 14]. It is also an exciting possibility that is relatively unexplored and under exploited.

Synthesis of nanophosphors using green chemistry received much attention by the researchers as it is clean, non-toxic, eco-friendly, free from unwanted byproducts, benign reaction media, non-hazardous, elimination of generated waste, lowering the reaction temperature etc.
Table 1.1 Members of Euphorbiaceae family.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Agent used</th>
<th>Medicinal use</th>
<th>Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Jatropha curcas</em></td>
<td>latex</td>
<td>Toothache</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><em>Euphorbia caducifolia</em></td>
<td>latex</td>
<td>treatment of bleeding wound, cutaneous eruption and other skin diseases.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><em>Synadenium grantii</em></td>
<td>latex</td>
<td>to treat various neoplastic diseases</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><em>Euphorbia-tirucalli</em></td>
<td>latex</td>
<td>Traditional medicine for asthma, cough, earache, neuralgia, rheumatism, toothache, and warts</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><em>Euphorbia resinifera</em></td>
<td>latex</td>
<td>cancer treatment and as analgesic</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><em>Euphorbia milii</em></td>
<td>latex</td>
<td>folk medicine</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td><em>Poinsettia pulchherima</em></td>
<td>latex</td>
<td>Pharmacological properties</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Euphorbia poinsettia)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Submicron or even nanosized products have been synthesized by various wet-chemistry methods all over the world for the past several years, including hydrothermal synthesis, co precipitation, sol–gel process, combustion synthesis, etc. Although significant progresses have been achieved, there are problems. For example, sol–gel process uses metal alkoxides as the starting materials, which are very expensive and extremely sensitive to the environmental conditions such as moisture, light and heat. Moisture sensitivity makes it necessary to conduct the experiment in dry boxes or clean rooms. Co-precipitation processes involve repeated washing in order to eliminate the anions coming from the precursor salts used, making the process complicated and very time consuming. Furthermore, it is difficult to produce large batches by using most of the wet-chemical solution processing routes.

1.2 Green combustion method

Green combustion synthesis is wet-chemical method, which has been proved to be an excellent technique for preparing several grams micro/nanocrystalline phosphors due to its short processing time, low processing temperature and low cost as well as good ability to achieve high purity in making single or multiphase complex oxide powders at the as-synthesized state. This technique is based on exothermic redox reactions that undergo self-sustaining combustion. Mixtures of oxidizer (usually metal nitrates) and reducer (plant latex) undergo spontaneous combustion under heating and the chemical energy from the exothermic reaction heats the precursor mixture to high temperatures. Such a high temperature leads to formation and crystallization of phosphor materials. In comparison with other methods, the products obtained by the combustion synthesis method are generally more homogeneous, have less impurity and have higher surface areas than powders prepared by conventional methods. Until now, this technique has been
employed to produce a variety of materials such as oxides, borates, silicates and aluminates.

1.3 Nanomaterials

In the past few years, nanomaterials have become one of the thrust areas of current research in material science and technology. The physical properties such as structural, magnetic, optical, dielectric, thermal, electrical etc. of nanophase materials is very much affected from those of the bulk materials due to quantum confinement effects. The manipulation of material properties by one dimensional, two-dimensional and three-dimensional confinement will revolutionize the luminescence area with huge advances in digital memory storage, image processing, optical telecommunication, photonics, etc [15-18].

Nanomaterials have been attracting increasing interest for their unique chemical and physical properties and potential technological applications. The properties of nanomaterials depend on the grain size and distribution of nanomaterials, the chemical composition of the constituent phases, the presence of interfaces, more specifically grain boundaries, hetero phase interfaces or the free surface and the interaction between constituent ions/atoms.

In nanomaterials, the ratio of particle surface area to volume is much larger than that in bulk material. One can imagine that the surface state such as surface defects, surface disorders and surface void bands will influence the luminescence properties of nano materials. Thus, surface modification is necessary to decrease the surface defects and increase the luminescence efficiency of nanomaterials. The amorphous phase, which
exists at the surface of the enclosed nanocrystalline phase, can decrease surface defects effectively and lower the non-radioactive emission in just the same way as surface modification. In nanoscale, the majority of the atoms will be located on the surface of the particles. In such a state, the intrinsic properties of the material will change.

Nanotechnology has more advantages over other conventional processes due to the availability of more components by biological entities for the formation of nanostructures. The rich biodiversity of such biological entities should be explored for the synthesis of nanomaterials. Esterases contained plant latex mediated syntheses have been used extensively for the production of various inorganic nanoparticles. It has received considerable attention due to the growing need to develop environmentally benign technologies in material synthesis.

