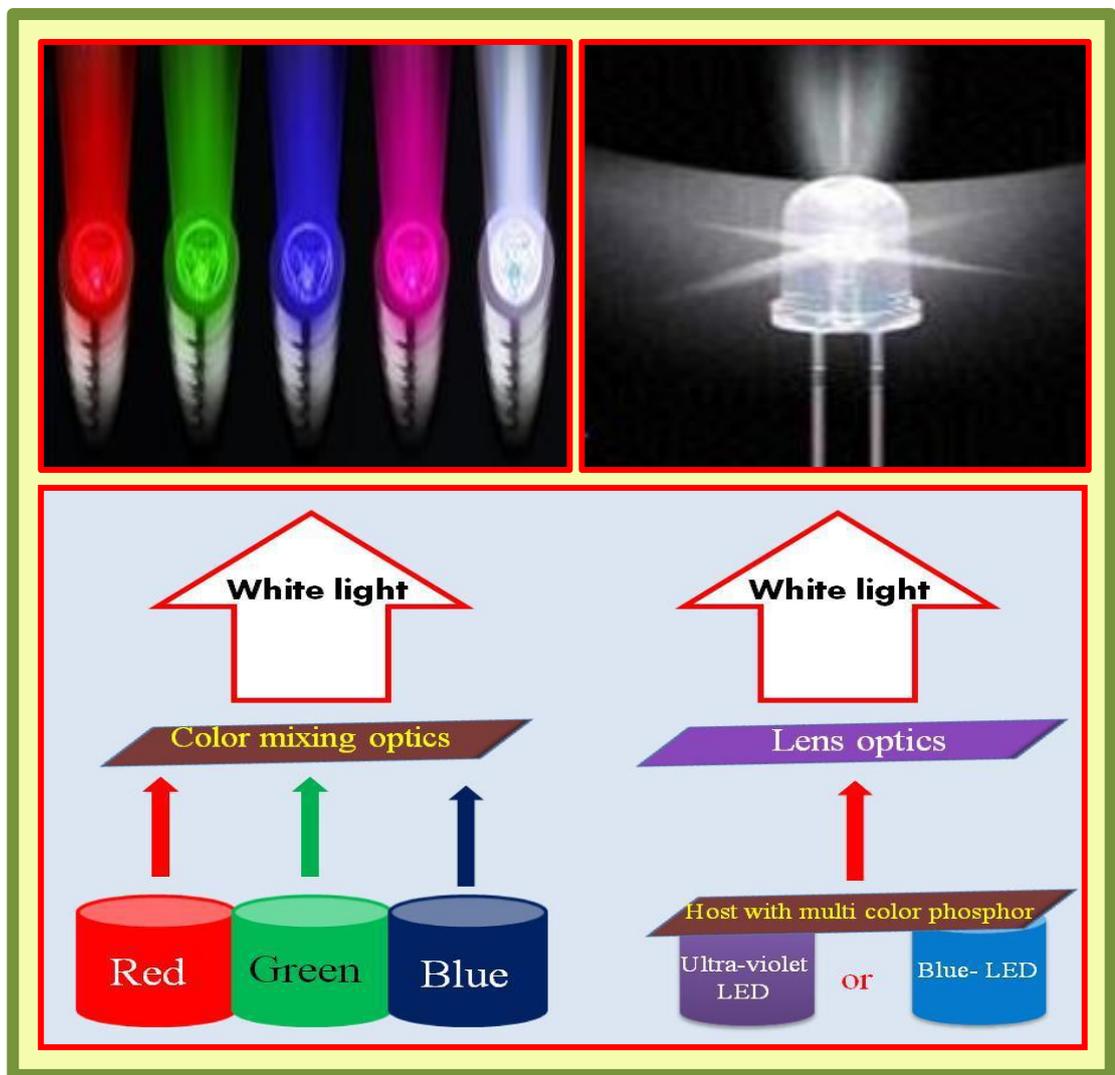


Chapter 1

Introduction



Chapter 1 provides the outline of introduction, applications, significance and different synthesis routes of nanophosphors. It deals with types of luminescence, light emission mechanism in phosphors and scope of the present work.

1.1 Nanomaterials and Nanotechnology

Recently, nanomaterials gaining widespread concentration in material science research in their view of the unique properties and massive amount of potential applications. Nanomaterials are actually a set of substances with length scale dimension is less than few (typically 100) nanometers, which consists of 10^1 - 10^5 atoms which are too large to be considered as molecules and too tiny for the bulk material, belong to a new class of materials called nanoparticles [1]. Nanomaterials with various size and shape (nanoparticles, nanowires, nanotubes nanorods and nano composites) are as of now gaining much attention because of their potential for innovative technological applications. This increase in interest changed into began via the acknowledgment that after the molecule size is reduced to the nanometer scale.

Nanomaterials have a much greater surface area to volume ratio than their traditional forms, that can result in greater reactivity and affect their strength. Additionally on the nano scale, quantum effects can emerge as much essential in determining the materials properties and characteristics, leads to novel optical, electrical and magnetic properties of the material and is responsible for the increase of energy difference between energy states and band gaps. The Schematic representation of band gaps in materials at nano and bulk size is shown in Fig.1.1

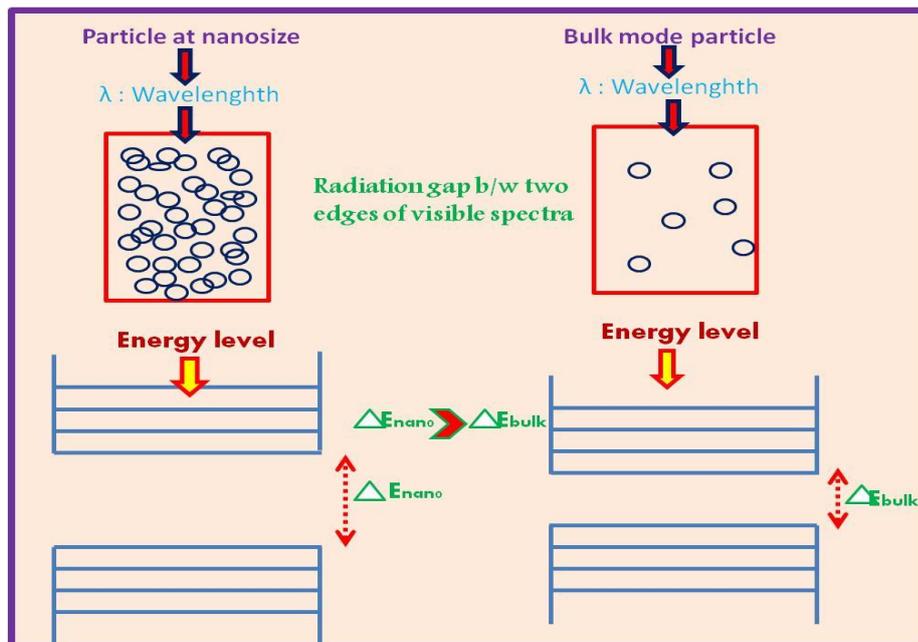


Fig.1.1 Band gap structure of the material at nano and bulk form.

When the size of the nanoparticle reduced, highest percentage of atoms are found on the surface compared to those inside, for example when the size is decreased to 3 nm, 50 % of its atoms are present on its surface, for 10, 30 nm size 20 and 5 % of its atoms present on its surface respectively. Among the surface atoms, edges and corners atoms are more reactive than those sitting in planes. Atomic proportion (%) increases with decrease in the particle size at the edges and corners of the surface, thus particles in nano size are at the leading edge of the rapidly developing field of nanotechnology both in scientific knowledge and in commercial (luminescence, catalysis etc) applications [2-6].

In the present era nanotechnology became an interdisciplinary research in which many physicists, chemists, biologists, materials scientists and other specialists are involved. The ability of scientist to manipulate the matter virtually atom by atom has been supported by the development of new instruments and approaches that allow the investigation of material properties with a resolution close to the atomic level. Such new tools had allowed extensive understanding of the remarkable physical and chemical properties characterizing the matter at the nanometer scale, opening up the way to the employ of nanomaterial in a wide variety of applications involving material science, engineering, physics, chemistry and biology [7, 8].

1.2 Important Applications of nanomaterials

Nanomaterials found wide range of applications in various field such as, fuel cells, batteries, agriculture, food industry and medicines etc..

1.2.1 Fuel cells

Fuel cell is an electrochemical device which converts the chemical energy from fuel and oxidizing agent into electricity. Electrodes are usually called as heart of the fuel cell. The performances of fuel cells are often optimized in two different methods; by means of enhancing the physical structure and with the aid of using high active electro catalyst.

1.2.2 Catalysis

Nanocatalysts generally tend to have excellent surface activity. Compared to bulk aluminium, reaction rate is very high in nano aluminium which can be used as a solid-fuel in rockets for propulsion, whereas the bulk aluminum is widely used in

utensils. Aluminium in nano form highly reactive and provides the sufficient thrust to propell into space.

1.2.3 Next-Generation Computer Chips

Microelectronic industry is failed to achieve significant reduction in circuit size (Transistors, resistors ,capacitors) due to loss of ultrafine precursors. Nanomaterials helps to the industry to break these barriers by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity and long lasting, durable interconnections. Example: Nanowires for junction less transistors. Researchers are succeed to design the junction less transistor (using silicon nanowire) with ideal electrical properties which potentially operate more faster and use less power than any conventional transistor in the market.

1.2.4 Elimination of Pollutants

Nanomaterials acquires very good chemical, physical, and mechanical properties due to which nanomaterials can be used as catalysts to react with noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

1.2.5 Sun-screen lotion

Skin burns due to the continuous exposure of sun (UV rays) rays, nano-TiO₂ used in manufacturing body lotion or sun screen lotion which not only provides better protection during eliminating stickiness and also protect the skin by sitting onto it rather than penetrating into the skin. Also retain the natural skin color due to transparent nature of TiO₂.

1.2.6 Nanoparticles in fire protection and detection

Nanomaterials are doped into the cement during the manufacturing process and the obtained product called as nanocement, which has the ability to create new paradigm in this area of application due to the resulting product can be used as a tough, durable, high temperature coating which increase the fire resistance.

1.2.7 Phosphors for High-Definition Monitors

Resolution of the monitor or display greatly depends on the pixel (pixel made of materials referred to as Phosphors) size. Reduction of pixel or phosphor size is necessary to enhance the resolution, with this regard, sol-gel and combustion route synthesized zinc selenide, zinc sulfide, cadmium sulphide, etc nanocrystallines are potential candidates for enhancing the resolution of monitors. Usage of nanophosphors is estimated to reduce the fee of those displays as a way to render high definition televisions (HDTVs) and personal computers inexpensive to be buy.

1.3 Phosphors

A material which has the ability to absorb energy and re-emitting it in other form of visible light is referred as Phosphor (or substance that emit light upon the illumination of excitation source is referred as phosphor) which are basically crystalline in nature. Excitation source may provide energy in the form of electrons, photons, heat etc. Source provides energy in the form of photons then the excitation is referred as optical excitation, however source may gives energy in the form electrons and heat then excitation is referred as electronic and thermionic excitations [9-11]. High brightness with good stability phosphors is essential for the development and improvement of modern light emission devices. Doping of rare earth (RE) ions into the phosphors are essential to get better luminescent characteristics with desired wavelength. However, phosphor hosts plays an vital role to achieve better luminescence. With this regard, host material should have the properties such as

- compatible with the emission centres. (accommodate the emission ions and allow them to involve in the emission process)
- should not react with the luminescent ions to form compounds.
- should be stable during fabrication of lamps.
- should be stable to highly energetic electrons, ultraviolet radiation and mercury (Hg) vapour.

1.3.1 Possible Light Emission Mechanism in Phosphors

Phosphors are the solid inorganic materials consisting of a host lattice, plenty of trivalent rare earth / transition cations are used as the luminescent activators in the

area of material science for outlining effective phosphors for lasers, optical gadgets, solar cells and bio-imaging applications. The major function of the activators in phosphors is to convert UV, NUV or blue light radiation to visible light (Fig.1.2b). When the phosphor undergo irradiation from the external light, phosphorescence process (light absorption, excitation, relaxation, and emission) occurs in the material, during which excitation light energy may be absorb by the phosphor host or by activators shown in Fig.1.2a.