1.4 Phosphor

Phosphors, are called luminescent materials, or optical transducers, which convert certain types of energy into electromagnetic radiation over and above thermal radiation. The electromagnetic radiation emitted by a luminescent material is usually in the visible range. Depending upon nature of the excitation energy, the resulting phosphors and luminescence are given in Table 1.2.
Table 1.2: Types of luminescence and its applications.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Phosphors</th>
<th>Luminescence</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low energy photons</td>
<td>Photophosphors</td>
<td>Photoluminescence</td>
<td>Lamps and display</td>
</tr>
<tr>
<td>(Ultraviolet/visible/VUV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat</td>
<td>Thermophosphor</td>
<td>Thermoluminescence</td>
<td>Radiation Dosimetry, Environment Protection</td>
</tr>
<tr>
<td>Cathode rays (Electrons)</td>
<td>Cathodophosphors</td>
<td>Cathodoluminescence</td>
<td>Cathod ray tube (CRT), Field emission display (FED), Vacuum fluorescence display</td>
</tr>
<tr>
<td>X-rays</td>
<td>X-ray phosphors</td>
<td>X-ray luminescence</td>
<td>Storage panels, Interfacing screens, Computation tomography</td>
</tr>
<tr>
<td>Ions (particles)</td>
<td>Ionophosphors</td>
<td>Ionoluminescence</td>
<td>Device fabrication</td>
</tr>
<tr>
<td>Mechanical forces</td>
<td>Tribophosphors</td>
<td>Triboluminescence</td>
<td>Crash prevention (car crash)</td>
</tr>
<tr>
<td>Electric field strength</td>
<td>Electrophosphors</td>
<td>Electroluminescence</td>
<td>Electronic Discharge, EL Panels</td>
</tr>
<tr>
<td>Biochemical</td>
<td>Biophosphors</td>
<td>Bioluminescence</td>
<td>Chemical Assay, Oxygen Detection</td>
</tr>
</tbody>
</table>

Phosphor (lamp phosphor) in fluorescence lamps (tube lights) converts UV to visible (white) light. Several other phosphors like TV (cathode-ray) phosphors, X-ray and $\gamma$-ray phosphors (scintillators) are also known. These phosphor materials find wide applications in lightining, scintillators, communication and as a diagnostic tool in medicine and biology. General perspectives of the luminescence of solids can be found in various textbooks [19-22].
A phosphor consists of a host lattice in which activator ions are incorporated. The activator creates a center, which absorbs excitation energy and converts it into visible radiation (Fig. 1.2(a)). Eu$^{3+}$ doped yttria ($Y_2O_3:Eu^{3+}$) is a typical example wherein the excitation radiation is absorbed by the Eu$^{3+}$ (activator), raising it to an excited state. Then it returns to the ground state by emission of radiation, mostly in the visible region. When an activator with the desired emission does not have a significant absorption for the available excitation energy, a sensitizer has to be used. The sensitizer absorbs the excitation energy and then transfers this energy to the activator, which can then emit its characteristic luminescence (Fig. 1.2(b)).

![Fig. 1.2. Representation of luminescence process (a) activator (A) in a host (H) and (b) sensitizer (S) & activator (A) in a host (H).](image_url)
1.5 Requirements for lamp phosphors

Luminescent properties of lamp phosphors are affected by structure of hosts, activator, types of fuel etc.

In order to get good luminescence, phosphor hosts should have the following characteristics.

- They should be compatible with the luminescent centers. i.e. accommodate the luminescent ions and allow them to involve in the luminescence process. Further, they should not react with the luminescent ions to form compounds.
- They should be stable during fabrication of lamps.
- They should be stable to highly energetic electrons, ultraviolet radiation and Hg vapor.