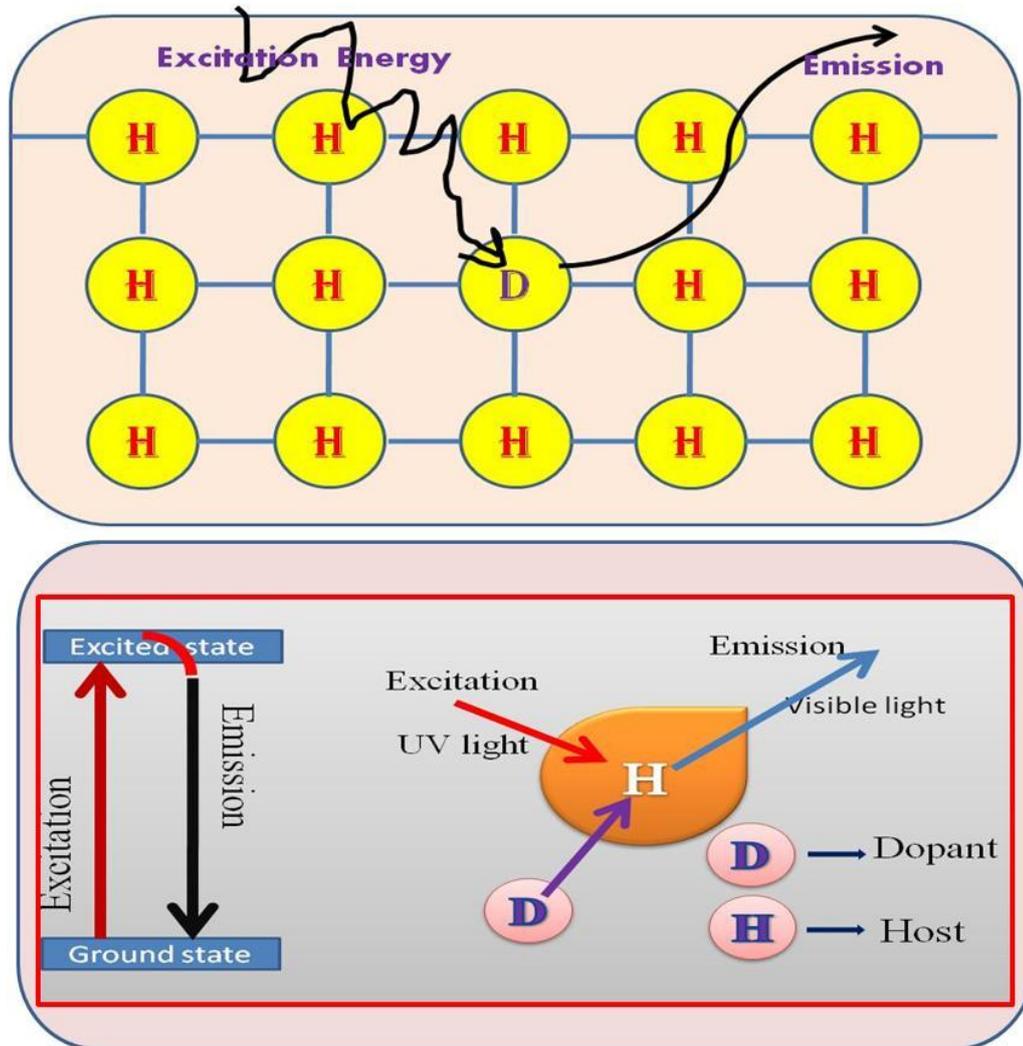


Fig.1.2. a) Representation of luminescence process, b) proposed mechanism of conversion of UV, NUV or Blue light into visible light

When the absorbed energy transmitted to dopant atom from host, the dopant emits visible light by relaxation of photo excited electron to lower energy state. Eu^{3+} doped Zn_2TiO_4 is a classic example in which the excitation light is absorbed by the Eu^{3+} and raising it to an excited state then returns to the ground state by means of

emission of radiation. However, a sensitizer can be utilized when an activator fails to emit required emission radiation with the available excitation energy. Sensitizer absorbs energy and transfers it to dopant, which emit radiation in visible region. A well-known example for this type of luminescence is $\text{Ca}_5(\text{PO}_4)_3\text{F,Cl:Sb}^{3+},\text{Mn}^{2+}$ in which UV radiation could not be absorbed by Mn^{2+} . Under UV irradiation, the emission consists partly of blue emission (Sb^{3+}), and partly of yellow emission (Mn^{2+}). The sensitizer transfers energy to Mn^{2+} there by emission takes place and corresponding energy transfer and emission process is shown in the Fig.1.3.

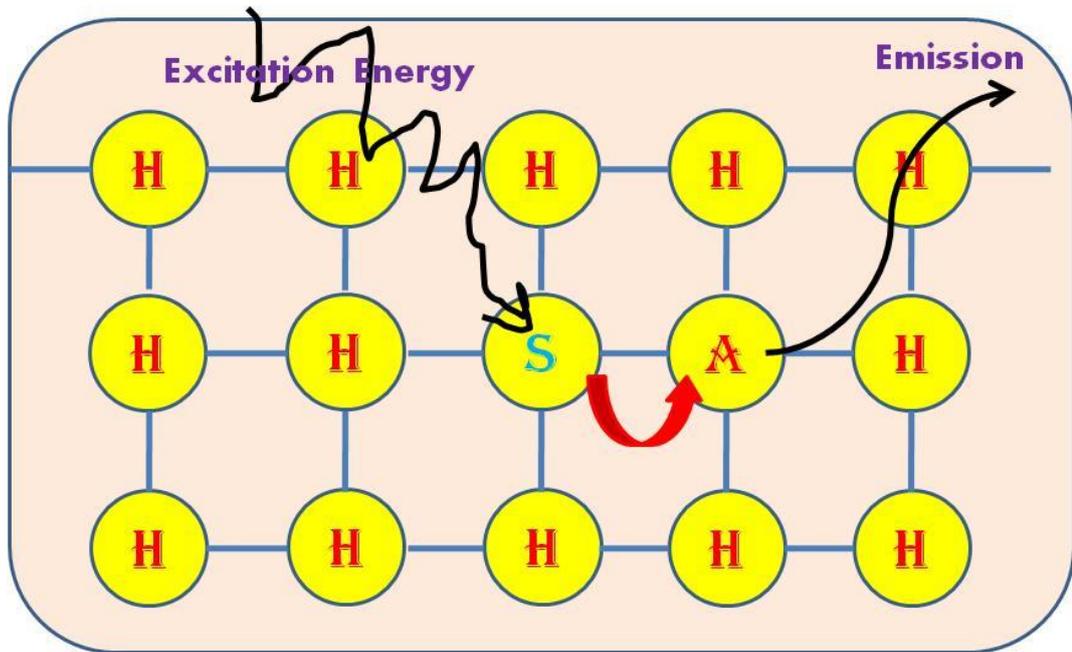


Fig. 1.3 Representation of luminescence process (a) sensitizer (S) & activator (A) in a host (H).

In the last few years, researches showing a much interest in the development of rare earth doped luminescent nanophosphors to fabricate white light emitting diodes (WLEDs) [12]. WLEDs are prominent candidates for the replacement of traditional luminescent light sources due to the higher efficiency of energy conversion, good stability, environmental friendly, long life time etc [13]. Presently, the combination of a blue LED (InGaN) with YAG: Ce^{3+} yellow-emitting phosphors used to generate white light [14-16]. When the sufficient current is provided, blue light was emitted by the InGaN chip through electron-hole recombination in the p-n junctions. Some of the blue light from the LED excites the YAG: Ce^{3+} phosphor to emit yellow light, and then the rest of the blue light was mixed with the yellow light to generate white light. Also another approach to generate white light is by combining red/green/blue tricolour phosphor with near-UV LEDs and the general

mechanism of generation of white light as illustrated in the Fig 1.4. Thus, it is necessary to prepare good quantum efficiency yellow phosphors to approach the needs of WLEDs with remarkable performance [17].

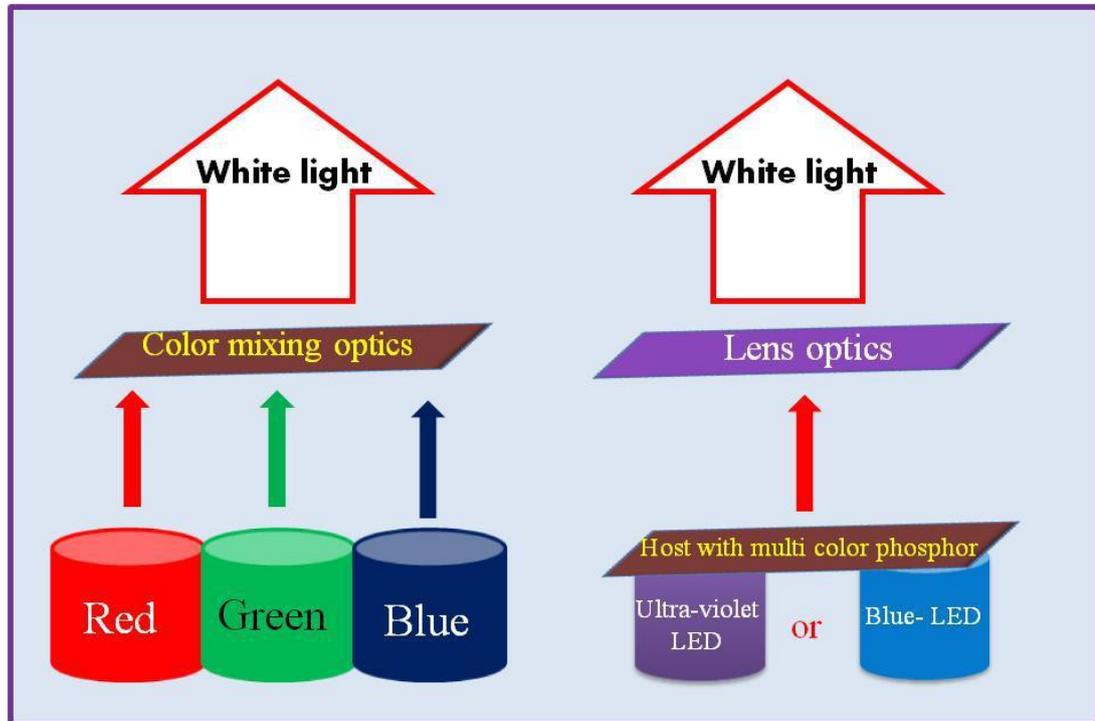


Fig1.4 General Mechanism of fabrication of white light

1.4 Preparation of phosphors

Nowadays material scientists are facing major problem in preparation of nanomaterials with desired composition, structures, and properties for specific applications. The physicochemical properties of many materials are determined by the choice of synthetic methods. Selection of the synthetic route is crucial to control the composition, structure and morphology of a chosen material. Top down and bottom up are two approaches to prepare nanophosphors

Top down approach: it is a Physical route in which the synthesis starts from macro/micro size to a required nanosize. Ex: Ball milling, etching, electron beam deposition, lithography, etc [18].

Bottom up approach: it is a Chemical route in which synthesis begins from molecular level to required nano size. Ex: Sol-gel, coprecipitation, microwave, hydrothermal, combustion, etc [19]. A brief review of different synthesis techniques utilized development of nanophosphors.

1.4.1 Sol-gel technique

The sol-gel method is one of the conventional wet chemical route to produce metal oxide nanoparticles through chemical processes in which precipitated tiny particles agglomerate to form long networks which are spread continuously throughout a liquid in the form of gel, Sols are the colloidal particles suspended in a liquid medium from which gel can be formed. In sol-gel method, metal alkoxides are used as a reactive metal precursor and hydrolyzed with water. By adding of the appropriate reagents, homogeneous gels can be produced through the processes of hydrolysis and gelation. After gelation, the precipitate is subsequently washed, dried, and then sintered at an elevated temperature to obtain crystalline metal oxide nanoparticles and the size of the prepared particle can be easily controlled by varying the initial concentration of the starting materials [20-22].

1.4.2 Ball Milling Method (Top Down approach)

Benjamin developed ball milling method in the late 1960s, in this method bulk material is broken into nanosize. Ball milling method is an effective method to fabricate fine, uniform dispersions of oxide particles (Al_2O_3 , Y_2O_3 , ThO_2) which cannot be done by other traditional methods. Chemical reactions in this method generally occurs either by changing the reaction rates or by inducing chemical reactions during milling.