Rare earths are well known for their extensive use in luminescent materials. The RE ions doped inorganic nanophosphor is one of the most promising materials for a variety of applications in solid state lightening, solid-state lasers, lighting and displays and optical communication fields such as fluorescent lamps, cathode ray tubes, and field emission displays. Many luminescent particles of different chemical compositions, shapes and size distributions have been prepared by different kinds of methods. In comparison, luminescent particles prepared by green combustion synthesis are more attractive than many other methods, in producing fine particle size, synthesizing homogeneous phosphor at relatively low temperature and with reduced processing time as well as low cost method for production of various industrially useful materials. Previous studies were reported on the optical properties of ZnO, CeO₂, Gd₂O₃ as a promising host material doped with Eu³⁺, Er³⁺, Nd³⁺ and Tm³⁺ ions due to its good chemical, photo thermal and photochemical stabilities as well as its low phonon-energy.
A significant practical application for nanostructured materials is X-ray medical imagery, because it is necessary to use dense materials in order to enable absorption of high energy photons. An important requirement of these materials is UV-Visible range emission produced by X-ray excitation, which can be influenced by the particle size. Europium doped ZnO, CeO₂ and Gd₂O₃ are well known red phosphor. Moreover, nanophosphors of Gd₂O₃ codoped with Tb³⁺, Eu³⁺ increase their light yield by energy transfer between Tb³⁺ and Eu³⁺ [23].

There has been an ever increasing interest in rare earth phosphors since 1980 as evidenced by the number of international conference held, technical reports and reviews [24-36] published. Phosphors activated by rare earth ions exhibit some peculiarities [37]. In the energy level diagram of the rare earths, luminescence processes often correspond to electronic transitions within the incompletely filled 4f shell. Consequently, these phosphors have narrow band spectra which are to a great extent independent of the nature of the host lattice. Because of the low interaction with the crystal lattice, the luminescence quantum yield of phosphors activated with rare earths is often high compared to other phosphors. Quenching occurs only at higher temperatures or higher activator concentrations. Europium (II and III) and terbium are of interest as activators [38-40].

1.6 Chemical aspect of doping

Chemically, the most important question to be dealt with, is the doping of the activators in the host. The problem is thoroughly discussed by Kroger [41]. The size of the ions is important: KCl can easily be activated by Tl⁺, but NaCl cannot be (K⁺=1.33 Å; Tl⁺=1.44 Å; Na⁺=0.95 Å). Since NaI also can be activated by Tl⁺, the ionic radius is not the only factor. The free energy of doping must be the deciding factor, but this quantity
can be calculated only in the simplest crystal lattices. A point of particular interest is the valency of the activator. When the activator atom has the same valency as the metal atom of the host crystal, it may replace the atoms of the host crystal substitutionally, without further complications. However, when it has a different state of valency, substitution at lattice sites must be accompanied by vacancies or interstitials. This seems to affect the efficiency of the phosphor adversely. Kinney et al. [42] reported that the partial substitution of sodium for calcium in calcium pyrophosphate increased the efficiency of the luminescent emission. The enhancement of luminescence is attributed to compensation of valence; Sb\(^{3+}\) and Na\(^+\) compensating for two Ca\(^{2+}\) in the lattice. Froelich [43] found that the chemical stability of Ca\(_3\)(PO\(_4\)_2):Ce\(^{3+}\), Mn\(^{2+}\) was improved by adding sodium. According to Crosby [44] addition of sodium greatly helps in simplifying the preparation of cerium-activated calcium magnesium silicate.

1.7 Physical aspect of luminescence

Since the luminescent properties of oxidic luminescent materials are explained on the basis of single configurational coordinate (SCC) model [45, 46], it would be appropriate to outline briefly the salient features of this model. Fig. 1.3 shows configuration curves for the ground state and an excited state. Electronic transitions are represented by vertical lines because they occur in a very short time compared to atomic displacements.

If the transition involves only inner orbitals, the equilibrium distance is not modified (\(\Delta r=0\)) [Fig. 1.3]; the parabola of the excited state has the same shape as that of the ground state. Since the two parabolas are parallel, all transitions have nearly the same energy. The corresponding spectrum consists of a narrow line at the same position in absorption and emission. If the transition involves an external orbital, the equilibrium
distance is changed ($\Delta r \neq 0$) [Fig. 1.3]. Transitions from a vibrational level of the ground state end on different vibrational levels of the excited state. The absorption spectrum consists of a band, which broadens with increasing levels of the ground state. The energy distribution of transitions has approximately a Gaussian shape.

After excitation, the ion returns to the ground state by the following processes:

a. relaxation to the bottom of the excited state parabola (transitions A$\rightarrow$B, Fig. 1.3) by emitting phonons (i.e. by giving up heat to the lattice), in a time of the order of $10^{-13}$ s;

b. radiative emission (transitions B$\rightarrow$ C); if emission occurs during excitation and upto $10^{-8}$ s is called fluorescence, while it continues longer than $10^{-8}$ s is known as phosphorescence.

c. relaxation to the minimum of the ground state parabola with phonon emission (transitions C$\rightarrow$O).