Steps to synthesize nanomaterials in ball milling method

- ❖ Ball milling method consists of cylindrical mill container, consists of hard and heavy balls which are made up of tungsten carbide or silicon carbide. The material powder is placed into the steel container with 2:1 ball to powder ratio.
- ❖ As the chamber is rotated around in its axis, balls move up words, due to gravity dropdown and hit the powder sample with high speed, powder samples subjected to high energetic impact and get crushed. Ball milling is done about 100 to 200 hr to obtain uniform powder with nanosize.
- ❖ In order to provide pulling force, magnet is fixed outside the container and this magnetic force enhances the milling energy when milling container or chamber rotates the metal balls.

1.4.3 Solution Combustion Synthesis (SCS)

Prof. K.C. Patil invented SCS (fire synthesis) route in 1988, also referred to as self-propagating high temperature synthesis (SHS). It is an exothermic redox reaction between fuel and an oxidizer. An oxidizer, fuel and temperature are plays an important role in production of fire, which is an uncontrolled combustion that generates heat, light and ash. SCS method can be employed to prepare ceramic oxide nano powders with the combination of metal nitrates (Oxidizer) in an aqueous solution with a fuel. Particularly fuels such as glycine and urea are outstanding candidates because they are amino acids which can serve as a complexing agent of the metal ion in the solution and also serve as fuel for the synthesis of nanocrystalline metal oxides. Combustion reaction mainly depends on fuel, water content, flame temperature and gaseous products [23, 24].

Role of fuels

Fuel helps in burning the reaction mixture by breaking C-H bonds or gaining electrons. Example: carbohydrazide (CH), oxalyl dihydrazide (ODH), malonic dihydrazide (MDH), urea, glycine, etc.

Water content

During the preparation of nanomaterials, water added into the reaction mixture for uniform dispersion of atoms. If excess of water is left during combustion, the water content may reduce the flame temperature, as a result complete burning of redox mixture does not takes place resulting in incomplete crystallization compound and also surface area decreases with increase in water content.

Importance of gaseous products

During combustion, large amount of gases are released such as H₂O, CO₂ and N₂, etc. The increase in release of gaseous products increases the surface area of the material by creating micro and nano porous structure.

Flame temperature

The exothermicity of the redox mixture plays an import role in SCS for the formation of the different phases of the compound. The flame temperature mainly depends on the decomposition of fuels by releasing large number of gaseous products. As the amount of gas increases the flame temperature decreases.

Series of steps involved during combustion synthesis for the preparation of phosphor particles is shown in Fig.1.5.

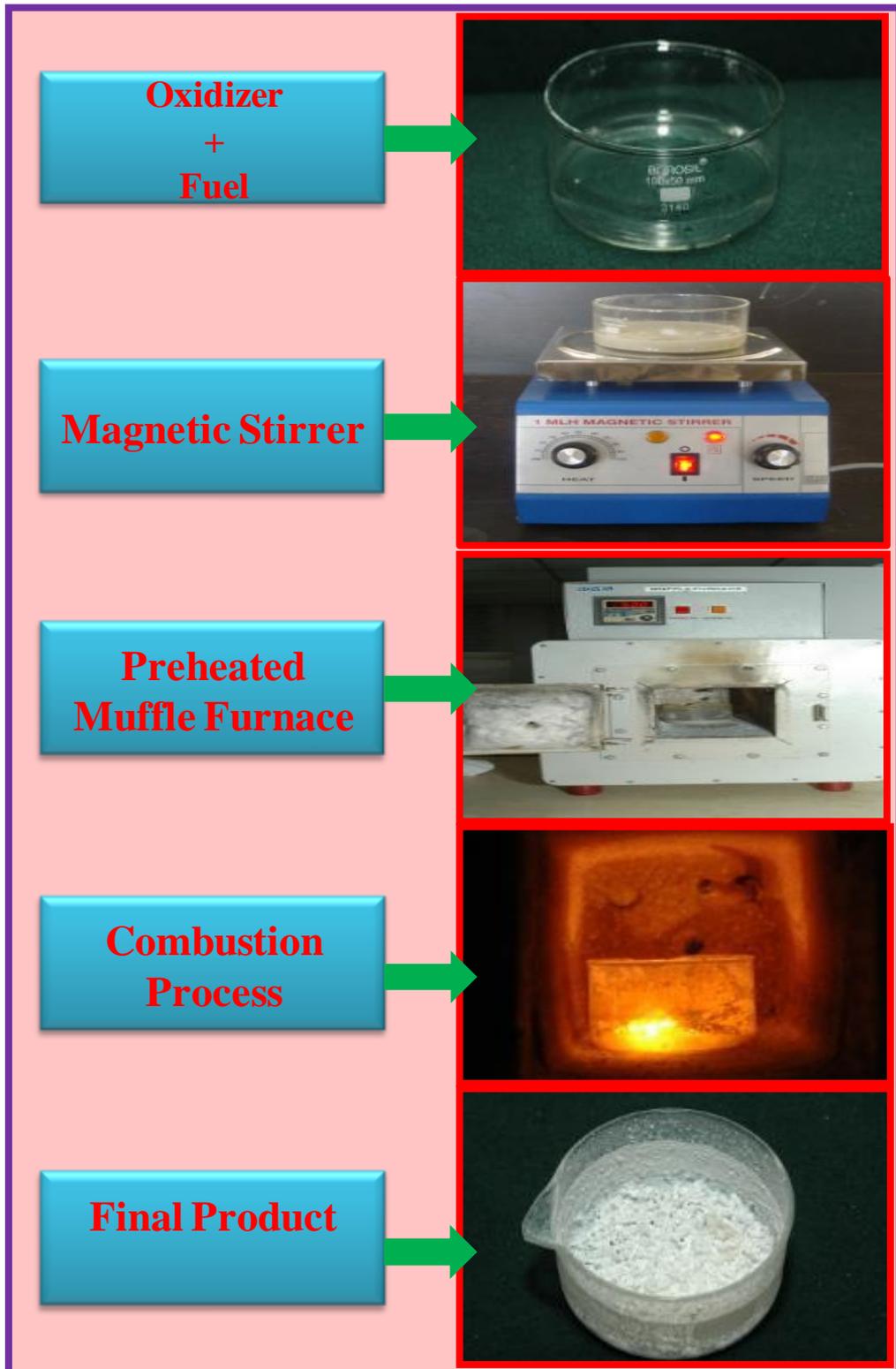


Fig.1.5 Schematic diagram for the preparation of materials in combustion process

Advantages of SCS

- It is simple and fast process
- self propagating reaction
- It is exothermic
- High level of atomic mixing
- Size and structure of the products can be controlled
- It requires less temperature
- It is economical
- It is single step method
- purity powders is high
- Compound obtained is homogeneous

1.5. Luminescence

Luminescence is defined as the phenomenon in which the electronic state of a substance is excited by a kind of external energy and the excitation energy is given out in the form of light. Now a day's luminescence is one of the most useful and fast growing analytical techniques due to their applications in various areas such as microelectronics, physics, chemistry, biology, biochemistry, medicine, toxicology, pharmaceuticals, and clinical chemistry. The tremendous interdisciplinary appeal for luminescence techniques has resulted in a growing number of researchers. Luminescence can be classified into fluorescence and phosphorescence according to the duration time of the after-glow.

1.5.1. Types of Luminescence

To illustrate the diversity of luminescence emissions, the following represent some of the more commonly observed types of luminescence based on the nature of excitations:

Electroluminescence

It is electro optical phenomenon in which a substance emits light during the flow of an electric current or electric field [25]. Example: a gas discharge lamp, solar cell (Fig.1.6)

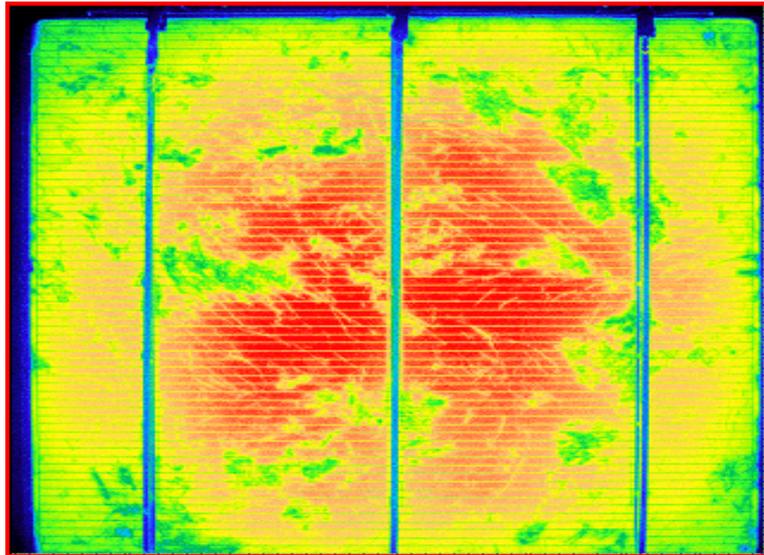


Fig.1. 6 Emission of light by solar cell

Radioluminescence (RL)

RL is the phenomenon in which light is emitted in substance by bombardment with ionizing radiation such as alpha, gamma and beta particles [26]. Example: luminous radium watch dial (Fig.1.7).



Fig.1.7 Emission of light by radium watch dial

Triboluminescence

It is the phenomenon in which light is generated through the breaking of chemical bonds in a substance when it is pulled apart, ripped, scratched, crushed, or rubbed.

The word tribo is originating from the Greek word which means to rub. Example: A jewel (diamond) may start to sparkle while being rubbed [27] and certain kinds of sugar crystals.

Sonoluminescence (SL)

SL is a charming effect of the emission of light from the gaseous bubbles in liquids when excited by sound. SL is the conversion of sound energy into light energy. it was discovered in 1934 by German scientists as a results of their experiment with solar [28].

Chemiluminescence (CL)

CL is an optical phenomenon in which light is emitted during chemical reaction, which does not generate any considerable amount of heat (temperature). It occurs when a highly oxidized molecule (peroxide) reacts with another molecule (iron or copper) [29]. Crystalloluminescence is another variant from chemiluminescence, which is produced light occasionally during crystallization.

Bioluminescence

Luminescence produced by the living organism is known as BL. The word BL is derived from Greek and Latin words bios (means living) and lumen (means light). Biological entities such as fireflies, mushrooms (few) also some bacterias generate luciferin (a pigment) and luciferase (an enzyme) chemicals in which luciferin reacts with oxygen to generate light where as luciferase acts as a catalyst to boost up the reaction [30]. Example. Emission of light by Fire flies is shown Fig.1.8.

Cathodoluminescence (ChL)

ChL is the process in which light is generated when a luminescence substance is stimulated by an electron beam. A well-known example is the emission of light by an electron beam scanning the phosphor-coated inner surface of the screen of a television that uses a cathode ray tube [31].



Fig. 1.8 Firefly attracting females with lit up behind.

1.6 Photoluminescence (PL)

PL derives its energy from the absorption of light energy (most commonly in the wavelength ranges of infrared, ultraviolet or visible light). Photoluminescence is further divided into the categories of fluorescence, delayed fluorescence and phosphorescence. Today they are defined via the emission based quantum mechanical mechanism for the orbital angular momentum multiplicity of the emitted electron (i.e. the singlet or triplet excited state). However, before the advent of quantum theory photoluminescence was defined solely on the basis of empirical evaluation of the duration of emissive lifetime.

Fluorescence

It is defined as a photoluminescent emission that arises from the singlet electronic state. In this process, particle absorbs radiation and gets excited from the electronic ground state to excited state and this excited state is generally the first excited singlet state (Fig. 1.9), particle reaches an excited singlet state and returns to the ground state in few nanoseconds by emitting photon and this process is called fluorescence. To the human eye fluorescence is observed only when the exciting light source shines on the radiator.