The emission spectrum consists of a band at longer wavelengths than the absorption band. The energy difference between the two bands is called the Stokes shift. Because phonon energies in the excited state are smaller, the excited parabola is wider and hence the emission band is broader than corresponding absorption band.

Transitions between the inner 4f orbitals produce narrow lines in the absorption and emission spectra of lanthanide ions. In contrast, those involving external orbitals, such as the 4f$\rightarrow$5d transitions of rare earths or s$\rightarrow$p transitions of mercury-like ions, give rise to broad bands. This is also the case for transitions within the 3d$^n$ configurations when they occur between orbitals of different symmetry, for instance from t$_{2g}$ to e$_g$ orbital in the case of an octahedral environment. All spin allowed d$\rightarrow$d transitions give rise to broad absorption bands. Configurational coordinate diagrams can be established
from the shape of absorption and emission bands. It must be stressed that the validity of the model is limited by the assumption of a single vibrational mode.

![Configurational coordinate diagrams for (a) negligible and (b) strong offset, $\Delta r$, $r =$ cation-anion distance.](image)

1.8 Effect of dopant ions on luminescence

The influence of dopant ions on luminescent of Gd$_2$O$_3$:Eu$^{3+}$ has been investigated extensively. Park et al. [52] studied europium-doped cubic Gd$_2$O$_3$ nanoparticles containing various activator content in the range of 5-15 wt % by a liquid-phase reaction method. The phosphors showed an initial increase in luminescence and then a subsequent decrease with further doping (above 10 wt %). The decay time was reduced with increasing Eu loading; however, it decreased significantly above the 10% Eu doping.
From spectroscopic studies, the Eu$^{3+}$ doping ion distribution is uniform and homogeneous up to the 10 wt% loading because no concentration quenching effect is observed. However, further Eu$^{3+}$ doping above 10 wt% reduced the luminescence due to the concentration quenching effect, as deduced from the shortening of the decay time.

1.9 Silver Nanoparticles

Silver nanoparticles are one of the promising products in the nanotechnology industry. The development of consistent processes for the synthesis of silver nanomaterials is an important aspect of current nanotechnology research. One of such promising process is green synthesis. Silver nanoparticles can be synthesized by several physical, chemical and biological methods. However for the past few years, various rapid chemical methods have been replaced by green synthesis because of avoiding toxicity of the process and increased quality \[53-62\].

1.10 Importance of silver nanoparticles

1) It is used for purification and quality management of air, biosensing, imaging, drug delivery system.

2) Biologically synthesized silver nanoparticles have many applications like coatings for solar energy absorption and intercalation material for electrical batteries, as optical receptors, as catalysts in chemical reactions, for biolabelling, and as antimicrobials.

3) Though silver nanoparticles are cytotoxic but they have tremendous applications in the field of high sensitivity bimolecular detection and diagnostics, antimicrobials and therapeutics, catalysis and micro-electronics.
4) It has some potential application like diagnostic biomedical optical imaging, biological implants (like heart valves) and medical application like wound dressings, contraceptive devices, surgical instruments and bone prostheses.

5) Many major consumer goods manufacturers already are producing household items that utilize the antibacterial properties of silver nanoparticles. These products include nanosilver lined refrigerators, air conditioners and washing machines.

1.11 Oxide nanoparticles

The powder is widely used as an additive for numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. ZnO is present in the Earth crust as a mineral zincite; however, most ZnO used commercially is produced synthetically. ZnO is nontoxic and is compatible with human skin making it a suitable additive for textiles and surfaces that come in contact with human body. The increase in surface area of nanoscale ZnO compared to bulk has the potential to improve the efficiency of the material function. Rare earths (RE) sesquioxides find wide applications in display devices, solid state lasers, X-ray radiography, luminescent materials. These materials show stable host for powerful lasers, high chemical, thermal stability and maximum power output.

1.12 Importance of oxide nanoparticles

1) It is used in paints, cosmetics, sunscreens, plastic and rubber manufacturing, electronics and pharmaceuticals products etc.

2) potentially used to treat leukemia and carcinoma cancer cell

3) a strong antibacterial agent
4) used as drug carrier
5) industrial sectors including environmental, synthetic
textiles, food, packaging, medical care, healthcare, as well as construction and decoration.