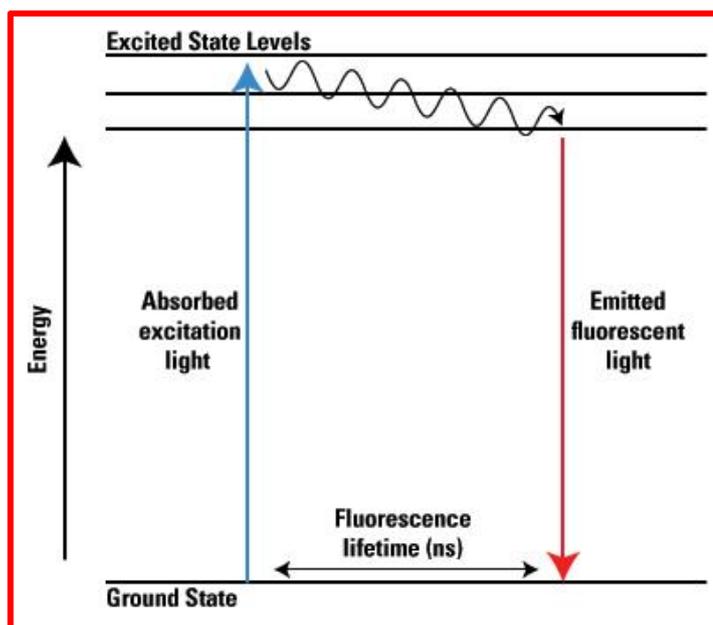


Fig 1.9 Different states involved in the fluorescence process

Phosphorescence

It is defined as a photoluminescent process that originates from the triplet electronic state (Fig.1.10). Emissions from the triplet state are from 10 to 10,000 times longer than fluorescence; therefore, to the eye these radiators appear to emit after the excitation radiation is removed.

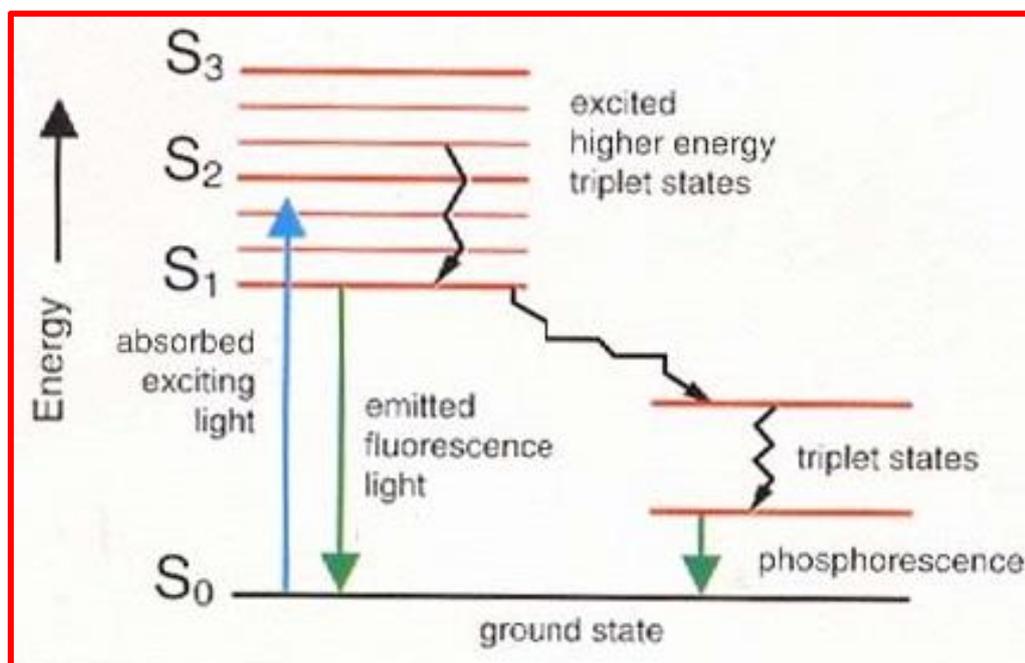


Fig 1.10 Different states involved in the phosphorescence process

1.7 Importance of Titanate hosts in solid state lighting

Titanates are one of the prominent candidates for luminescent centers owing to its outstanding chemical and thermal stability. When rare earth ions or transition metal ions doped into silicate/oxide materials becomes phosphor powder, which produces brilliant luminescence in the blue, green and red region. Such kind of phosphor has been generally utilized in color television, flat panel display screen and cathode ray luminescence tubes. Titanates materials gaining significant attention in the area of material industry due to their (i) stable crystal structure (ii) high physical and chemical stability (iii) better formability (iv) long persistence time (v) relatively easy preparation (vi) multi-color phosphorescence and resistance for acid, alkali and oxygen.

Titanium based inorganic materials have been studied vigorously due to their excellent properties and potential applications in various fields. Among the titanates, Zinc titanate is a functional inverse spinel material with cubic structure used for many applications because of their few important properties like good chemical and thermal stability and good mechanical resistance, particularly high permittivity, low dielectric losses make this material a suitable candidate for microwave applications. Zn_2TiO_4 is a promising, versatile luminescent host phosphor due to the extensive range of multi-colors that can be obtained from various activator ions. In the present work, Zn_2TiO_4 chosen as a host material in view of the industrial and immense potential applications.

1.8 Review of literature

Number of efforts has been made for the synthesis of low cost and efficient luminescent materials by various preparation routes. Among the phosphors which are accessible in the market, rare earths and transition metal ions activated zinc titanates nanophosphors are the novel luminescent materials for lamps, cathode ray tubes (CRTs), plasma display panels and solid state lighting applications. A concise literature review of host, dopant, preparation route and its applications is given in Table.1.1

From the table it was observed that, a very limited work has been accounted on the synthesis and luminescence studies of solution combustion derived zinc

titanate host materials. Thus in the present work, zinc titanate nanophosphors were synthesized by solution combustion route oxalyl diformyl hydrazine (ODH) as a fuel.

1.9 Objectives of the present study

The objectives of the present study are:

- Preparation of pure and RE³⁺ doped Zn₂TiO₄ nanophosphors by conventional SCS route.
- Characterization of synthesized phosphor by PXRD, SEM, TEM, FTIR, UV-VIS, etc.
- To optimize excitation wavelength for an intense emission by PL technique.
- To tune the emission wavelength by doping suitable rare earth and optimize the dopant concentration.
- To compare the relative efficiencies of doped phosphors under exposure of energetic radiations like gamma rays, Ultraviolet rays and Electron beam.
- To achieve colored and white light emission by the phosphors with higher efficiencies and longer radiative lifetimes.