1.13 Present status and outlook

Jose-Yacaman and co-workers [63] first reported the formation silver nanoparticles by living plants. Very recently green silver nanoparticles have been synthesized using various natural products like green tea (Camellia sinensis) [64], neem (Azadirachta indica) leaf broth [65], natural rubber [66], starch [67], aloe vera plant extract [68], lemongrass leaves extract [69,70] leguminous shrub (Sesbania drummondii) [71], etc.

ZnO, CeO₂, Gd₂O₃ are an inorganic oxide nanoparticles which has a wide and direct band gap [72]. The ZnO-NPs has numerous applications such as catalysis [73], piezoelectric devices [74], pigment [75], chemical sensors [76], and cosmetic material especially for transparent UV protection [77]. It is important to prepare ZnO-NPs by a simple, costeffective, and eco-friendly process that has potential to yield nanoparticles of uniform particles in size. Yang et al [78] reported green synthesis of ZnO nanophosphors from Zn₅(CO₃)₂(OH)₆ and H₂O₂ at room temperature (RT) for various durations (24-72 h) under atmospheric pressure.

Sangeetha et al [79] studied the structural and optical properties of ZnO nanophosphors prepared by Aloe barbadensis miller leaf extract. Spherical shape and size was highly influenced on the concentration of leaf broth solution. Hudlikar et al [80] prepared ZnS nanophosphors by green synthesis method using Jatropha curcas L. plant
latex. The cyclic peptides of curcacycline A, curcacycline B and curcain acts as both reducing and stabilizing agents in the latex *Jatropha curcas* L. Further, plant latex acts as a source of sulphide (S\(^{-2}\)) ions which were donated to Zn ions.

Most of the nanoparticles prepared by synthetic physicochemical methods reported till date were heavily on the use of organic solvents and toxic reducing agents. Many of these chemicals were highly reactive and pose potential environmental and biological risks. With the increasing interest in elimination of hazardous chemicals, the development of biological, biomimetic and biochemical approaches were highly desirable. Therefore, biological approach has advantages over physicochemical methods [81-84]. Therefore, ecofriendly synthesis of nanoparticles have proven to be better methods due to friendliness, high yield, nontoxic nature, environmentally benign solvents etc [85-87]. Till date most of the commercially produced oxide phosphors were prepared by solid state reactions. It involves various process namely raw materials, blending, high temperature treatment, washing, milling, filtering, drying and sieving etc [88, 89].

Further, the phosphor synthesized in this method generally degrades luminescent efficient due to grinding, larger surface defects as a result required resolution was not achieved in display devices. Therefore, efficient alternate method was required for the synthesis of nanophosphors. Green combustion synthesis is an attractive alternate ecofriendly method for the preparation of nanophosphors using various biological materials, low process temperature, reduced time, simple experimental setup. During the exothermic decomposition of metal nitrates and organic fuel complexes at low temperature, sufficient heat is generated locally to form crystalline materials. The
different parts of the plant were used in medicine for the treatment of painful muscular spasm, dysentery, fever, rheumatism, asthma and as an expectorant purgative etc [90, 91].

Another interesting application of CeO₂ is as luminescent layers because of its good compatibility with silicon-based optoelectronics. Recently, violet/blue luminescence from the CeOₓ film and CeO₂ film has been reported. Ceria shows weak emission characteristics which limits its application as light emitting phosphor and its identification in biological and cellular studies. It has been observed that the luminescence properties of weakly emitting particles can be improved by doping of the parent matrix with elements which can emit by itself upon excitation in the UV-visible range of the spectrum [92]. The comparable ionic radius of cerium ions and europium ions favors the latter’s extensive solubility in the ceria matrix. There are a few reports on doping ceria with Eu³⁺ [93-95]. In all the cases, red emission has been obtained from the Eu³⁺ dopant ion. The enhancement of photoluminescence of host ceria through doping as been observed only in a few of them. Recent advances in ultraviolet (UV) light emitting diodes based on wide-gap semiconductors have facilitated solid-state white lighting using red, orange, yellow, green and blue phosphors. White light emitting diodes (LEDs) are widely used due to their many advantages, such as energy saving, long life time and safety [96, 97]. CeO₂, with no 4f electron can be a promising photoluminescence host material because of strong light absorption through the charge transfer from O²⁻ to Ce⁴⁺. If this energy can be transferred to the doped rare earth ions in ceria, characteristic emission from the latter would be observed and a correct combination of the dopants can lead to a white light source. However, to the best of our knowledge, there is no report on white light emission from doped ceria nanophosphor. Eu³⁺ is considered as a suitable dopant for enhancing emission in CeO₂ due to (i) it can be excited from UV-visible light (ii) ionic radius of
Eu$^{3+}$ (0.1066 nm) being close to Ce (Ce$^{3+} = 0.097$ nm), favours extensive solubility with the CeO$_2$ lattice (iii) it increases the trivalent state of Ce, with further enhance the biological activity of CeO$_2$.

Over the past several years, phosphors have been considered as key and technologically important components as the prerequisites to the functionality and success of many lighting and display systems [98-105]. At present, RE-based phosphors with efficiencies close to the theoretical value is 100% employed in different fluorescent tubes, X-ray imaging and color televisions. Such applications depend on the luminescent properties of RE ions, e.g. sharp lines, high efficiency and high lumen equivalent.

The interest in nanocrystalline oxide is due to its potential applications in lamp and display phosphor, contrast agent for MRI, fluorescence imaging, etc. oxides are considered one of the best host materials for luminescent centers due to their excellent chemical and thermal stability when mixed with RE ions, become excellent luminescence in the blue, green and red regions of the spectrum. Stable crystal structure, high physical and chemical stability, good formability, long persistence time relatively easy preparation, multicolor phosphorescence and resistance to acid, alkali and oxygen

In general electric transitions are influenced by the symmetry of luminescent centers. If inversion symmetry is present, the electric dipole transitions are forbidden, so that the emission is restricted to magnetic-dipole $^5D_0 \rightarrow ^7F_1$ transition. If inversion symmetry is absent, forced electric-dipole transitions are allowed. The red emission of Eu$^{3+}$ is due to radiative transitions $^5D_0 \rightarrow ^7F_J$ [106]. In this special case they are restricted to the transitions $^5D_0 \rightarrow ^7F_{J=2,4,6}$ [107]. The broad absorption and reflection spectra of the
Eu$^{3+}$ ion in oxides is ascribed to a charge-transfer transition in which an electron is promoted from the highest-filled oxygen-orbital to the 4f shell of the Eu$^{3+}$ ion. For Eu$^{3+}$ in six-coordination, the charge transfer band is observed at ~238 nm and does not depend markedly on the host lattice [108].

1.14 Scope and objectives of present study

(i) Scope

Microorganisms producing various diseases are developing resistance to multiple antibiotics. Organic agents have limited their applications due to their low heat resistance, high decomposability and short life [109]. Therefore there is growing interest in developing new bactericides based on inorganic materials to substitute the traditional organic agents. Researchers have also recommended the use of silver and copper ions as superior disinfectants for wastewater generated from hospitals containing infectious microorganisms [110]. However, residual copper and silver ions in the treated water may adversely affect human health [111]. In this context, metal oxide nanoparticles which ensure a slow release of ions can serve as an alternative. Metal oxide nanoparticles with bactericidal activity can be immobilized and coated on to surfaces, which may find application in various fields, i.e., medical instruments and devices [112-114], water treatment and food processing [115]. In comparison with Ag [116, 117] Cu nanoparticles (CuNPs) are less studied, because copper is easily oxidized, although they show a significant promise as bactericidal agent [118].

The latex of Euphorbiaceae family plants would be suitable for biological application and to the best of our knowledge a few reports are available not been used as
a matrix for synthesis of metallic nanoparticles. The present method has several advantages.

(i) The synthesis is prompt, easy and involves only dilute aqueous solution of latex.

(ii) Latex itself acts as capping and stabilizing agent. In case of silver it also acts as reducing agent.

(iii) The nanoparticle solution can be directly utilized for antimicrobial and in vitro cytotoxicity studies.

The present investigation deals with the preliminary characterization of oxides synthesized by green combustion method using esterases containing *E. Tirucalli* plant latex. Luminescence and photocatalytic activities of rare earth doped oxide nanoparticles of the above plant latex have been described.

(ii) Objectives

- Synthesis, characterization and luminescence properties of Silver nanoparticles using *E. Tirucalli* as a reducing agent.
- Synthesis, characterization, luminescence and photocatalytic activity of undoped and Eu$^{3+}$ doped ZnO nanoparticles using *E. Tirucalli* latex.
- Synthesis, characterization and luminescence properties of undoped and Eu$^{3+}$ doped CeO$_2$ nanoparticles using *E. Tirucalli* latex.
- Synthesis, characterization and luminescence properties of undoped and Eu$^{3+}$ doped Gd$_2$O$_3$ nanoparticles using *E. Tirucalli* latex.
References