Table 1.1.

| Host material | Preparation route | Characterisation | Luminescence Studies | Outcomes | Authors |
|---|--------------------------|-----------------------------|----------------------|--|----------------------------|
| Zn ₂ TiO ₄ | Rf sputtering | XRD, SEM, TEM, HRTEM | | GaN-based MOS Dielectric applications | C.Y. Hsiao et.al.[32] |
| Zn ₂ TiO ₄ | flame spray pyrolysis | XRD, SEM, TEM, HRTEM, EDS | | High purity product preparation . | C. Siriwong, et.al.[33] |
| Zn ₂ TiO ₄ | floating zone method | XRD- | | Large-sizeandhigh-quality single crystal. | L. Li, et al. [34] |
| ZnTiO ₃ | Sol-gel | XRD, FTIR, FE-SEM, TEM, AFM | | Thin films with 40-45 nm powders size | Mohammadi, et al. [35] |
| Zn ₂ TiO ₄ | high-energy ball milling | XRD- | | Phase transformation kinetics | Manik, et al. [36] |
| Zn ₂ TiO ₄ | Polymer precursor method | XRD, IR | PL | Increased luminescence with doping | Chaves, et al. [37] |
| Zn ₂ TiO ₄ | Solid state reaction | XRD, SEM | - | Good material for dielectric resonator applications | Sandeep, et al. [38] |
| ZnTiO ₃ and Zn ₂ TiO ₄ | Ball milling method | XRD , XANES XAFES | - | Good agreement of EXAFS results and crystal structure data. | Guvanc, et al. [39] |
| Zn ₂ TiO ₄ | Thermal oxidation | XRD, FE-SEM, Raman | | Belt-like nanostructures of cubic Zn ₂ TiO ₄ | Santhaveesuk,, et al. [40] |
| ZnTiO ₃ and Zn ₂ TiO ₄ | Solid state Reaction | PXRD,FTIR,Raman and DRS | PL | Zn ₂ TiO ₄ showed a strong PL band at 510 nm and a small PL band at 395 nm in the green and violet | Madhusudhana, et al. [41] |

Table 1.1.

| Host material | Preparation route | Characterisation | Luminescence Studies | Outcomes | Authors |
|---|----------------------------|------------------------------|------------------------|--|--------------------------|
| Zn ₂ TiO ₄ : Eu, Er, Tm ³⁺ | Sol- Gel | XRD, DTA, DGA, SEM | - | regions A new crystalline phase of RE pyrochlorates has been observed for RE concentrations higher than this limit | Jan Mrazek, et al. [42] |
| ZnTiO ₃ and Zn ₂ TiO ₄ | Mechanochemical activation | XRD ,SEM FTIR, UV visible | - | The mechanochemically obtained mixture of zinc titanates displays photocatalytic activity towards the degradation of malachite green after 150 min irradiation time | Iordanova, et al. [43] |
| ZnTiO ₃ and Zn ₂ TiO ₄ | Mechanical Activation | XRD, SEM | - | Zn ₂ TiO ₄ ceramics can be obtained by mechanical activation after a certain time without additional thermal treatment.. | Obradovic, et al. [44] |
| Li ₂ ZnTi ₃ O ₈ | Sol-gel | XRD, TGA , DTG | - | Li ₂ ZnTi ₃ O ₈ electrode makes it a promising anode candidate for high performance lithium ion batteries | Xinxi L, et al. [45] |
| (Ca, Zn)TiO ₃ : Eu ³⁺ | Sol-gel | XRD, SEM | PL CIE chromaticity | Promising red phosphor for white LEDs.. | Y. Wu, et al. [46] |
| Li ₂ ZnTi ₃ O ₈ | Molten-salt | XRD,SEM,TEM | - | large specific capacities, good crystallinity, small particle size and low charge-transferresistance of Li ₂ ZnTi ₃ O ₈ . | B. Chen, et al. [47] |
| ZnTiO ₃ : :Eu ³⁺ | Sol-gel | XRD,SEM,TEM EDS | PL CIE chromaticity | The intense red emission at 614 nm corresponding to the transition of ⁵ D ₀ → ⁷ F ₂ was dominant in the emission spectra, and the <i>R</i> value calculated for ZnTiO ₃ :2 mol %Eu ³⁺ sample was about 3.81, which suggested that Eu ³⁺ ions mainly occupied the lattice site without inversion symmetry. | LI Mengting, et al. [48] |

Table 1.1.

| Host material | Preparation route | Characterisation | Luminescence Studies | Outcomes | Authors |
|--|-------------------------|---------------------------------|----------------------|--|-----------------------------|
| ZnTiO ₃ | Physicochemical method | XRD,SEM,TEM UV-visible,FTIR | | The value of energy band gap of as prepared ZnTiO ₃ nanocomposite was found 4.10 eV, Rapid sensor response, good sensitivity, and stability sensor for LPG applications . | Yadav, et al. [49] |
| ZnTiO ₃ | Atomic layer deposition | XRD,SEM,TEM | | ALD ZnTiO ₃ coatings also exhibited improved tribological properties compared to CVD-like ZnTiO ₃ coatings.Mechanistic friction | Ageh, et al. [50] |
| ZnTiO ₃ | Combustion Synthesis | XRD,SEM,TEM UV-Visible,FTIR | | Good adsorption capacity for MG dye | Raveendra, et al. [51] |
| Zn ₂ TiO ₄ :Pt | flame spray pyrolysis | XRD, SEM, TEM, HRTEM, EDS | | Agglomerated nanospheres with an average diameter of 10–20 nm.. | C. Siriwong, et.al.[52] |
| Zn ₂ TiO ₄ core shell | Solid state reaction | XRD, SEM, TEM IR spectra- | | Zn ₂ TiO ₄ composite catalyst in applications of photocatalytic degradation of air pollutants. | Liyuan Wan, et al. [53] |
| ZnTiO ₃ , Zn ₂ TiO ₄ , ZnTi ₃ O ₈ | Hybrid DFT | Uv-Visible | | Promising candidates for constituting robust visible light-active photocatalysts, | J. C. Conesa, et al. [54] |
| ZnTiO ₃ :Sr | Solid state reaction | XRD,SEM | | Addition of Sr makes the sintered ZnTiO ₃ more porous. | Yee-Shin Chang, et al. [55] |

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